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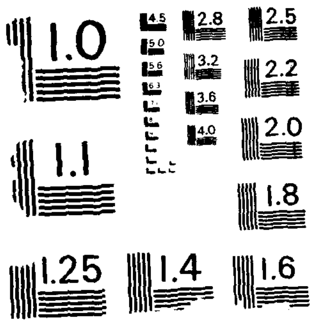
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Analysis of Low-Pressure Gas-Phase Pyrolytic Reactions by Mass Spectrometric Techniques

Lars Carlsen

Chemistry Department,
Risø National Laboratory, DK-4000 Roskilde, Denmark
January 1989

This we learned from famous men,
Knowing not its uses,
When they showed, in daily work,
Man must finish off his work -
Right or wrong, his daily work -
And without excuses.
(R. Kipling)

TO MY PARENTS

IN MEMORIAM

Denne afhandling, i forbindelse med 18 tidligere publicerede arbejder, er af Institut I ved Roskilde Universitetscenter antaget til offentligt at forsvares for den Naturvidenskabelige Doktorgrad

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ANALYSIS OF LOW-PRESSURE GAS-PHASE PYROLYTIC REACTIONS BY MASS SPECTROMETRIC TECHNIQUES.

Lars Carlsen

ABSTRACT

The report is divided into seven chapters: Chapter 1 gives a short introduction to applications of pyrolysis techniques in different areas of chemical research. Chapter 2 is devoted to the application of mass spectrometric techniques for the analysis of gas-phase reactions. The applicability of field ionization and collision activation mass spectrometry is illustrated by studies on isomerization reactions of carboxylic acid esters and the thermal decomposition of 1,2-oxathiolane. The importance of reference structures is discussed. Chapter 3 gives details on the sample/inlet systems applicable to the pyrolysis-mass spectrometry system. Chapter 4 discusses the low-pressure pyrolysis reaction, with special emphasis on reactors based on the inductive heating principle. The temperature control of the reactors is discussed in terms of a 'multitemperature' filament, as the basis for the concept of Pulse Pyrolysis. The influence of surface composition on the course of reaction is discussed, advocating for the application of gold coated surfaces to minimize surface-promoted reactions. Chapter 5 deals with low-pressure gas-kinetics on the basis of an empirical 'effective temperature' approach. Chapter 6 gives a short summary of the main achievements, which are the basis for the present report and Chapter 7 is the reference list. A Danish summary and 18 appendices, consisting of previously published papers in the period 1980-1986 are included as separate sections.

Risø May 1987

CONTENTS

PREFACE 7

1. INTRODUCTION 11

2. THE DETECTION SYSTEM 19
   2.1. Mass spectrometry 19
        2.1.1. Isomerization reactions 27
   2.2. Static systems 37
        2.2.1. 1,2-oxathiolane 38
   2.3. The importance of reference structures 44

3. SAMPLE/INLET SYSTEM 49

4. THE PYROLYSIS REACTOR 53
   4.1. The Knudsen reactor 55
        4.1.1. Simulation of molecular movement through
               low-pressure reactors 59
   4.2. Temperature control 62
        4.2.1. Pulse pyrolysis 67
   4.3. Surface influence 68
        4.3.1. Nitroso-ethene 76
        4.3.2. Direct surface involvment 77

5. GAS KINETIC CONSIDERATIONS 81
   5.1. Experimental determination of k 84
   5.2. The effective temperature approach 85

6. SUMMARY 91

7. REFERENCES 97

ACKNOWLEDGEMENTS 105

RESUME (in Danish) 107

APPENDIX 1 113

APPENDIX 2 127

APPENDIX 3 143

APPENDIX 4 153

APPENDIX 5 159

APPENDIX 6 175

APPENDIX 7 189

APPENDIX 8 197

APPENDIX 9 205

APPENDIX 10 213

APPENDIX 11 221

APPENDIX 12 227

APPENDIX 13 231

APPENDIX 14 237

APPENDIX 15 245

APPENDIX 16 251

APPENDIX 17 261

APPENDIX 18 265

And we all praise famous men -
Ancients of the College;
For they taught us common sense -
Tried to teach us common sense -
Truth and God's Own Common sense,
Which is more than knowledge!
(R. Kipling)

PREFACE

The present report highlights applications of mass spectrometric techniques in the analysis of low-pressure pyrolytic reactions, based on work carried out at the Chemistry Department, Risø National Laboratory. The Risø contributions to this field of research started in 1979. The studies at Risø have all been carried out in close collaboration with Helge Egsgaard. Other collaborators have been Ernst Schaumann (Hamburg), David N. Harpp (Montreal), Gordon H. Whitham (Oxford), Susanne Elbel (Hamburg), and Elfinn Larsen, Palle Pagsberg, and Peter Bo (Risø).

The work was originally initiated in an attempt to extend a study on the photolysis of thioketene S-oxides (L. Carlsen and E. Schaumann, J.Chem.Soc. Faraday Trans. 1, 75 (1979) 2624) to include also the thermal fragmentation patterns of these species.

The major part of the work summarized in the present report has previously been published in the below mentioned 18 papers. Reprints of these papers are included in this report as appendices 1-18. For a more detailed description of the technique, and especially the applications the appendices 1-7 and 8-18, respectively, should be consulted.

1) 'An effective approach to flash vacuum thermolytic studies'
Thermochim.Acta 38 (1980) 47-58
(with Helge Egsgaard)

2) 'Real-time collision activation mass spectrometry of pyrolysis products'
J.Anal.Appl.Pyrolysis. 4 (1982) 33-46
(with Helge Egsgaard and Elfinn Larsen)

3) 'Gold-plated filaments for Curie-point pyrolysis'
J.Anal.Appl.Pyrolysis. 5 (1983) 1-7
(with Helge Egsgaard)

4) 'Heterogeneous catalysis in gas phase reactions studied by Curie-point pyrolysis. Gas phase pyrolysis of methyl dithioacetat'
J.Anal.Appl.Pyrolysis. 5 (1983) 257-259
(with Helge Egsgaard)

5) 'Continuous-flow inlet systems for low pressure Curie-point pyrolysis. Introduction of pulse-pyrolysis'
J.Anal.Appl.Pyrolysis. 7 (1984) 1-13
(with Helge Egsgaard)

6) 'Pulse pyrolysis: Gas kinetic studies in an inductively heated flow reactor'
J.Anal.Appl.Pyrolysis. 8 (1985) 3-14
(with Helge Egsgaard and Peter Bo)

7) 'Direct surface participation in gas-phase Curie-point pyrolysis: The pyrolysis of phenyl azide'
J.Anal.Appl.Pyrolysis. 10 (1986) 83-87
(with Helge Egsgaard)

8) 'Gas phase thermolysis of a thioketen-S-oxide'
J.Chem.Soc. Perkin Trans. II (1980) 1206-1211
(with Helge Egsgaard and Ernst Schaumann)

9) 'Gas phase thermolysis of silylated thionocarboxylic acid derivatives: A route to thioketens?'
J.Chem.Soc. Perkin Trans. II (1980) 1557-1562
(with Helge Egsgaard, Ernst Schaumann, Herbert Mrotzek and Wolf-Rüdiger Klein)

10) 'Gas phase thermolyses of thietan 1-oxide and 1,2-oxathiolan 2-oxide. Evidence for the intermediacy of 1,2-oxathiolan'
J.Chem.Soc. Perkin Trans. II (1981) 1166-1170
(with Helge Egsgaard and David N. Harpp)

11) 'Thermally-induced rearrangement of methyl acetate in the gas phase'
J.Chem.Soc. Perkin Trans. II (1981) 1256-1259
(with Helge Egsgaard and Palle Pagsberg)

12) '1,2-Oxathiolan'
J.Chem.Soc. Chem.Commun. (1981) 742-743
(with Helge Egsgaard, Gordon H. Whitham and David N. Harpp)

13) 'Gas-phase thermolysis of 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide. On the intermediacy of 1,2-oxathietan'
J.Chem.Soc. Perkin Trans. II (1982) 279-282
(with Helge Egsgaard)

14) 'Gas phase thermolysis of methyl and ethyl monothioacetates'
J.Chem.Soc. Perkin Trans. 2 (1982) 1081-1085
(with Helge Egsgaard)

15) 'Unimolecular gas phase thermolysis of ethyl acetate'
Int.J.Mass Spectrom. Ion Phys. 47 (1983) 55-58
(with Helge Egsgaard)

16) 'Thermal decomposition of 1,2-oxathiolane in the gas phase'
Chem.Ber. 117 (1984) 1393-1399
(with Helge Egsgaard)

17) 'Gas-phase pyrolysis of methyl dithioacetate. The absence of a 1,3-methyl group migration'
J.Chem.Res. synop. (1984) 340-341
(with Helge Egsgaard)

18) 'Pyrolysis of $H_4N_4S_4$. First evidence for the formation of sulphur diimide'
Sulfur Letters 3 (1985) 87-93
(with Helge Egsgaard and Susanne Elbel)

These papers are included in the list of references and are referred to as are other references through out the report.

1. INTRODUCTION

Pyrolysis, e.g. reactions initiated by high temperatures, is a widely used technique within rather different areas of chemistry, ranging from pure physical chemistry over physical organic/inorganic chemistry, preparative organic/inorganic chemistry to characterization studies in geochemistry, food chemistry, polymer-, biological/medical-, and forensic sciences.

The application of pyrolysis in the characterization studies mentioned typically involves pyrolytic degradation of solid material to gaseous products, which can be detected by gas chromatography and/or mass spectrometry. The resulting chromatograms, often named pyrograms, and mass-spectra are frequently used as finger prints for these materials otherwise characterizable only with diffculty, such as humic substances, coals, bacterial samples, skin-samples and paints. A series of detailed reports of these applications of pyrolysis can be found in recent reports on Analytical and Applied Pyrolysis (Voorhees, 1984, Schulten, 1985). Reports on these subjects are to be found typically in J. Anal. Appl. Pyrolysis (published by Elsevier, Amsterdam).

Pyrolysis in preparative organic chemistry appears as an effective technique for generating a variety of species, which cannot, or only with difficulty, be achieved by ordinary synthetic procedures (Wiersum, 1984). Also the formation of reactive species, which subsequently can be trapped and used as reaction partners is of great importance. Available literature up to the end of 1977 in this field has comprehensively been compiled by Brown (1980) in his monograph 'Pyrolytic Methods in Organic Chemistry'.

Within the field of physical organic/inorganic chemistry pyrolysis are often used as the technique for generating highly reactive species in diluted gas-phase in order to study these compounds spectroscopically. The analysis can be carried out either directly on the gaseous reaction mixture (microwave spectroscopy (Bak and Svanholt, 1983), photoelectron spectroscopy (Bock and Solouki, 1981), mass spectrometry (Holdiness, 1984)) or following trapping of the pyrolyzates on a cold KBr or quartz plate, the product mixture being analyzed by low-temperature infra-red or electronic absorption spectroscopy (Mayo, 1972). The physical organic/inorganic chemistry application of pyrolysis also covers the area of mechanistic studies elucidating high-temperature-initiated reaction pathways such as fragmentations, isomerizations, and rearrangements (Carlsen and Egsgaard, 1980, Egsgaard, Larsen and Carlsen, 1982).

Whereas the former application, i.e. identification of a new highly reactive species, is rather closely connected to the above-mentioned preparative use, the latter, i.e. the mechanistic studies, is on the borderline of pure physical chemical pyrolytic studies. Typically the latter deals with gas-phase kinetics of well-known reactions, an area which has been developed to a high degree of sophistication (Quack, 1984). The complicated (at least from an organic chemists point of view) mathematics requires extensive use of computers.

An important factor in gas-phase pyrolysis studies is the mean residence time, t_{mr}, of the molecules in the pyrolysis reactor, i.e. the hot zone. In order to avoid the occurrence of consecutive reactions, i.e. repyrolysis of primary generated products, it is desirable that t_{mr} be as low as possible. Generally, the term Flash Vacuum Pyrolysis (FVP) is used when the mean residence time is less than 1 sec. (Seybold, 1977). However, in the case of low-pressure pyrolysis, mean residence times several orders of magnitude lower are often used, typically in the range of 1-100 ms (Hedaya, 1969). For the latter type of studies Golden, Spokes and Benson (1973) introduced the term Very Low Pressure Pyrolysis (VLPP). In these set-ups the reactors are typically constructed in such a way that they fulfil the requirements for a so-called Knudsen reactor, which means that the mean residence time of the molecules in the reactor is a function of the reactor geometry and -temperature alone. Thus, t_{mr} is independent of the internal pressure.

The present report focuses on the physical organic/inorganic application of pyrolysis, advocating for the superiority of direct analysis techniques, as mass spectrometry of low-pressure gas-phase pyrolytic reactions. In the present context, low-pressure pyrolysis refers to reactions carried out at high temperature, in general above 750K, at pressures typically below 10^{-3} torr, *ensuring in practice* that only unimolecular reactions take place.

Schematically the experimental set-up can be illustrated as in the block diagram Fig. 1-1.

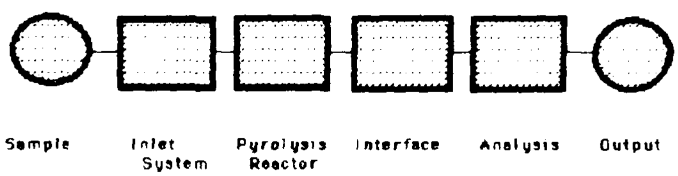


Fig. 1-1. Block diagram for pyrolysis experiment.

The aims with the present study have been to develop a pyrolysis system based on mass spectrometry as detection system, as well as to demonstrate its applicability to mechanistic problems within organic chemistry.

These investigations have involved studies in the area of inlet systems, reactor design and analysis techniques. One main achievement has been the introduction of the inductive heating principle for gas-phase pyrolytic studies, including the development of the 'multi-temperature filament'. A second achievement of major importance has been the unique application of field-ionization mass spectrometry (FIMS) and collision activation mass spectrometry (CAMS) to studies of gas-phase pyrolysis reactions. Especially the avantageous application of stable isotopes as ^{2}H, ^{13}C, ^{18}O, and ^{34}S is strongly emphasized.

With regard to the applications new information obtained on isomerization reactions of esters and mechanistic studies on the thermal stability of the 1,2-oxathiolane system can be regarded as being of major importance. These results, which exemplify the versatility and capabilities of the pyrolysis - mass spectrometry system, could most probably only with difficulty, if at all, have been obtained applying different techniques.

The gas-phase pyrolysis reactions may be carried out in a flow system, which in general will be the most suitable. However, the mass spectrometer used for the studies described in this report, is equipped with a thermostatable gas inlet system, which may be used for studies in a static system.

In Figs. 1-2 and 1-3 flow charts summarize the course of an analysis of a w-pressure gas-phase pyrolytic reaction by mass spectrometric techniques. In the following sections the single parts of the pyrolysis system (cf. Fig. 1-1) will be treated in detail separately. However, to secure the understanding of the fundamentals of the mass spectrometric techniques applied, the analysis part will be treated first. A final section is devoted to preliminary studies on gas kinetics.

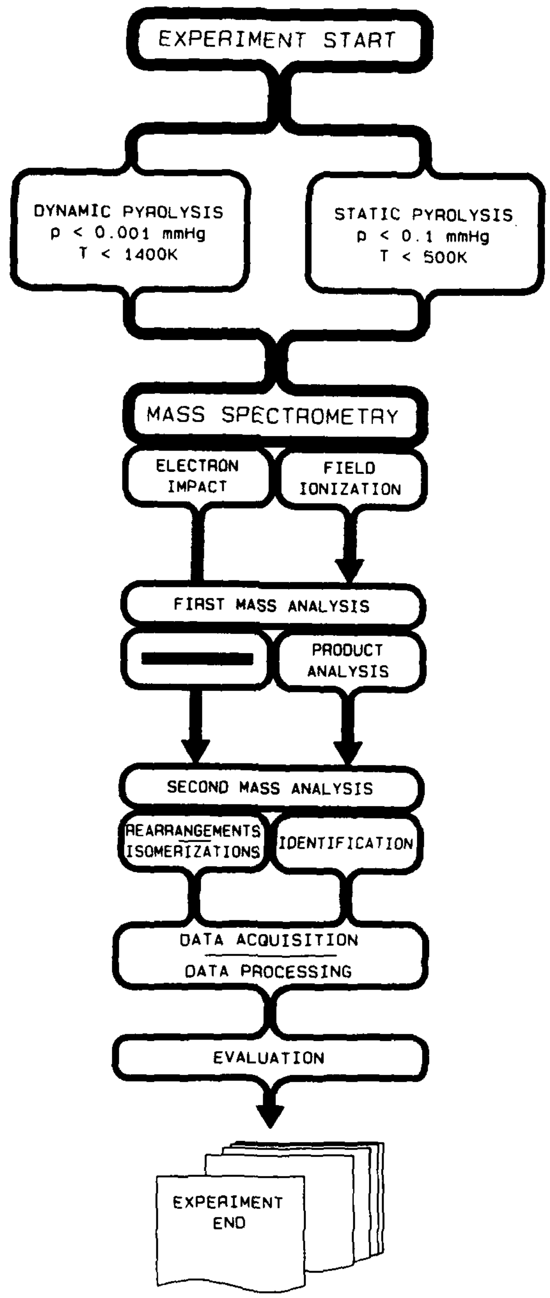


Fig. 1-2. Flow chart for low-pressure pyrolysis - mass spectrometry studies.

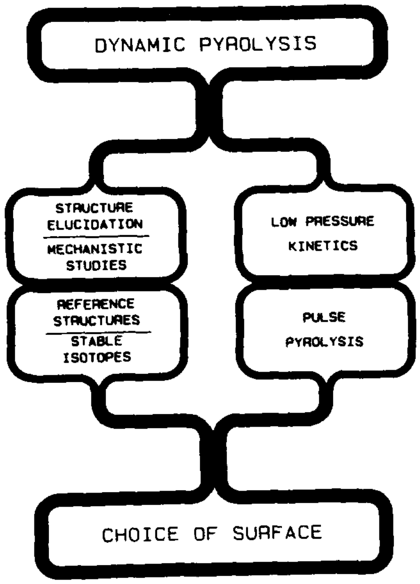


Fig. 1-3. Flow chart for dynamic low-pressure pyrolysis studies.

2. THE DETECTION SYSTEM

Usually three different detection systems are applied in the direct analysis of low pressure pyrolytic reactions. These are microwave spectroscopy, photoelectron spectroscopy, and mass spectrometry. All three types of detection systems exhibit advantages as well as disadvantages. In the following the applicability of mass spectrometry as detection system is summarized.

Often significant discrepancies can be observed studying pyrolysis reactions applying different systems. A variety of factors may account for these apparent controversies. Among others reactor geometry and material, temperature distribution and transfer time from reactor to analysis equipment can be mentioned as possibly being responsible. A detailed discussion of these problems is, however, outside the scope of the present study.

2.1. Mass Spectrometry

The application of mass spectrometric techniques in the study of low pressure gas phase pyrolytic processes appears without doubt as the more versatile course.

Mass spectrometry as detection system for pyrolysis studies has been applied as early as 1948 (Madorski and Strauss, 1948) and in connection with flash vacuum pyrolytic studies Hedaya (1969) used mass spectrometry in the study of nickelocene pyrolysis. The utility of mass spectrometry in gas phase kinetic studies has been outlined by Golden, Spokes and Benson (1973), a feature which will be dealt with in a proceeding section. In the field of solid state pyrolysis the combination of Curie-point pyrolysis units and mass spectrometers has been reported by several authors (cf. Meuzelaar et al., 1973, Meuzelaar et al., 1984, Schmid and Simon, 1977; and references cited therein).

Recently we introduced the Curie-point pyrolysis principle for gas phase reactions (Carlsen and Egsgaard, 1980), the method being based on a direct combination of the pyrolysis unit and the ion source of a mass spectrometer. The introduction of the so-called soft ionization modes, as field ionization mass spectrometry (FIMS) (Jason and Parr, 1976, Beckey, 1971) as well as MS-MS techniques as collision activation mass spectrometry (CAMS) (Levsen and Beckey, 1974) has opened up a new dimension in the analysis of low pressure pyrolytic reactions, which advantageously has been used for the gas phase Curie point pyrolysis-mass spectrometry technique (Carlsen and Egsgaard, 1980; Egsgaard, Larsen, and Carlsen 1982), the experimental set-up being visualized in Fig. 2-1.

The advantageous pairing of the direct combination of the pyrolysis unit with field ionization mass spectrometry, in contrast to the classical electron impact mass spectrometry (EIMS) is to be sought for in the principle of field ionization (Jason and Parr, 1976, Beckey, 1971). Since field ionization takes place with no excess energy to the neutral molecule, excluding polarization induced by the high electric field (Jason and Parr, 1976), this ionization mode gives rise to molecular ions - even of highly unstable molecules - accompanied by very few, if any, fragment ions, generally of low intensity (<1%) (Beckey, 1971). Hence, the detection system offers the possibility of analyzing even very complex reaction product mixtures. Electron impact ionization, on the other hand, may result in complicated fragmentation patterns, which eventually may lead to confusion as they are to be described as superpositions of EIMS spectra of several, and often unknown, reaction products.

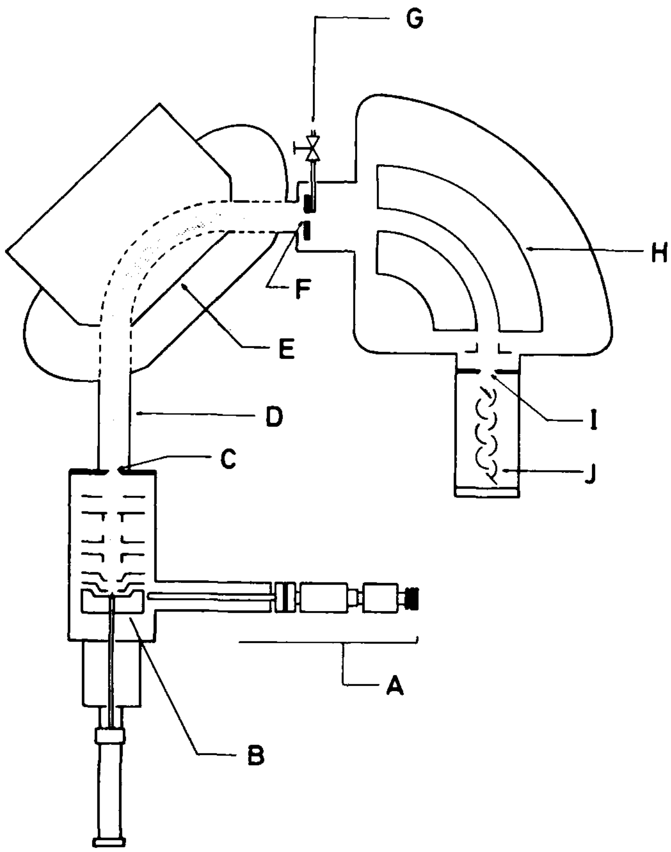
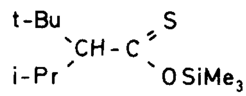


Fig. 2-1. Thermolysis unit - mass spectrometer set-up. A, Thermolysis unit; B, EI/FI/FD ion source; C, entrance slit; D, analyser tube; E, magnetic sector; F, intermediate focus slit; G, needle valve; H, electric sector; I, collector slit; J, detector (SEM).

The applicability of FIMS, in contrast to EIMS, as detection system of pyrolysis studies is convincingly elucidated by the spectra depicted in Fig. 2-2, showing the FIMS, 13 eV EIMS, and 70 eV EIMS spectra, respectively, following pyrolysis of 3,3-dimethyl-2-isopropyl (thiobutanoic)acid O-trimethylsilyl ester (I) (Carlsen et al., 1980) at 1043K (Carlsen and Egsgaard, 1980).



I

Without discussing the rather confusing complex product composition, which e.g. includes the three possible ketenes and carbenes (Carlsen and Egsgaard, 1980), Fig. 2-2 visualizes the difficulties associated with the use of EIMS, even low-voltage EIMS, as a detection system. Apparently compound I, as well as the pyrolysis product, strongly fragments under 70 eV EIMS conditions. Thus, in several cases, in contrast to the FIMS spectra, no molecular ions are observed. The low voltage EIMS spectrum may seem even more confusing in the present case, as it exhibits more pronounced molecular ions together with the fragment ions originating from the more energetically favoured fragmentation pathways. In other words, the latter spectrum to a certain extent can be regarded as a superposition of the FIMS and the 70 eV EIMS spectra.

A clear disadvantage using field ionization mass spectrometry in the present context is the inability of this technique to detect small inorganic fragments, which are often generated by pyrolysis of organic molecules, due to very low FI sensitivities, as well as for ion source geometric reasons (Beckey, 1971).

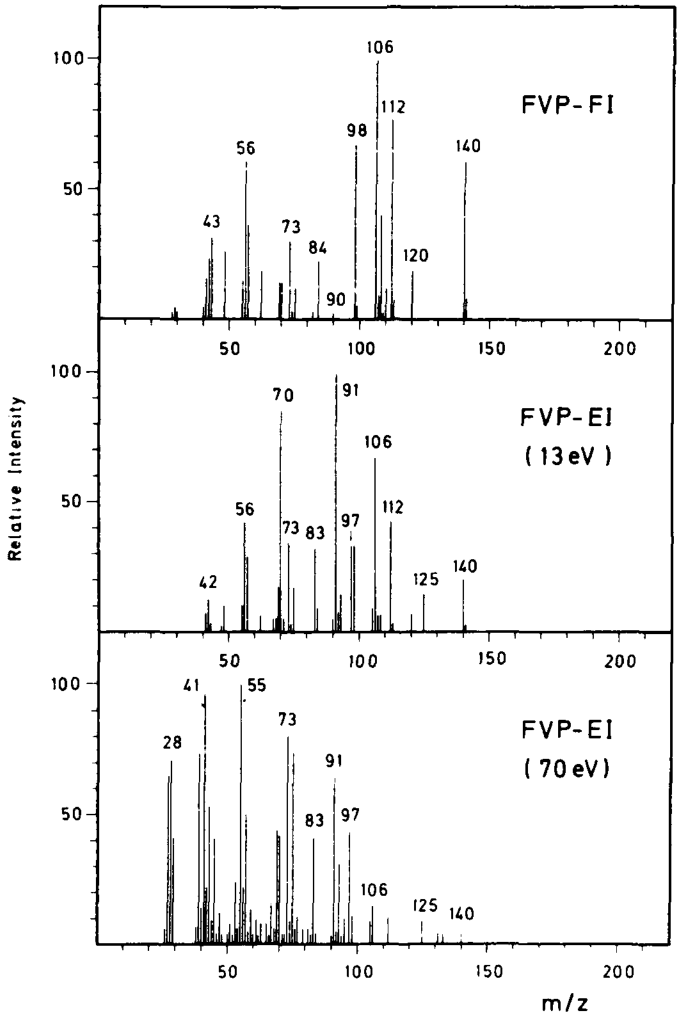
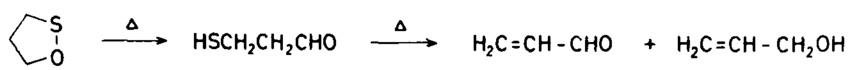


Fig. 2-2. FI-MS, 13 eV EI-MS, and 70 eV EI-MS spectra obtained following flash vacuum thermolysis of I at 1043 K. Since I is totally degraded at this temperature no molecular ion (M = 246) is observed.

Although extremely valuable important primary information on product compositions are obtained, obviously field ionization mass spectrometry alone does not give the eventual answer as to the identity of the single species, since only molecular weights are determined. To elucidate the nature of the single components further collision activation mass spectrometry appears as a highly effective tool (Egsgaard, Larsen, and Carlsen, 1982).

Due to comparable internal energies of the fragmentating ions generated by collision activation and electron impact as well as their residence time in the field-free regions and the ion source, respectively, CA and EI mass spectra resemble each other to a certain extent (McLafferty et al., 1973a, McLafferty et al., 1973b, Levsen and Schwarz, 1976). Hence, the fragmentation pattern of single components in the pyrolysis mixture can be obtained without interference from even large quantities of other species. This means that valuable structural information may be obtained by applying the fragmentation rules known from electron impact mass spectrometry.

Much more important, however, is the possibility of comparing CAMS spectra of single field ionized pyrolysis products with those of possible authentic samples, whereby unequivocal verification can be obtained. To illustrate this procedure, the gas phase pyrolytic decomposition of 1,2-oxathiolane (II) to acrolein and allyl alcohol, formed, respectively, by H_2S and S extrusion from the intermediary mercaptopropanal may serve as an example (Carlsen, Egsgaard, and Harpp, 1981; Egsgaard, Larsen, and Carlsen, 1982; Carlsen and Egsgaard, 1984a).



II

In Fig. 2-3 the partial collision activation mass spectra of the field ionized C_3H_6O pyrolysis product is visualized together with those of three possible structures, i.e. propanal, oxetane, and allyl alcohol, showing close resemblance between the latter and the pyrolysis product. It is important to note that application of EIMS combined with CAMS in this case leads to incorrect conclusions concerning the identity of the pyrolytically formed C_3H_6O isomer, since the predominant fraction of m/z 58 observed in the EI mass spectrum appears to be an EI induced fragment of the molecular ion m/z 90, exhibiting a different ionic structure.

The major pyrolysis product, acrolein, was easily identified by comparing the collision activation mass spectrum of the pyrolytically generated product with that of an authentic sample.

Despite the advocating of applying of field ionization mass spectrometry combined with collision activation mass spectrometry, noted above, it is emphasized that in studies of isomerizations and rearrangements, where both the starting material as well as the isomerized/rearranged product of necessity exhibit the highest molecular weight of the reaction mixture, the CAMS analysis can be carried out advantageously using electron impact ionization, leading to a significantly increased signal-to-noise ratio (Egsgaard, Larsen, and Carlsen, 1982).

The analysis of isomeric compounds constitutes a common problem in pyrolysis experiments. The CAMS analysis technique may be applied with advantage to such studies, which can be illustrated by the investigations on the pyrolytic isomerization of methyl acetate and the corresponding mono- and dithio analogues.

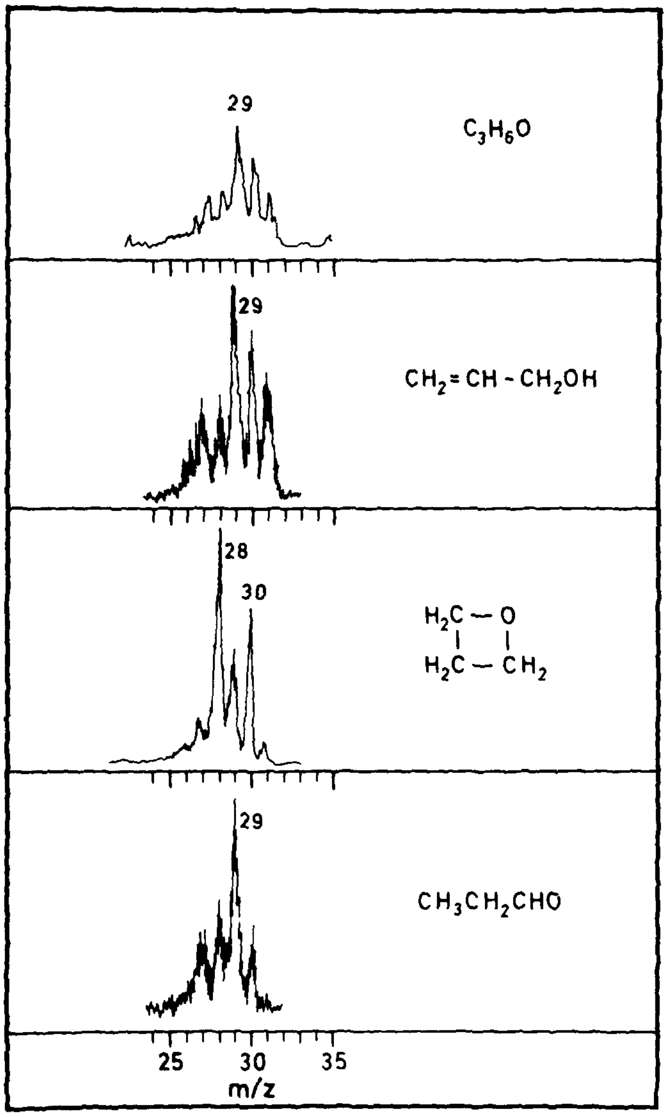


Fig. 2-3. Partial collision activation mass spectra of field induced molecular ions of (a) propanal, (b) oxetane, (c) allyl alcohol, and (d) the C_3H_6O isomer formed pyrolytically from 1,2-oxathiolane.

2.1.1. Isomerization Reactions

The isomerisation of alkyl thionoacetate into the corresponding thiolo acetates have been reported by Oele et al. (1972), Bigley and Gabbott (1975) and Carlsen and Egsgaard (1982a).

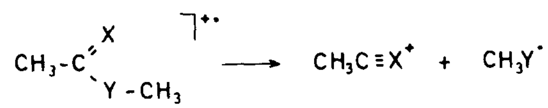
The activation data for the reactions have been estimated: $E_a \approx 45$ kcal/mol, log A ≈ 13 s^{-1}, the thermodynamical stabilization of the thiolo isomers amounting approximately 20 kcal/mol (Oele et al., 1972, Bigley and Gabbott, 1975).

As a part of an investigation of the possible formation of thioketenes from O-trimethylsilyl esters of thiocarboxylic acids (Carlsen et al. 1980) we reinvestigated the progress of isomerization of methyl thionoacetate to the corresponding thiolo ester as a function of pyrolysis temperature (Carlsen and Egsgaard, 1982a) applying collision activation mass spectrometry. Based on the CA mass spectra (Fig. 2-4) the degree of isomerization, expressed as the thiono/thiolo ratio was calculated to be 9, 1.0, and < 0.05 following pyrolysis at 1043, 1253 (not shown), and 1404K, respectively.

The unimolecular thiono-thiolo isomerization proceeds, of necessity, through a four-membered transition state, which most probably exhibits a planar structure as supported by theoretically obtained results, based on semiempirical MNDO MO calculations.

The possible isomerizations of carboxylic acid esters and the corresponding dithio derivatives cannot be studied directly, due to the identity of the starting material and the isomerized product, in contrast to the monothio species, where two distinctly different compounds, although with identical molecular weights, were to be detected. Thus, the differencies in the collision activation mass spectra (cf. Fig. 2-4) facilitates the elucidation of the thiono-thiolo isomerization.

Owing to the fragmentation pattern of the molecular ions under CA conditions, an analogous separation of the starting material at the isomerized product appeared possible studying methyl acetate and methyl dithioacetate artificially labelled with ^{18}O and ^{34}S, *respectively*, in the carbonyl/thiocarbonyl function, respectively (Carlsen, Egsgaard, and Pagsberg, 1981; Carlsen and Egsgaard, 1984b).



X	Y	m/z	m/z	m/z
^{18}O	^{16}O	76	45	31
^{16}O	^{18}O	76	43	33
^{34}S	^{32}S	108	61	47
^{32}S	^{34}S	108	59	49

The existence of a pyrolytically induced isomerization of methyl acetate was unequivocally demonstrated (Carlsen, Egsgaard and Pagsberg, 1981) studying the collision activation mass spectra of the electron impact-induced molecular ion following pyrolysis of methyl[^{18}O]acetate at different temperatures in the range 1043-1404K (Fig. 2-5).

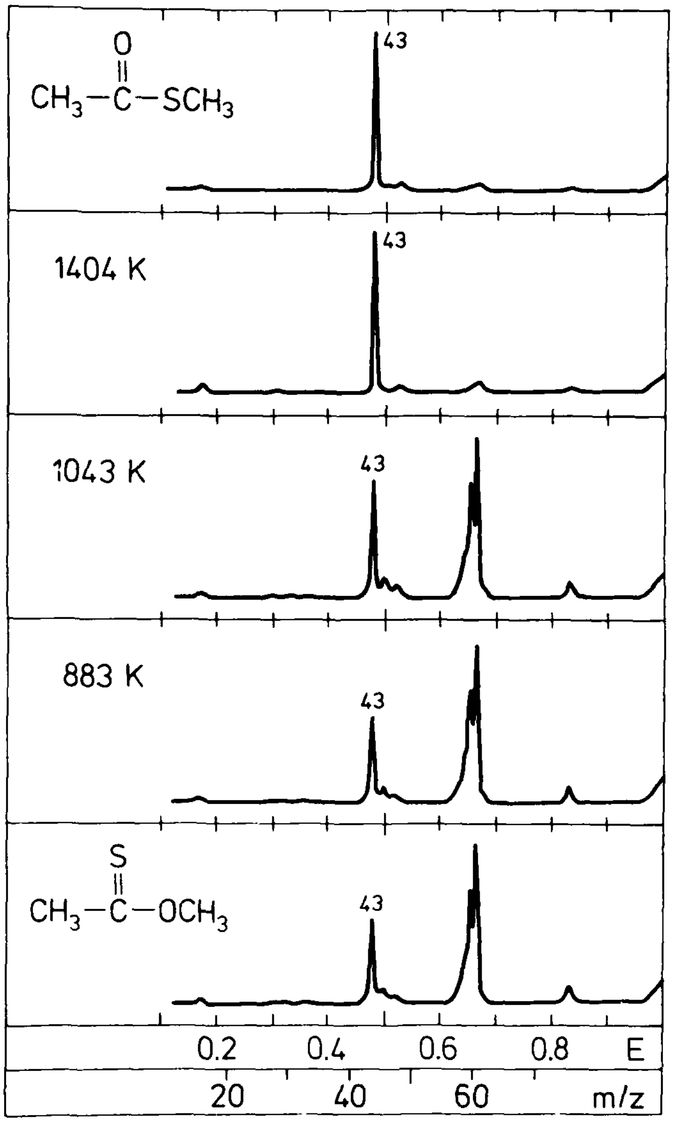


Fig. 2-4. Collision activation mass spectra of the electron impact-induced molecular ions of methyl thionoacetate without thermolysis (a), following thermolysis at 883 K (b), 1043 K (c), and 1404 K (d), respectively, and unthermolysed methyl thioloacetate (e).

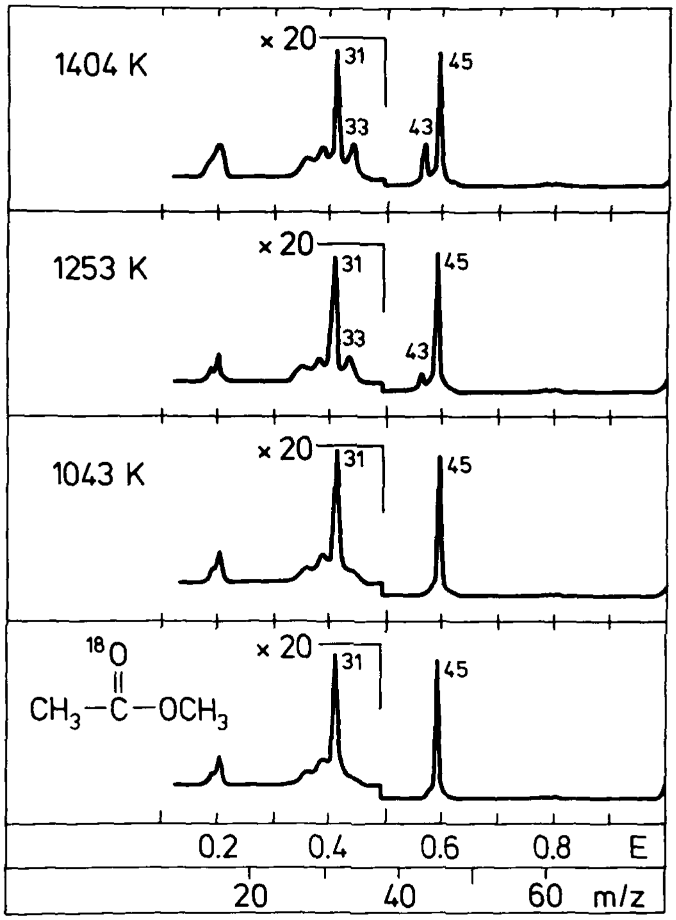
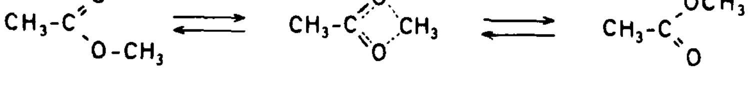


Fig. 2-5. Collision activation mass spectra of the electron impact induced molecular ion of methyl [^{18}O]acetate without thermolysis (a) and following thermolysis at 1043 K (b), 1253 K (c), and 1404 K (d), respectively.



The increased intensities of the peaks m/z 43 and m/z 33 were, according to the above discussion associated with an increasing amount of $CH_3C(O)^{18}OCH_3$ in the pyrolyzate.

Based on kinetic considerations, as well as on cross-over experiments (pyrolyzing a mixture of $CH_3C(^{18}O)OCH_3$ and $CH_3C(O)OCD_3$) we (Carlsen, Egsgaard, and Pagsberg, 1981) excluded the involvement of an acetoxyl/methyl radical pair, as a result of a homolytic $O-CH_3$ bond cleavage, in the isomerization reaction, concluding the intermediacy of a planar, symmetric four-membered transition state.

It appears reasonable to formulate the reaction as a result of vibrational excitation of two specific normal modes in methyl acetate, i.e. the OCO and the COC bends, which bring about the methyl group transfer. This suggestion finds strong support in infra-red spectroscopic studies on gaseous methyl acetate, which demonstrated that the ester, processing E-configuration, exhibits two in-plane bending modes ν_{15} 639 cm^{-1} (OCO bend) and ν_{17} 303 cm^{-1} (COC bend), as well as a combination mode 942 = 639 + 303 cm^{-1}, demonstrating a fairly strong coupling between the two normal modes (George, Houston, and Harris, 1974; Wilmshurst, 1957). Hence, the threshold energy should in principle be available through a critical set of quantum numbers (n_C, m_C) above which the two individual in-plane bending modes degenerate into one single 'hand-to-hand' vibration (Fig. 2-6). However, in practice it does not appear possible due to lack of knowledge of the actual shape of the bending potentials involved.

Based on semi-empirical MNDO MO calculations, we estimated that the isomerization of methyl acetate should be significantly more energy demanding than the methyl thiono methyl thiolo acetate isomerization by approximately 16 kcal/mol. This is in agreement with the considerably lower degree of isomerization,

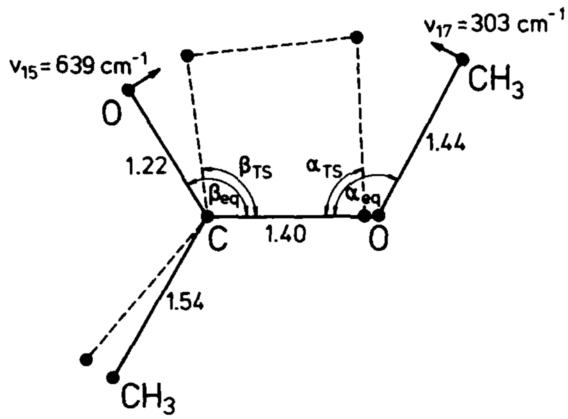


Fig. 2-6. Structure of methyl acetate (——) and the transition state for the thermally induced isomerization (·····).

at a given temperature for methyl acetate, than for the corresponding monothio derivative (compare Figs. 2-4 and 2-5). On the other hand, the possible isomerization of methyl dithio acetate was suggested to be slightly less energy demanding by 4 kcal/mol, i.e. an activation energy approximately 20 kcal/mol below that of the methyl acetate isomerization. Based on simple geometric considerations and the fact that the ester apparently posseses an E-configuration (cf. Scheithauer and Mayer, 1979), the isomerization of methyl dithioacetate appears as favourable as that of methyl acetate. On this background it appeared to be rather surprising that pyrolysis of methyl [^{34}S]dithioacetate unambiguously revealed the absence of a sulphur to sulphur methyl group migration, as demonstrated by the identity of the collision activation mass spectra of the ester before and after pyrolysis at temperatures up to 1253K (Fig. 2-7) (Carlsen and Egsgaard, 1984b).

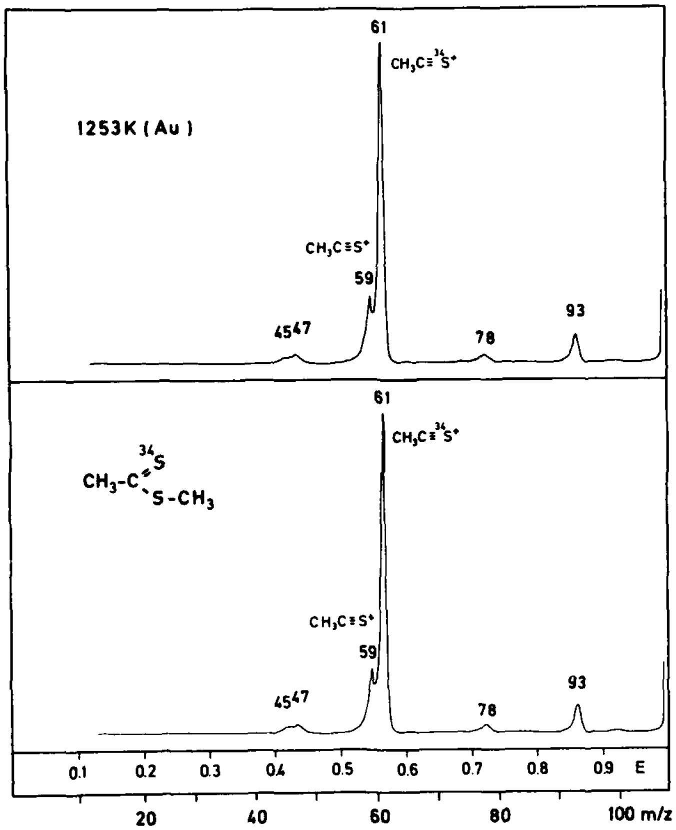


Fig. 2-7. Collision activation mass spectra of the electron impact-induced molecular ion of methyl [^{34}S]dithioacetate without pyrolysis and following pyrolysis at 1253 K.

Studies on several other dithio esters, including methyl [^{34}S]-2,2-dimethyl dithiopropionate and methyl [^{34}S]-dithiobenzoate (Carlsen and Egsgaard, unpublished) and methyl N,N-dimethyl [^{34}S]-dithiocarbamate (Carlsen and Egsgaard, 1987) analogously demonstrated the apparent absence of a sulfur to sulfur methylgroup migration.

As a consequence of the lacking S to S isomerization the possible operation of competing rearrangement reactions was studied. Thus, the absence of the expected isomerization of methyl dithioacetate was discussed in terms of a possible operation of an enethiolization reaction,[a] blocking the thiocarbonyl function. However, since no changes in the CA mass spectrum could be recorded (cf. Fig. 2-7) the reaction is supposed to be reversible (Carlsen and Egsgaard, 1984b).

Experimental support was obtained by pyrolyzing methyl dithioacetate in the presence of D_2O, resulting in an H-D exchange, apparently as a result of a reaction of the enethiole and surface bound D_2O, as convincingly demonstrated by studying the intensity of the m/z 107 ion (relative to m/z 106 and 108)[b] as the collision activation mass spectrum of m/z 107 before and after pyrolysis (in the presence of D_2O) (Fig. 2-8).

The spectra unambiguously demonstrated the incorporation of deuterium in the undecomposed ester (increase in m/z 107) as well as the eventual position of the deuterium in the acid methyl group (increase in the m/z 60 relative to m/z 59 in the CA spectrum), in accordance with the tautomerism suggested above.

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[a] enethiol tautomers of certain substituted dithioacetic acid esters have been discussed previously (Scheithauer and Mayer, 1979).

[b] before pyrolysis m/z 107 consists of isotopomers exhibiting the natural abundance of one ^{13}C or one ^{33}S.

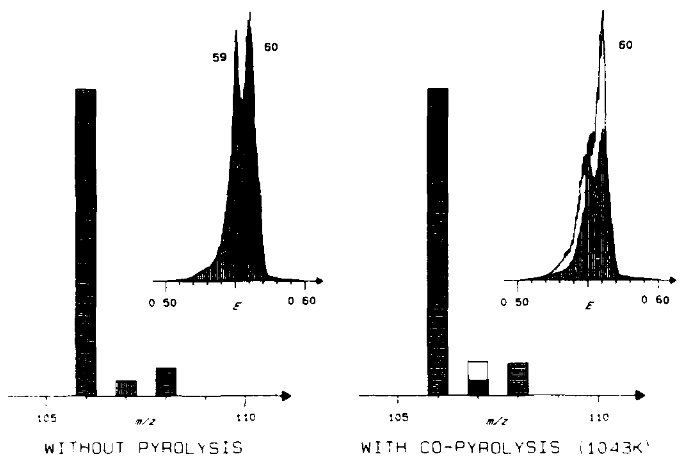
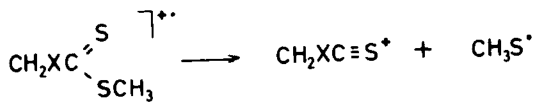


Fig. 2-8. Partial electron impact mass spectra and partial CA mass spectra (0.5-0.6 E) of the electron-impact-induced m/z 107 ion of methyl dithioacetate (a) in the presence of D_2O before pyrolyis and (b) after pyrolysis at 1043 K.



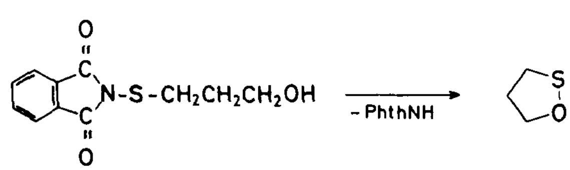
X (m/z 107)	relative abundance	m/z
H:		
$CH_3C(S)^{33}SCH_3$	0.16	59
$CH_3C(S)S^{13}CH_3$	0.23	59
$CH_3C(^{33}S)SCH_3$	0.16	60
$CH_3{}^{13}C(S)SCH_3$	0.23	60
$^{13}CH_3C(S)SCH_3$	0.23	60
D:		
$CH_2DC(S)SCH_3$	1	60

The above discussed thiocarbonyl-enethiol-tautomerism constitutes obviously only part of the explanation for the apparent lack of isomerization. Pyrolysis of methyl [^{34}S]-2,2-dimethyl dithiopropionate gave no rise to information, which could indicate the operation of a competing isomerization, which, by analogy would yield the stable 1,1-di(methylthio)-2-methyl-1-propene. However, the propene could not be detected (Carlsen and Egsgaard, unpublished). Hence, the eventual answer as to the absence of sulphur to sulphur methyl group migration in methyl dithiocarboxylates apparently is pending.

2.2. Static Systems

Although the mass spectrometric analysis of gas phase pyrolytic reactions in general is associated with pyrolysis in flow reactors, the reactions may in certain cases be carried out under static conditions, maintaining the general analysis concept, however. In these cases the reactors appear as large thermostated reservoirs directly, through a needle valve, connected to the detection system. In principle, this technique may be applied to all types of detection systems. However, certain mass spectrometers are equipped with thermostatable gas-inlet systems (temperatures up to 500 K available), which constitute an excellent reactor for gas phase reactions (see e.g., Carlsen and Egsgaard, 1984a). A disavantage, which should be taken into account, is the relatively high operating pressure (ca. 0.1 torr), which is up to several orders of magnitude higher than commonly used in flow reactors.

As obvious substrates to be studied applying the static pyrolysis system are such species, which are reasonably stable in diluted gas-phase at ambient temperature, however, decomposing slowly ($t_{1/2}$ > 5 min) at higher temperature. Typical examples would be gaseous species produced by cracking solid material as e.g. 3-mercapto propanal from the corresponding oligomer (Carlsen et al., 1984) or 1,2-oxathiolane from 3-(phthalimidothio)propane-1-ol, leaving the non-volatile phthalimid (Davis and Whitham, 1981, Carlsen et al., 1981), the first, and hitherto only unsubstituted cyclic sulphenate to be isolated.



We reported the intermediacy of 1,2-oxathiolane in the gas-phase pyrolyses of 1,2-oxathiolane 2-oxide and thietane 1-oxide (Carlsen, Egsgaard and Harpp, 1981), partly based on the observed pyrolysis products. These were acrolein and allyl alcohol. Analogously 1,2-oxathietane was suggested as intermediate in the pyrolyses of 1,2,3-oxadithiolane 2-oxide and thiirane 1-oxide (Carlsen and Egsgaard, 1982b).

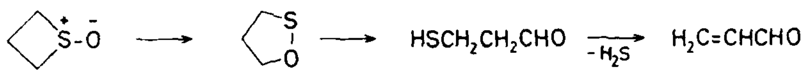
2.2.1. 1,2-Oxathiolane

We studied the thermal decomposition of 1,2-oxathiolane and thietane 1-oxide in a static system at temperatures in the range of 400-450K, the eventual product in both cases being acrolein alone (Carlsen and Egsgaard, 1984a). Following the progress of thermal decomposition of 1,2-oxathiolane by collision activation mass spectrometry of the electron impact-induced ion m/z 90 and comparing it to those of authentic 1,2-oxathiolane (Carlsen et al., 1981) and 3-mercapto propanal (Carlsen et al. 1984) demonstrated the intermediacy of the latter (Fig. 2-9), as the spectra depicted in Fig. 2-9b and c, unambiguously are to be assigned as superpositions of those given in Fig. 2-9a and d, respectively (Carlsen and Egsgaard, 1984a).

An analogous set of CA mass spectra elucidating the thermolysis of thietane 1-oxide is depicted in Fig. 2-10 (Carlsen and Egsgaard, 1984a).

A comparison of Figs. 2-10b and 2-9a strongly suggest the presence of considerable amounts of 1,2-oxathiolane in the reaction mixture responsible for the former spectrum. Prolonged thermolysis (Fig. 2-10c and d) resulted in fragments characteristic for 3-mercapto propanal (cf. Fig. 2-9d). This, combined with the fact that the eventual product being acrolein which also was observed as the only product upon thermolysis of authentic

3-mercapto propanal (Carlsen et al. 1984) unambiguously demonstrated the operation of the reaction sequence



Further elucidation of the fate of 1,2-oxathiolane was obtained by studying the thermal decomposition of the 5,5-dideutero substituded species (Carlsen and Egsgaard, 1984a). It appeared that two different acroleins, containing one and two deuterium atoms, respectively, were produced (Fig. 2-11).

Partly based on the collision activation mass spectra of the field ionized molecular ions of the single acroleins (Fig. 2-12) partly on the rationalization of the 3-mercapto propanal decomposition, the two acroleins could be assigned to CH_2=CH-CDO and CD_2=CH-CHO, respectively.

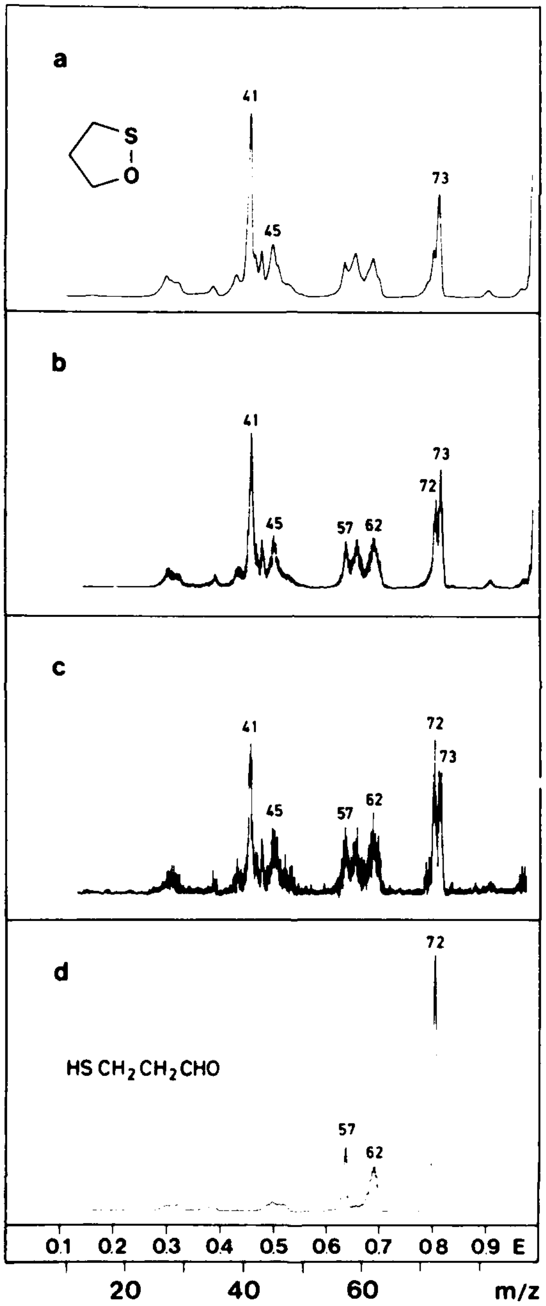


Fig. 2-9. Collision activation mass spectra (CAMS) of the electron impact-induced molecular ions of authentic 1,2-oxathiolane (a) and 3-mercaptopropanal (d), and of the ion m/z = 90 obtained following 35 (b) and 50 (c) min thermolysis (450 K) of 1,2-oxothiolane.

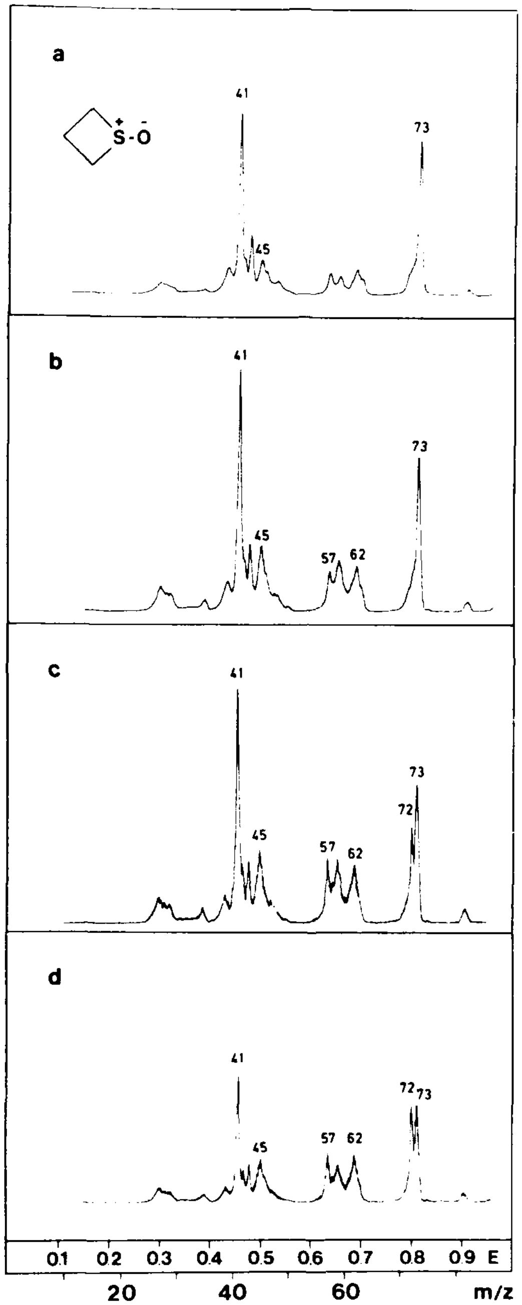


Fig. 2-10. Collision activation mass spectra (CAMS) of the electron impact-induced molecular ions of authentic thietane 1-oxide (a) and of the ion m/z = 90 obtained following 4 (b), 40 (c), and 80 (d) min thermolysis (450 K) of thietane 1-oxide, respectively.

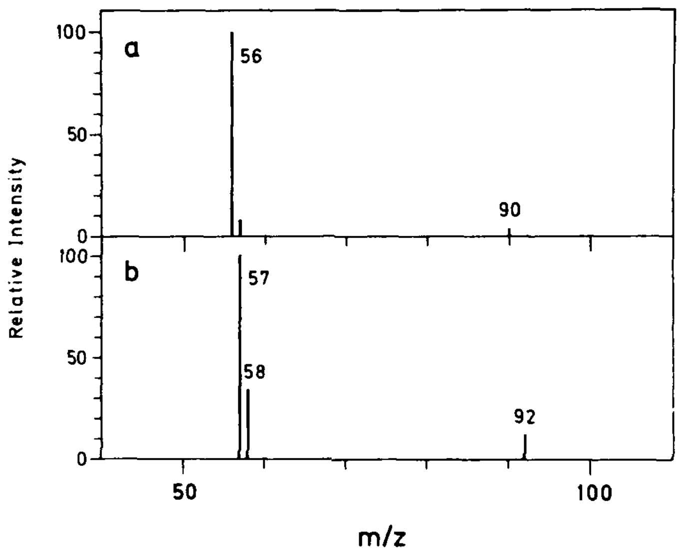


Fig. 2-11. Field ionization mass spectra obtained following 25 min thermolysis (425 K) of 1,2-oxathiolane (a) and [5,5-$^2H_2$]-1,2-oxathiolane (b).

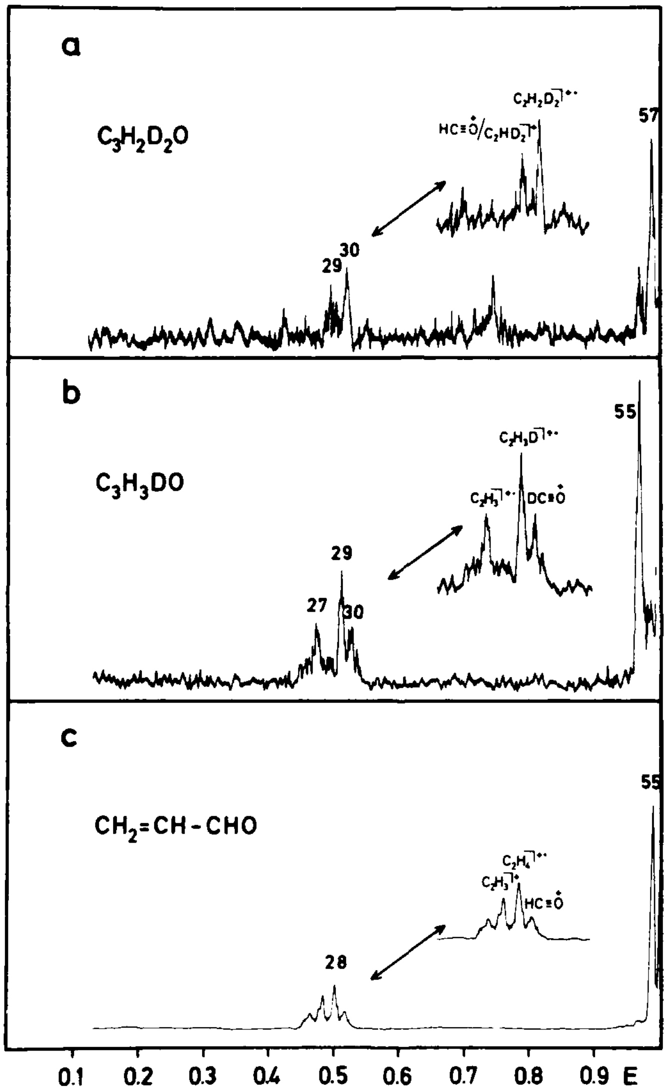
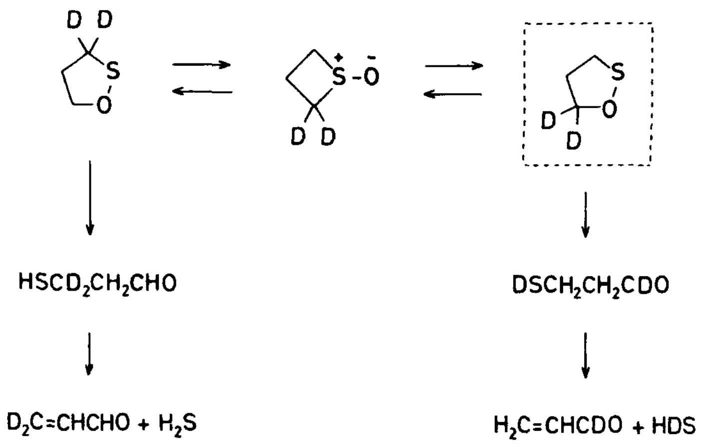


Fig. 2-12. Collision activation mass spectra of the field ionized molecular ions of acrolein (c), [1-^{2}H]acrolein (b), and [3,3-$^2H_2$]acrolein (a) obtained following thermolysis of 1,2-oxathiolane and [5,5-$^2H_2$]-1,2-oxathiolane, respectively.

Based on the information discussed above we rationalized the thermal decomposition of 1,2-oxathiolane as follows (Carlsen and Egsgaard, 1984a).



2.3. The Importance of Reference Structures

The application of pyrolytic techniques to generate reference structures for mass spectrometric studies has been reported, the profitable use of unimolecular gas phase pyrolysis being closely connected to the fact that this technique often constitute a route to otherwise non-accessible structures. This feature of gas phase pyrolysis is illustrated by the formation of N-phenylketenimine from acetanilide (Egsgaard, Larsen, and Carlsen, 1982) in connection with mass spectrometric studies of phenyl pyrazoles (Pande et al., 1981), phenyl imidazoles and phenyl triazoles (Larsen et al., to be published), as well as by the formation of isomeric phenyl azirines from "styryl azides"(Larsen, Egsgaard, and Jørgensen, to be published).

The reverse situation, i.e. mass spectrometric generation of reference structures for pyrolysis studies, is likewise of interest, as the elucidation of ion structures can be carried out by numerous methods. Hence, a well-defined ion can be the rational basis for the identification of an unknown neutral compound, e.g. formed pyrolytically, by the application of MS-MS techniques, as e.g. collision activation mass spectrometry. This aspect can be illustrated by the search for the neutral aci-tautomer of nitromethan among the products generated by low-pressure pyrolysis of nitroalkanes (Egsgaard, Carlsen, and Elbel, 1986). The reference ion (CH_2=N(O)$OH^{+\bullet}$) is easily accessible by specific electron impact-induced elimination of ethylene from the molecular ion of 1-nitropropane (Nibbering, deBoer, and Hofman, 1965).

As visualized in Fig. 2-13 collision activation mass spectrometry appears as highly specific, as the spectra of the two isomers exhibit destinct characteristics. Hence, the formation of even minor amounts of the aci-nitromethan among the pyrolysis products of nitroalkanes should easily be disclosed. However, all attempts remained negative, indicating high thermal lability on aci-nitromethan, if formed (Egsgaard, Carlsen, and Elbel, 1986).

As previously mentioned, the course of reaction may often, although not necessarily, be found to be dependent of the pyrolysis system used. Hence, the application of combinations of detection techniques may turn out to be advantageous in many cases. In the present context the combined use of mass spectrometry and photoelectron spectroscopy shall be emphasized.

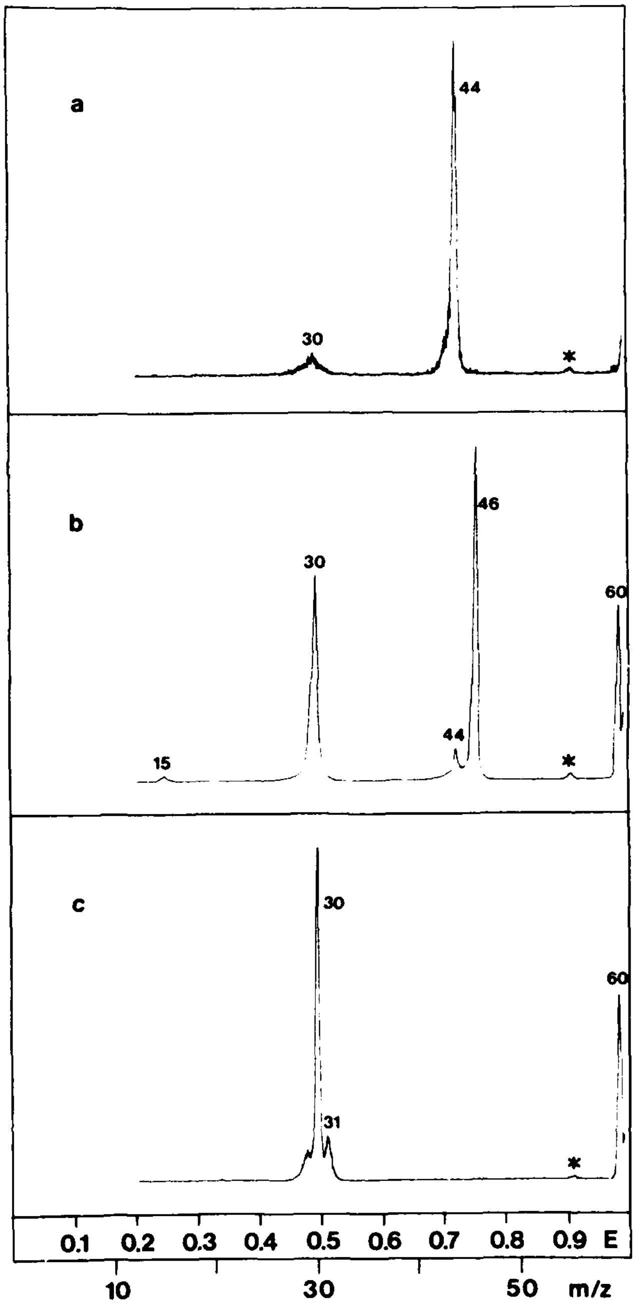


Fig. 2-13. Collision activation mass spectra of m/z 61 of 1-nitropropane (a) and the molecular ions of nitromethane (b) and methylnitrite (c).

An example of the advantageous combination of mass spectrometry and photoelectron spectroscopy is our studies on the 1,2-oxathiolan/3-mercaptopropanal system (Carlsen et al., 1981, Jørgensen and Carlsen, 1983, Carlsen et al., 1984). The existence of the species was established based on MS investigations, the electronic structure subsequently being elucidated by photoelectron spectroscopy. Likewise, the MS/PES interplay in the study of di-tert.-butylphosphazene(tBu-N=P-tBu) may serve as an illustrative example (Elbel et al., 1985).

In a recent study on the pyrolytic decomposition of the eight-membered tetrathiatetrazocine ($H_4N_4S_4$) ring, applying both mass spectrometric and photoelectron spectroscopic detection techniques, we (Carlsen, Egsgaard, and Elbel 1985) presented the first evidence for the formation of sulphur diimide. By mass spectrometry the formation of a compound with the molecular weight 62 was established, unambigiously exhibiting the molecular composition H_2N_2S. An analogous study of the corresponding tetramethyl derivative revealed a product with the molecular weight 90, the latter being assigned to $(CH_3)_2N_2S$. Photoelectron spectroscopy demonstrated, by comparison to known ionization potentials of dimethyl sulphur diimide (Schouten and Oskam, 1977) the identity of the "90". Hence, it was concluded by analogy that the "62" could be assigned to sulphur diimide.

$$R_4N_4S_4 \xrightarrow{\Delta} RN{=}S{=}NR$$

$$R = H, CH_3$$

The effectiveness of the combined use of mass spectrometry and photoelectron spectroscopy was also demonstrated by Elbel et al. (1986) in their study on the generation of gaseous $AsCl_4F$ from the salt $AsCl_4{}^+AsF_6{}^-$, and analogously PCl_4F from $PCl_4{}^+PF_6{}^-$ (Elbel et al. unpublished).

3. SAMPLE/INLET SYSTEM

The choice of inlet system is closely related to the nature of the sample. Thus, the problems concerning sample introduction can be subdivided according to whether the sample is (a) gaseous or easily evaporable, (b) a liquid exhibiting a moderate to low vapour pressure at ambient temperature, or (c) a solid. To the latter class of samples belong solid oligomeric species, whereby the monomeric species can be generated in the gaseous state by gentle heating.

In general a continuous flow of reactants into the pyrolysis reactor is desirable, which consequently will result in a constant flow of pyrolysis products from the reactor, greatly facilitating the analytic procedure. However, in certain cases involving liquid samples exhibiting only very low vapour pressures at ambient temperature, the latter can be introduced into the reactor by injection via a heatable injection block. Due to the very limited amount of material available by the injection technique only mass spectrometry appears to be sufficiently rapid to be applied as an analysis technique. As an alternative, the inlet system for solid samples (vide infra) may be used.

The main requirement to the inlet system is the supply of the necessary amount of reactant per unit time to the pyrolysis reactor, which eventually depends solely on the pressure requirement of the analytical system. In practice, the rate of gaseous sample introduction can be controlled by the temperature of the sample reservoir and/or by a constrictor between the sample reservoir and reactor, the pressure in the latter in general being several orders of magnitude below that of the reservoir.

In the case of gaseous or easily evaporable compounds a gas-inlet system, as commonly used in mass spectrometry, can be applied advantageously. The system consists of a closed reservoir connected to the reactor by a constrictor, which can be a needle valve or simply a glass capillary possessing an appropriate leak-rate. The substance-requirement for the mass spectrometric analysis is as low as ca. 0.1 μg/s (Egsgaard and Carlsen, 1984).

For substances exhibiting moderate to low vapour pressures at ambient temperature a combination of a heatable reservoir and a constrictor can be used to advantage. However, it is often necessary to heat the complete inlet system in order to avoid undesirable recondensation of the reactant in the colder parts of the latter. Furthermore, compounds of this type frequently appear to be adherent, and extensive flushing may be necessary to avoid interference from preceding experiments. In 1984 we reported a rather simple inlet system, applied to pyrolysis-mass spectrometry, consisting of a capillary leak only (Egsgaard and Carlsen, 1984). The liquid sample is placed directly into the leak cavity, the desirable amount of material (ca. 0.1 μg/s) evaporating continuously through the leak into the pyrolysis reactor. However, since the mass flow through the leaks is considerably higher under these conditions than with the gaseous samples, leaks possessing correspondingly lower leak-rates are used.

In the case of solid samples or liquid samples exhibiting only very low vapour pressures at ambient temperature, the flow of gaseous reactant from the reservoir into the pyrolysis reactor is advantageously controlled by the reservoir temperature in such a way as to maintain the desired mass flow per unit time.

For solid oligomeric substances, from which the gaseous monomeric species can be generated by smooth thermal cracking the "solid" inlet system described above appears favourable in gas-phase pyrolytic studies of the latter. However, application of the inlet to evaporate solids, or liquids with very low vapour pressures in general may well lead to problems due to condensations of the samples in the colder parts of the inlet system. A uniformly heated inlet system will, of course, remedy the problem in cases where this is possible.

In Fig. 3-1 the three different inlet systems, applicable to the pyrolysis-mass spectrometric system (Egsgaard and Carlsen, 1984) are visualized.

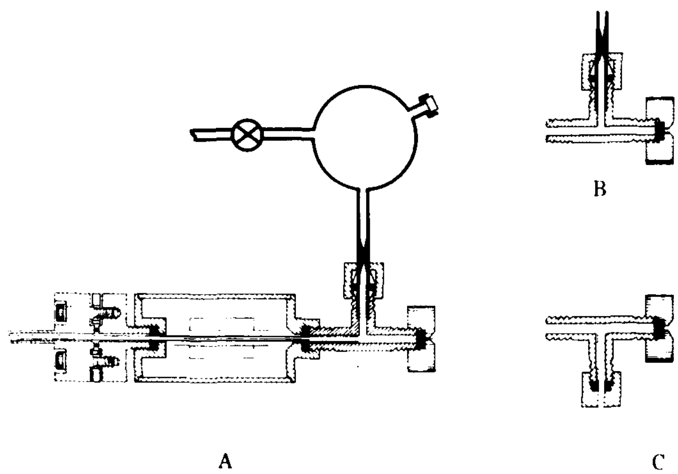


Fig. 3-1. Inlet systems for low-pressure Curie-point pyrolysis: (A) continuous gas inlet system assembled with the PV4000 pyrolysis unit. (B) the continuous "liquid" inlet system, and (C) the "solid" inlet system.

4. THE PYROLYSIS REACTOR

In the course of time a wide variety of pyrolysis reactors, differing in size, geometry, material, etc. have been used. Often the single research groups working in the field of gas phase pyrolysis construct their own reactors with special regard to the type of analytical tool to be applied. However, all these different types of reactors, which shall not be described here, are based on relatively few common principles. A series of these more or less different reactors has been reviewed by Brown (1980).

In most cases pyrolysis reactors constructed in quartz have been used, ranging from the simplest, where the reactor is merely a quartz tube passing through a furnace, as applied by Bock and co-workers (Bock and Solouki, 1981, and references therein) to highly sophisticated constructions that have the possibility of changing the area of the orifice (Golden, Spokes, and Benson, 1973). In all cases, when using quartz reactors electric heating is necessary. As an alternative to quartz reactors some groups prefer metal-based reactors, often of stainless steel. The heating of these reactors can be accomplished electrically or by electron bombardment, as recently reported by Elbel et al. (1981); this system is commercially available.

An alternative reactor design/heating technique in the study of gas phase pyrolytic reactions is based on the Curie point pyrolysis technique (Simon and Giacobbo, 1965), i.e. the high frequency inductive heating in ferro-magnetic materials. The technique is widely used as an analytical tool in connection with gas chromatography and/or mass spectrometry in the study of involatile substances (Irwin, 1979, cf. also Voorhees 1984, Schulten, 1985). The first report on the application of the technique to low-pressure gas phase pyrolytic studies appeared only recently (Carlsen and Egsgaard, 1980). However, it has been proved to be a highly effective technique in combination with mass spectrometry. In Fig. 4-1 the pyrolysis unit based on the Curie point principle mounted with a heatable injection block is shown (compare also with Fig. 3-1).

The more pronounced difference between the conventional reactor designs and the equipment for Curie-point pyrolyses is the nature of the heated zone. In conventional equipment the reactor as such is heated, i.e. all internal surfaces are heated to the pyrolysis temperature, whereas in the Curie-point pyrolyzer the walls of the reactor in principle maintain ambient temperature, and only the ferro-magnetic filament placed ideally in the center of the reactor constitutes the heated area.

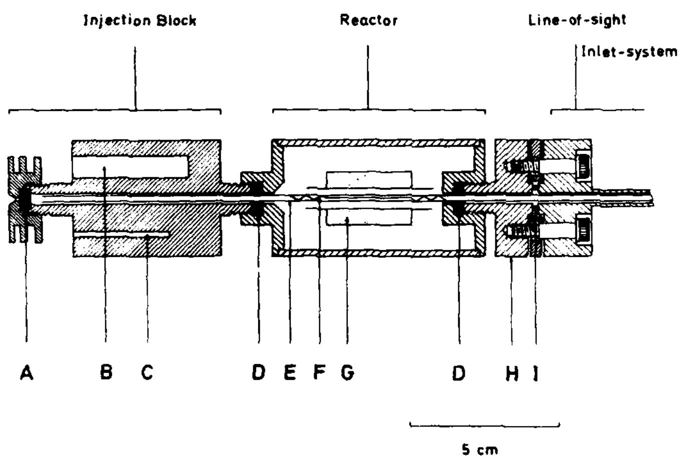


Fig. 4-1. Thermolysis unit. A, Septum; B, injection block heater; C, thermocouple for temperature readout; D, rubber washer; E, quartz lining tube; F, ferromagnetic wire; G, high frequency induction coil; H, adapter flange; I, gold wire sealing.

In contrast to the more conventional types of pyrolysis reactors the Curie-point pyrolysis technique, as generally applied suffers from some disadvantages: 1) the limited number of temperatures available, 2) the differencies in composition of the single ferro-magnetic filaments available, and 3) the enhanced possibility of reactions induced by collision between the reactant molecules and the hot, reactive metal sufaces as e.g. nickel or iron. The last of these disadvantages also applies to a certain extent to the more conventional reactors. Considerable efforts have been devoted to diminish or possibly remedy these problems.

It should be noted that a major advantage of the inductive heating technique is the very limited amount of reactor material which has to be heated in contrast to the completely heated conventional reactors. Hence, the heating rate by inductive heating is known to be very rapid, as the Curie-point can be reached usually within milliseconds to seconds, but also the subsequent cooling of the filament back to ambient temperature is rapidly achieved due to the limited ammount of heated material. This, of course, is a clear advantage when pyrolytic reactions are to be studied at different temperatures, in which cases the use of conventional reactor designs may be rather time consuming.

Furthermore, the fact that the heating can be achieved without introduction of electric wires into the low-pressure reactor, as would be necessary if electric heating of the filament were applied, must be regarded as a clear advantage.

4.1. The Knudsen Reactor

As mentioned previously, the low pressure in the pyrolysis reactor is required in order to exclude the possible operation of bimolecular reactions. In cases where mass spectrometry or photoelectron spectroscopy is used as detection system, this requirement is generally fulfilled, whereas it may be dubious if it always is the case using microwave spectrocscopy.

However, consecutive pyrolysis of primary-generated products may also disturb the eventual analytical interpretation. Hence, it is desirable that the mean residence time in the reactor (contact time in the hot zone) can be kept at a sufficient low level to avoid re-pyrolysis.

In low pressure pyrolysis reactors, fulfilling this requirement the mean free path for the molecules are typically larger than the diameter of the reactor. At these very low pressures the reactors fulfil the requirements for a Knudsen reactor (Seybold, 1977, Golden, Spokes, and Benson, 1973, Knudsen, 1909a, Knudsen, 1909b, Clausing, 1931/32, Venema, 1973) i.e. the mean residence time, t_{mr}, for a molecule depends on the actual reactor geometry, the temperature, and the molecular weight of the involved species only, and not the internal pressure in the reactor. The mean residence time can then be calculated according to the Knudsen formula (eqn. 4-1)(Golden, Spokes, and Benson 1973, Dushman, 1960:ch. 2).

$$t_{mr} = 4V/\bar{c}AK \quad \text{sec} \qquad (4-1)$$

Where V is the reactor volume, A the area of the orifice, K a constant, and $\bar{c}$ is the mean molecular rate, which can be estimated according to the kinetic gas theory (eqn. 4-2).

$$\bar{c} = 1.46 \times 10^{+4} \sqrt{(T/M)} \quad \text{cm sec}^{-1} \qquad (4-2)$$

In eqn. 4-2, T is the absolute temperature and M the molecular weight of the compound under investigation.

The collision frequency in the reactor, i.e. the frequency by which an average molecule collides with the walls, is given by

$$\omega = Z/t_{mr} = \bar{c}A_w/4V \qquad (4\text{-}3)$$

where Z is the collision number of the average molecule, $Z = A_w/AK$, and A_w is the area of the reactor surface.

The value of the constant K is dependent of the design of the interface between the reactor and the detection unit. The ideal value, K=1 is valid only if the thickness (l) of the wall, in which the orifice (radius = r) is located, is vanishingly small compared to r. If, however, the pyrolyzate leaves the reactor through an orifice which consists of a tube for which the l/r ratio is appreciable, the factor K, which is a dimensionless function of l/r, is less than 1 (Dushman, 1960:ch. 2, Venema, 1973). The factor K is the so-called transmission probability, i.e. the probability that a molecule entering the tube from the reactor will pass through the tube without having returned to the rector (Venema, 1973). The variation in K as a function of l/r is depicted in Fig. 4-2.

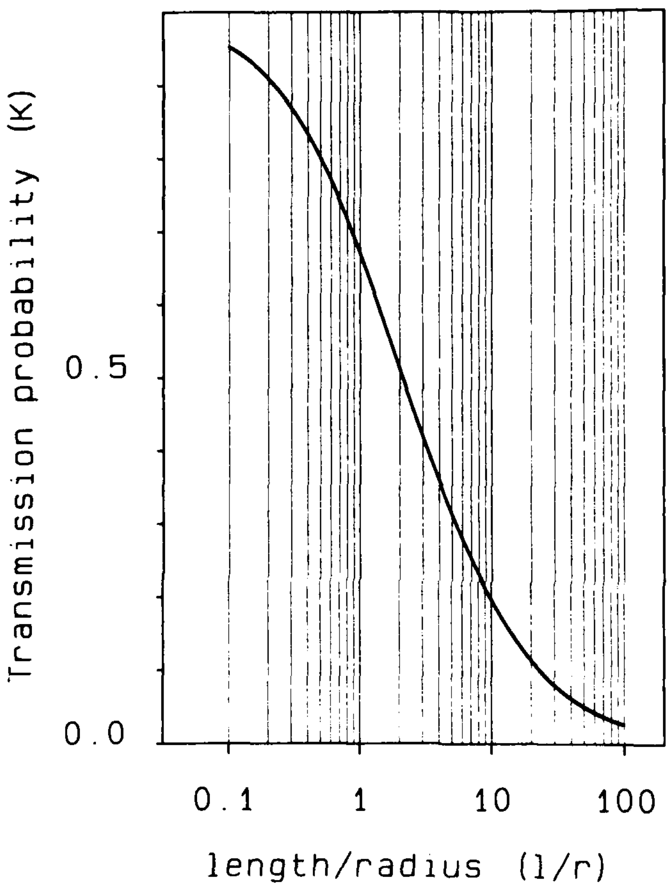


Fig. 4-2. Transmission probability (K) as a function of the length-to-radius (l/r) of a cylindrical tube.

In Table 4-1 values for $\bar{c}$ and t_{mr} for two molecules with molecular weight 100 and 200, respectively, are given as functions of temperature for a typical gas phase Curie point reactor ($V=0.13\ cm^3$, $A=0.03\ cm^2$) (Egsgaard and Carlsen, 1984).

Table 4-1 Mean molecular rate ($\bar{c}$)[a] and mean residence time (t_{mr})[b] as a function of temperature.

M\T	300		500		700		900		1100	
	$\bar{c}$	t_{mr}	$\bar{c}$	t_{mr}	$\bar{c}$	t_{mr}	$\bar{c}$	t_{mr}	$\bar{c}$	t_{mr}
100	2.53	6.85	3.26	5.31	3.86	4.49	4.38	3.96	4.84	3.58
200	1.79	9.69	2.31	7.51	2.73	6.35	3.10	5.60	3.42	5.06

[a] given in $cm\ sec^{-1} \times 10^{-4}$
[b] given as $sec \times K \times 10^{4}$

The reciprocal of the mean residence time, $k_e=t_{mr}^{-1}$, is defined as the so-called unimolecular escape rate constant, i.e. the rate constant for the discharge of the molecule from the reactor reactor through the orifice of area A.

4.1.1. Simulation of Molecular Movement through Low-Pressure Reactors

In order to design the optimal configuration of low-pressure pyrolysis reactors - for a given type of experiments - a knowledge of the fate of the gaseous molecules is of importance. Several factors are determining in this context, such as collision number, mean residence time and energy transfer from the surface to the molecule. In the case of a Curie-point pyrolysis reactor, the problem becomes even more complicated, as the molecule-surface interactions are divided in collisions between the hot filament surface and with the reactor surface, the latter typically exhibiting ambient temperature. Hence, thermal activation as well as deactivation must be considered (Egsgaard and Carlsen, 1987b).

Calculations on molecular movement in low pressure reactors are based on the following assumptions: a) the behaviour of a highly rarefied gas can be described on the basis of the individual behaviour of the single molecules (molecular flow (Knudsen 1909a, 1909b)), as the molecules are no longer in collective motion, i.e. there are no intermolecular collisions in the reactor. Thus, the molecules move linearly between the positions of the surface at which they collide; b) a molecule, striking the surface is repelled in a direction which is totally independent of the direction of the incidence, and the distribution of directions of an infinitely large number of molecules after reflection from a surface follows Lambert's cosine law for the reflection of light from a glowing body (typically the statistics are based on 1000 to 5000 molecules (Egsgaard and Carlsen, 1987b)); c) all molecules enter the reactor at a given position, this position, however, being left according to b) (Egsgaard and Carlsen, 1987b). In Figures 4-3 and 4-4 the simulated movement of a molecule through a conventional reactor and a Curie-point pyrolysis reactor, respectively, is shown. In Figure 4-4 the * denotes the collisions between the molecule and the hot filament surface. Evidently a series of molecule-wall collisions, i.e. thermal deactivation, take place between two molecule-filament collisions. Hence, the pyrolysis products observed apparently are results of single collisions between the substrate and the hot filament surface.

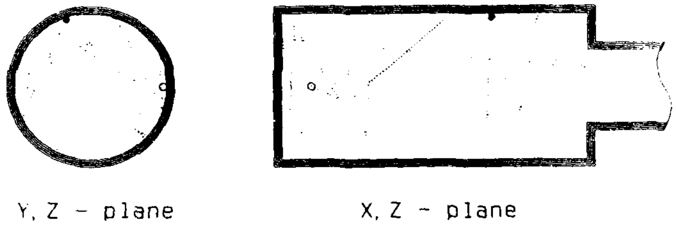


Fig. 4-3. Simulation of molecule movement (15 collisions) in a conventional low pressure pyrolysis reactor (o: start position, •: end position).

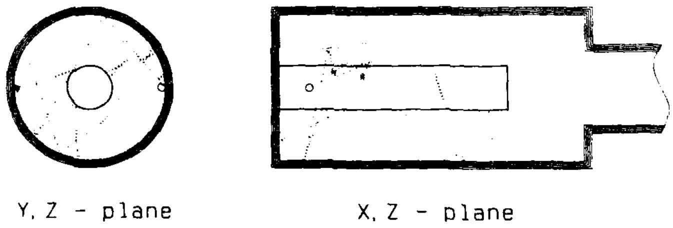


Fig. 4-4. Simulation of molecule movement (15 collisions) in a low pressure Curie-point pyrolysis reactor (o: start position, •: end position).

The movement of the molecules through the Curie-point reactor (visualized in Fig. 4-4) unambiguously demonstrates the single-collision nature of the pyrolysis reactions in this type of reactor. Thermal activation can take place only by molecule-filament collisions.

4.2. Temperature Control

The more common reactors for gas-phase pyrolysis are equipped with external heating, i.e. the entire internal surface of the reactor becomes heated to the pyrolysis temperature.

As mentioned in the previous section the use of the inductive heating principle in practice remedies the problem concerning the amount of material to be heated, as only the filament placed internally in the reactor is heated. However, as also mentioned, the Curie-point pyrolysis technique, as originally applied, permits pyrolysis only at a relatively limited number of temperatures, corresponding to the availability of ferro-magnetic filaments: e.g. 358, 480, 510, 610, 770, 980, and 1131°C. It can be mentioned that pure cobalt exhibits the highest Curie-point known (1131°C). On the other hand, it is important to note that a Curie-point of a ferro-magnetic material is extremely well defined, and since the material itself in principle controls the temperature by the ferromagnetic to diamagnetic transition at the Curie-point, one obtain highly reproducible and well-defined temperatures in applying the Curie-point pyrolysis technique.

In order to overcome the "temperature problem", however, maintaining the advantages of the inductive heating principle, e.g. reactor design (vide supra), rapid heating, the limited amount of material to be heated, we (Egsgaard, Bo, and Carlsen, 1985) reported an inductively heated flow reactor where arbitrarily chosen temperatures in the range from ambient to the Curie-point of the filament rapidly can be achieved. The temperature control was based on the application of a "multi-temperature" filament in combination with extensive computerization of the pyrolysis-mass spectrometry system.

The "multi-temperature" filament was constructed (cf. Fig. 4-5) by fixing a chromal-alumal thermocouple by gold-soldering inside a gold-plated iron tube (O.D.: 1 mm; I.D.: 0.8 mm). Eventually the assembled filament was gold-plated as described by Egsgaard and Carlsen (1983a) to ensure a low-catalytic surface (vide infra).

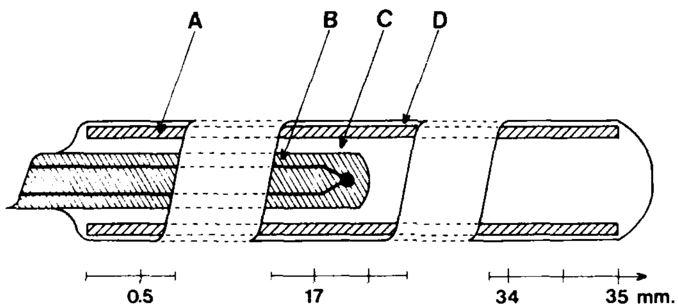


Fig. 4-5. "Multi-temperature filament" design. A, Ferromagnetic (e.g., Fe) tube; B, thermocouple; C, gold matrix; D, gold plating.

In contrast to the conventional Curie-point pyrolysis technique, where the high-frequency unit is operated continuously throughout the duration of the pyrolysis, the multi-temperature inductive heating method is based on a pulse-mode operated high-frequency unit. Attainment of a given arbitrary temperature appears as a three parameter process: 1) a rapid sequence of high-frequency pulses to obtain the temperature required, 2) a simple on/off procedure to gain thermal equilibrium in the filament, and 3) a final control based on high-frequency pulses delivered only if the temperature profile is decreasing and if the temperature is below the chosen value as summarized in Fig. 4-6.

In Fig. 4-7 temperature variations with time are shown for T_f= 400, 500, 600, and 700°C, whereas Fig. 4-8 illustrates the actual temperature stabilization, which in general can be achieved better than ± 1%.

The multi-temperature inductive heating method relies heavily on computerization, since the high rates of temperature increase obtained by this technique requires rapid control of the high-frequency unit (cf. Egsgaard, Bo, and Carlsen, 1985). The computerized pyrolysis - mass spectrometry system is visualized in Fig. 4-9.

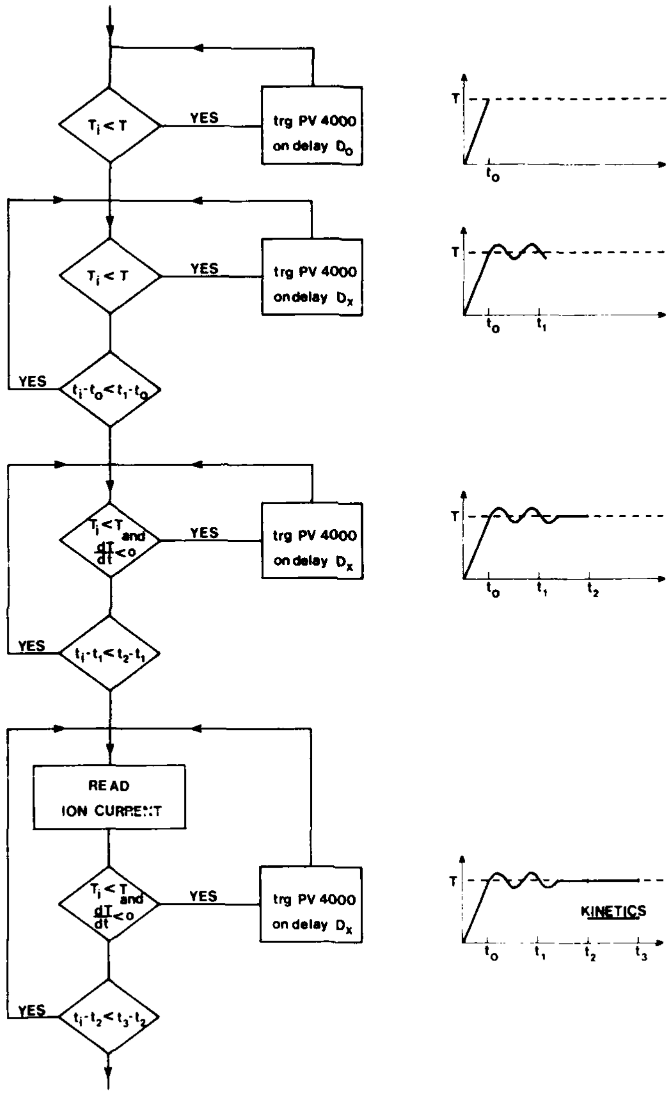


Fig. 4-6. Temperature control flow chart for "multitemperature filament".

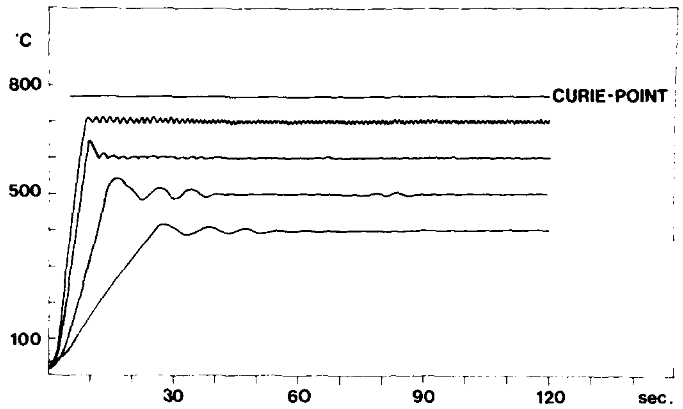


Fig. 4-7. Arbitrary temperature selection by "multitemperature filament" (T_f = 400, 500, 600 and 700°C).

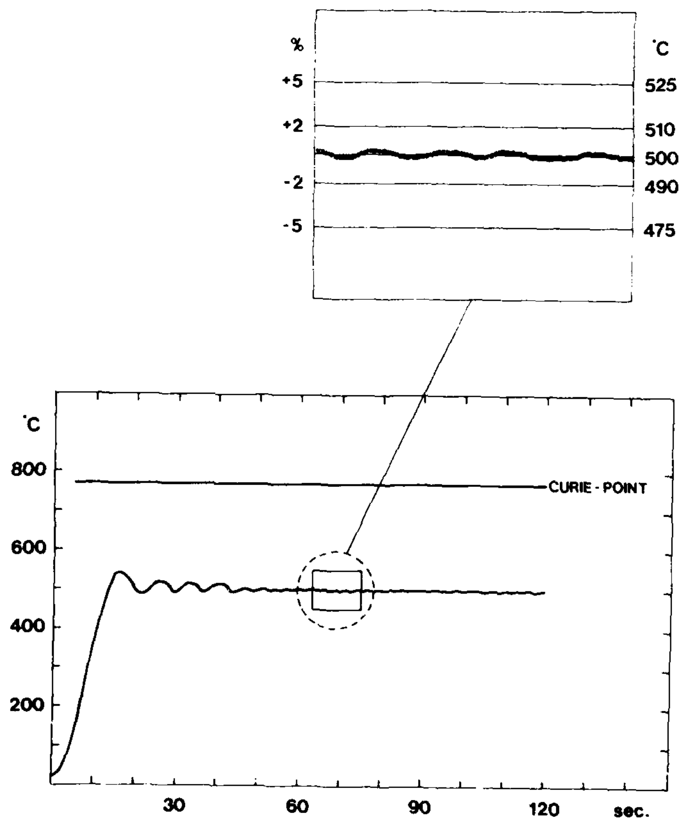


Fig. 4-8. Temperature stability of "multi-temperature filament" at T_f = 500°C.

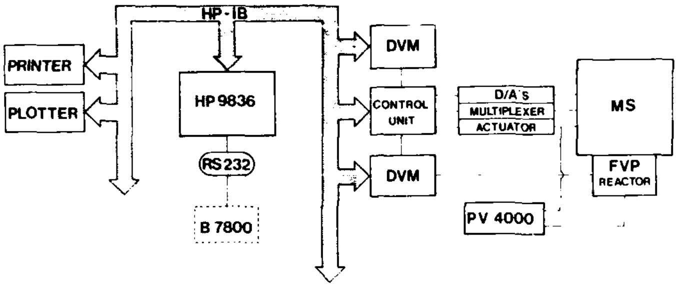


Fig. 4-9. Computerized pulse pyrolysis - mass spectrometry configuration.

4.2.1. Pulse Pyrolysis

The introduction of the continuous-flow inlet system for low pressure Curie-point pyrolysis studies (Egsgaard and Carlsen, 1984) opens up the possibility of carrying out gas kinetic studies using the inductive heating technique. Calculations of gas kinetic data, using mass spectrometry, involves experimentally determined ion intensities at ambient (I_{amb}) and pyrolysis (I_T) temperature (cf. section 5). These are conveniently obtained by single ion monitoring in sequences of pyrolyses and adequate cooling periods, i.e. pulse pyrolysis. In Fig. 4-10 the temperature profile created for six pyrolysis temperatures in the range 400 to 550^oC is visualized.

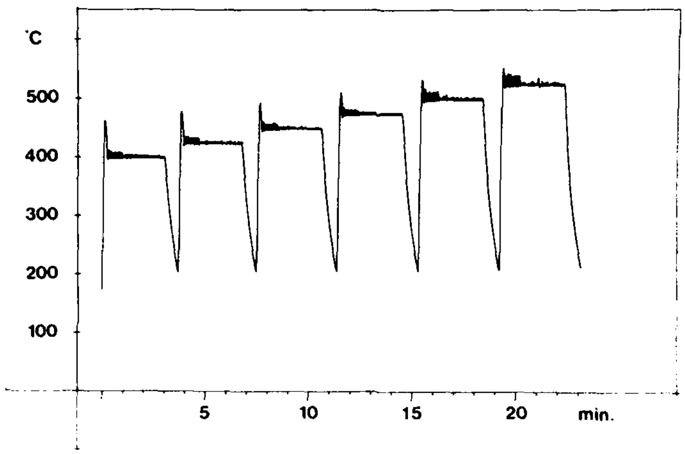


Fig. 4-10. Pulse pyrolysis sequence for kinetic studies.

4.3. Surface Influence

The importance of surface reactions in pyrolysis units is a well-recognized phenomenon both in the laboratory and in industrial scale units (Albright and Tsai, 1983, Nishiyama and Tamai, 1980). Typical reactions are coke formation, carburization of metal surfaces (i.e. formation of metal carbides) oxidation/reduction of metal surfaces, and sulfiding the surfaces (i.e. desulfiding the reactant).

These reactions are, however, of minor interest in the analytical studies of gas phase pyrolytic reactions, although they often occur and hereby diminish the yield of the gaseous products wanted.

From an analytical point of view it is much more interesting that the hot reactor surfaces may direct the pyrolysis towards certain products. However, these products are often due to extensive degradations, as results of reactions promoted by reactive sites at the surfaces, and thus unwanted in connection with studies of pure thermally induced reactions. On the other hand, selective choice of surface coating may advantageously be applied in an attempt to direct pyrolysis reactions in certain directions, e.g. heterogeneous catalysis.

In the Curie-point pyrolysis reactor, where the hot zone as mentioned consists of a metal wire, surface treatment appears relatively easy, since metal surfaces are fairly easily coated, e.g. by electro-plating, to give surfaces of known composition. Most metal surfaces are rather reactive at high temperatures giving rise to a series of unwanted products as mentioned above (Albright and Tsai, 1983). However, we found (Egsgaard and Carlsen, 1983a) that application of gold-plated filaments for gas phase Curie-point pyrolysis minimizes the degree of possible reactions induced by the presence of hot metal surfaces such as nickel and iron.

To illustrate the effect of gold-plating the gas phase pyrolysis of methyl dithioacetate presents an example (Carlsen and Egsgaard, 1983). It was observed that even at temperatures as low as 631 K (nickel surface) the dithioester degraded extensively (Fig. 4-11(a)), giving rise to products which could be assigned as C_3H_6S (m/z 74), dimethyl sulphide (C_2H_6S) (m/z 64), C_4H_6 (m/z 54), and methane thiol (m/z 48). Verification of the involvment of the hot nickel surface was obtained by comparison to the pyrolysis of methyl dithioacetat at 631K, however, applying a gold-plated filament. It was unambiguously demonstrated (Fig. 4-11(b)) that the compound was perfectly stable under these conditions. At higher temperatures (1253K cf. Fig. 4-11(c)), still applying gold-plated filaments the dithioester decomposed smoothly into the expected products, as are thioketene (m/z 58) and methane thiol (m/z 48), as a result of a simple 1,2-elimination.

The involvment of nickel surfaces in pyrolysis reactions has recently been reported by Bock and Wolf (1985), and Glebov et al. (1985) reported on the deoxygenation of alcohols and ketones on an iron catalyst.

A second example, also taken from the study of gas phase pyrolysis studies of organo-sulfur compounds, illustrates the abovementioned disulfiding reactions. Pyrolytic sulfur extrusion from the thioketen 1,1,3,3-tetramethyl 2-thiocarbonyl cyclohexane was observed applying a hot iron filament (1043K) (Carlsen, Egsgaard, and Schaumann, 1980), the reaction, however, unequivocally being associated with the nature of filament surface, as demonstrated (Egsgaard and Carlsen, 1983a) by comparison with an experiment using a gold-plated filament (1043K), under which conditions the thioketen (m/z 182) was found to be perfectly stable (Fig. 4-12). The findings are in agreement with the bond strength of the C=S bond, which is about 125 kcal/mol (Benson, 1978), i.e. the carbon-sulfur double bond should not be cleaved at 1043K by pure thermal induction.

Gold-plating is not the optimal choice in all cases, as it can be observed that unwanted reactions in several cases are minimized, but not necessarily completely suppressed (Egsgaard and Carlsen, 1983a). This is demonstrated in the study of the pyrolysis of nitromethane (Egsgaard, Carlsen, and Elbel, unpublished) and nitrobenzene (Egsgaard and Carlsen, 1983a).

Figure 4-13 visualizes the product distribution following pyrolysis of nitrobenzene at 1043K applying a gold-plated iron filament and an iron filament, respectively.

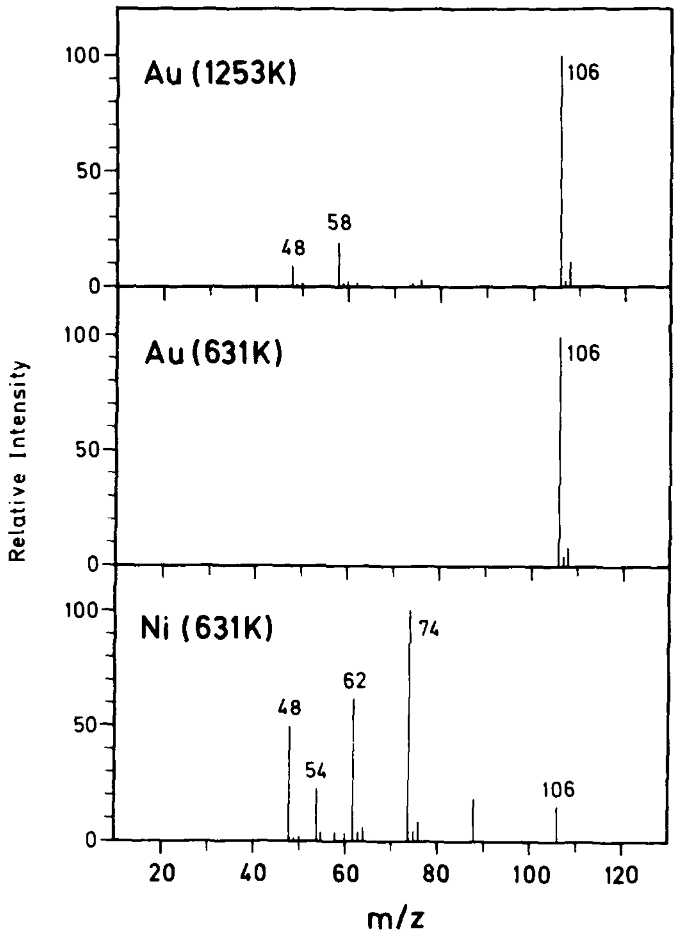


Fig. 4-11. Field ionization mass spectra of methyl dithioacetate following gas-phase thermolyses at 631 K (nickel), 631 K (gold) and 1253 K (gold).

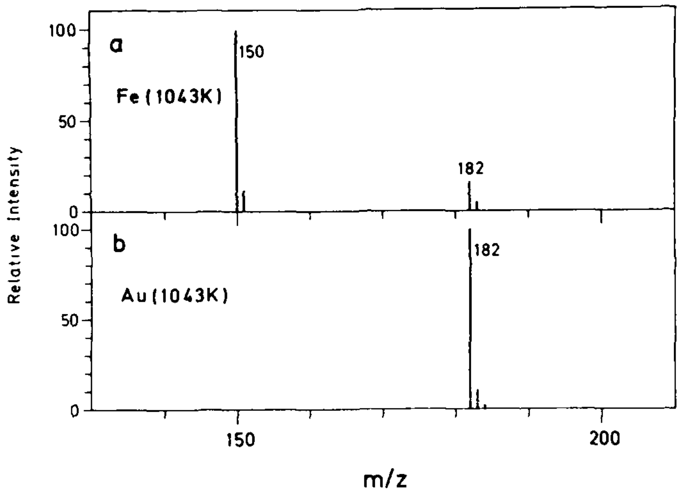


Fig. 4-12. Field ionization mass spectra after pyrolysis of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane at 1043 K using (a) an iron filament and (b) a goldplated iron filament.

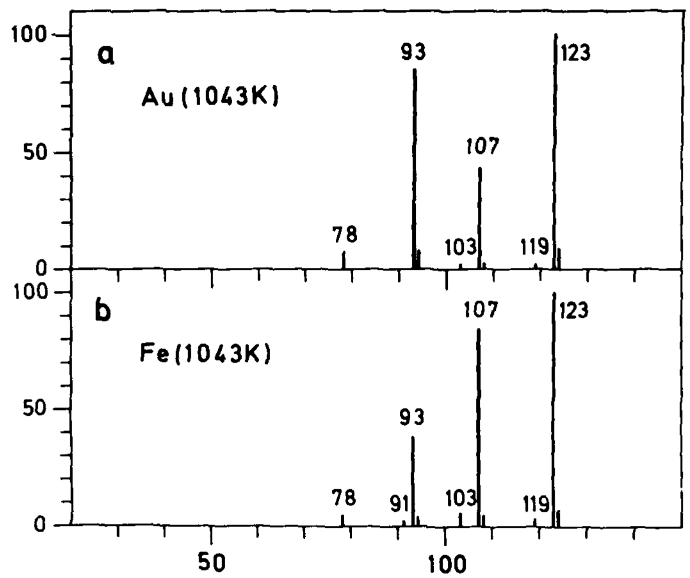
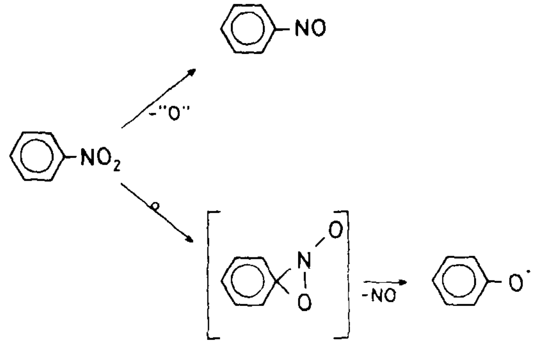
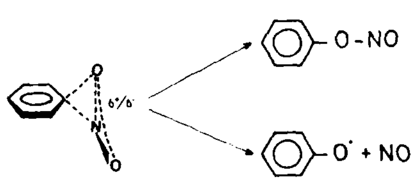


Fig. 4-13. Field ionization mass spectra after pyrolysis of nitrobenzene at 1043 K using (a) a gold-plated iron filament and (b) an iron filament.

In both cases two products appear dominant, exhibiting molecular weights of 93 and 107 which were assigned to the phenoxy radical and nitrosobenzene, respectively. The formation of these two products could be explained by the operation to concurrent reactions, i.e. rearrangement followed by NO elimination and formel atomic oxygen extrusion.



Phenoxy radicals have been postulated as intermediates in the pyrolysis of nitrobenzene by McCarthy and O'Brian (1980) and by Fields and Meyerson (1975). These authors formulated the reaction as removal of NO from an intermediate phenyl nitrite, possibly formed as a consequence of consecutive radical reactions (cf. Batt, 1982), which, however, is not possible under pure unimolecular reaction conditions as applied by us (Egsgaard and Carlsen, 1983a, 1984). Thus, the formation of the C-O bond of necessity involves a three-centred transition state, which in principle may ring-open to give the nitrite or directly eliminate NO to yield the phenoxy radical.



Study of the m/z 123 ion by collision activation mass spectrometry before and after pyrolysis of nitrobenzene (Egsgaard and Carlsen, 1984) resulted in identical spectra suggesting the absence of the phenyl nitrite in the pyrolyzate, as nitro compounds in general are expected to result in spectra differing from those of the corresponding nitrites (Budzikiewicz et al., 1967, Egsgaard, Carlsen, and Elbel, 1986). However, taking the thermal lability of nitrites into account, the intermediacy of the latter cannot definitely be ruled out.

By comparing the two spectra depicted in Fig. 4-13, the most striking feature appears to be the significant variation in the phenoxy radical: nitrosobenzene (m/z 93: m/z 107) ratio. Obviously the pyrolysis of nitro benzene is shifted in favour of phenoxy radical formation applying gold-plated filaments, in agreement with the involvement of the hot reactive iron surface in the apparent loss of an oxygen atom from the nitro group, a reaction, which surprisingly cannot be surpressed fully upon gold plating.

In this connection it should be noted that in few cases gold surfaces may catalyze gas phase reactions as demonstrated by Meyer and deMeijere (1976) in a study on the thermally induced rearrangement of strained small ring hydrocarbons.

Nevertheless, gold metal has been found as the least catalytically active metallic material (Cramers and Keulemans, 1967). The authors therefore recommended gold for flow reactors for gas kinetic studies. Gold-based reactors has been applied by Kwart et al. (1969), Egsgaard and Carlsen (1983a) and Carlsen and Egsgaard (1983)[c].

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[c] In later studies by the Risø group, gold-plated filaments have been routinely used unless stated otherwise.

On the other hand, the above described pyrolysis of nitrobenzene illustrates the possibility of directing a pyrolysis reaction towards certain products by carefully selecting the filament surface.

4.3.1. Nitroso-Ethene

The surface-promoted deoxygenation of nitro compounds has recently been applied to generate nitroso-ethene (Egsgaard and Carlsen, 1987a), the latter hitherto being known only as trapped by cyclopentadiene (Faragher and Gilchrist, 1979) or as model substance in theoretical studies (Faragher and Gilchrist, 1979, Schmidt Burnier and Jorgensen, 1983, Petukhov et al., 1984).

Pyrolysis of nitro-ethene at 883K (surface Ni: 72%, Fe: 28%) gave rise to the formation of three products exhibiting molecular weights of 57, 41, and 30, respectively, as visualized in Figure 4-14, together with unpyrolyzed starting material (M: 73) (Egsgaard and Carlsen, 1987a).

Based on CA mass spectrometic fragmentation of m/z 57, leading to ions m/z 27 ($C_2H_3^+$) and m/z 30 (NO^+), it appeared possible to exclude alternative structures, such as 4*H*-1,2-oxazete, 2*H*-azirine-1-oxide and acetonitrile *N*-oxide as being responsible for this ion, leaving nitroso-ethene (H_2C=CH-NO) as the only possibility.

In agreement with the study of Bock, Dammel and Aygen (1983), reporting acetonitril as the eventual product following pyrolysis of vinyl azide, the compound being responsible for the m/z 41 ion (Fig. 4-14) was, in accordance with CA mass spectrometry, identified as acetonitril. Apparently the formation of acetonitrile can be ascribed to a rearrangement of primary generated vinyl nitrene, the latter, in the present context, being a result of a consecutive surface-promoted deoxygenation of the nitroso-ethene.

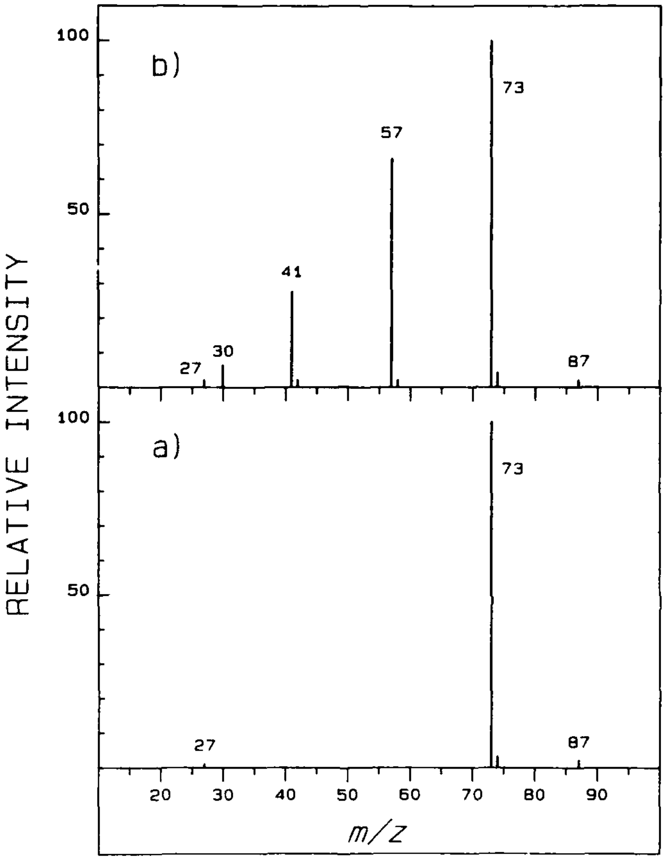

Fig. 4-14. Field ionization mass spectra of nitro-ethene without pyrolysis (a) and following pyrolysis at 883 K (filament composition: Ni: 72%, Fe: 28%) (b).

4.3.2. Direct surface involvment

In the preceeding sections it has been demonstrated that hot metal surfaces in certain cases may promote the formation of otherwise, from a thermodynamic point of view, difficult accessible species. However, hot surfaces may also take directly part in the reactions by supplying additional atoms to primary pyrolytically generated reactive species.

Scrutiny of the FI mass spectrum obtained following pyrolysis of nitrobenzene, applying an iron filament (Fig. 4-13 b) reveals the formation of minor, but significant amounts of a compound with molecular weight 103, identified as benzonitrile (Egsgaard and Carlsen, 1983a). Obviously, compared to the starting nitrobenzene, this product contains an additional carbon atom.

By analogy to the apparent consecutive double deoxygenation of nitro-ethene (cf. section 4.3.1.), it appeared most reasonable to formulate the benzonitrile formation as a reaction between intermediary phenyl nitrene and elemental carbon deposited on the iron filament. This mechanism was most convincingly confirmed by studying the pyrolysis of phenyl azide, applying a carbon-coated gold-plated filament, benzonitril (M = 103) being established as one of the major products (Egsgaard and Carlsen, 1986) (Fig. 4-15). Hence, reactive species, as e.g. nitrenes, may be converted into thermodynamically stable compounds by picking up atoms delivered by the surface.

Obviously the reaction between nitrenes and carbon must lead to isocyanides, which, however, are rapidly rearranged into the corresponding nitriles.

Finally, it shall be noted that the products exhibiting molecular weights 91 and 93 were identified as 1-cyano 1,3-cyclopentadiene and anilin, respectively (Fig. 4-15). Both products are results of the presence of an intermediary phenyl nitrene, which rearranges or picks up two hydrogens from the surface, respectively.

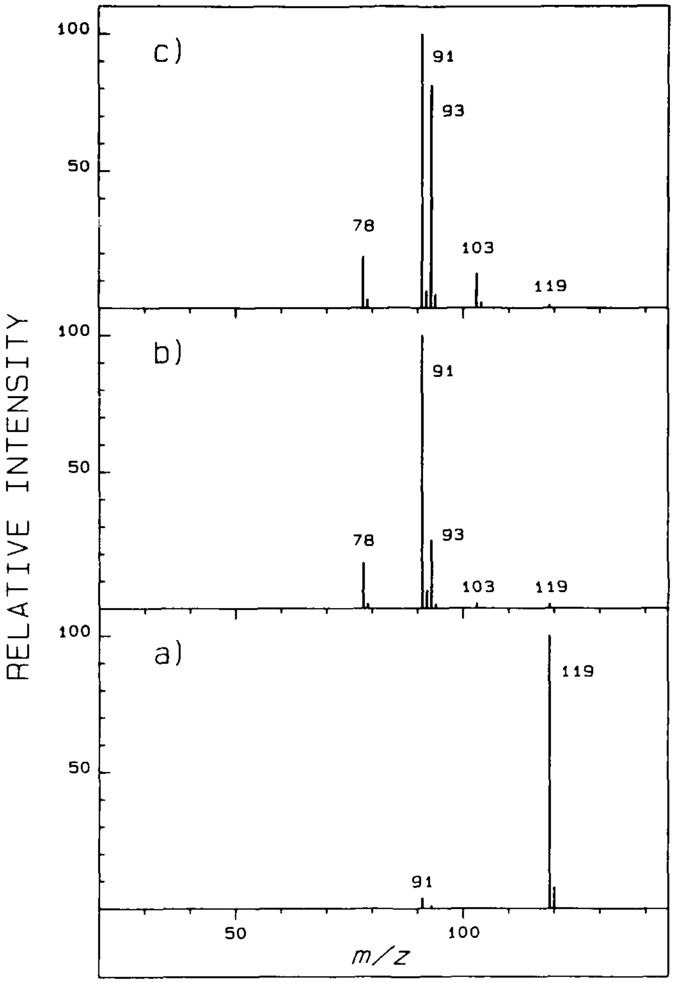

Fig. 4-15. Field ionization mass spectra of unpyrolyzed phenyl azide (a) and following pyrolysis of pheny' azide at 770°C at gold (b) and gold/carbon (c) surfaces.

In the present context, it can be mentioned that the parent nitrene, imidogene, produced by pyrolysis of azoimide, also reacts with elemental carbon forming hydrogen cyanide, which may well be considered as an alternative route to interstellar HCN (Carlsen and Egsgaard, 1988).

5. GAS KINETIC CONSIDERATIONS

Gas kinetic studies may be crucial in connection with mechanistic investigations. The theory of the unimolecular gas phase reaction has been a subject of detailed studies (cf. Robinson and Bolbrook, 1972). However, in the present context the application of highly sophisticated mathematics may seem somewhat exaggerated. Furthermore, some of the figures, e.g. vibrational frequencies of transition states, are certainly not immediately available for the compounds, which are normally within our sphere of interest.

A unimolecular reaction may be represented by the elementary process

$$A \xrightarrow{k} \text{products} \qquad (5\text{-}1)$$

the corresponding rate constant, k, obeying a first-order kinetic law

$$-\frac{1}{[A]}\frac{d[A]}{dt} = k \qquad (5\text{-}2)$$

The expression (Eqn. 5-1), however, is to be regarded only as an overall expression, as a large number of reactions, which kinetically obey the first order law, are not elementary prosesses in the sense that only a single step is involved in the reaction. Thus, the source of energy in thermal reactions must be of a collisional nature, i.e. molecule-molecule or molecule-wall collisions, which may involve activations as well as deactivations (Lindemann, 1921, Hinshelwood, 1927)

$$A + M \xrightarrow{k_1} A^* + M \tag{5-3}$$

$$A^* + M \xrightarrow{k_{-1}} A + M \tag{5-4}$$

$$A^* \xrightarrow{k^*} \text{products} \tag{5-5}$$

Based on equations 5-3 to 5-5, the pressure dependence of unimolecular gas phase reactions is obvious. Under steady-state conditions the equations lead to the pseudo-first order rate constant

$$-\frac{1}{[A]}\frac{d[A]}{dt} \equiv k = k_1[M]k^*/(k_{-1}[M] + k^*) \tag{5-6}$$

the limiting pseudo-first order low pressure rate constant, k_0, and the limiting true first order high pressure rate constant, k_∞, are given by Equations 5-7 and 5-8, respectively

$$\lim_{[M]\to 0} k \equiv k_0 = k_1[M] \tag{5-7}$$

$$\lim_{[M]\to\infty} k \equiv k_\infty = k_1 k^* / k_{-1} \qquad (5-8)$$

An application of Equations 5-6 to 5-8 yields the following expression

$$k = k_\infty (k_0/k_\infty / 1 + k_0/k_\infty) < k_\infty \qquad (5-9)$$

using k_0/k_∞ as a simple pressure scale, to interpolate k between k_0 and k_∞. Hence, the unimolecular rate constants, k, measured in the low pressure pyrolysis studies, are in general not equal to the high pressure limiting rate constant, k_∞.

Consequently the Arrhenius parameters A_∞ and E_∞, as defined by Eqn. 5-10, cannot be derived directly by application of the temperature variation of k.

$$k_\infty = A_\infty e^{-E_\infty/RT} \qquad (5-10)$$

To avoid the rather complicated mathematical treatment of low-pressure kinetics (cf. Robinson and Holbrook, 1972), we introduced (Egsgaard, Bo and Carlsen, 1985) the empirical Effective Temperature Approach based on experimentally determined rate constants in a "calibrated" reactor.

5.1. Experimental Determination of k

Looking at an irreversible unimolecular reaction in the low-pressure flow reactor as described by Eqn. 5-1 the specific flux (Dushmann, 1960, Golden, Spokes and Benson, 1973, Egsgaard and Carlsen, 1984) of the species A is given by

$$F_A = k_e [A] + k [A] \tag{5-11}$$

where k_e and k are the unimolecular escape-rate constant for A from the reactor and the unimolecular rate constant for the reaction A → products, respectively. For k = 0, $F_A = k_e [A]_o$, k_e is defined as the reciprocal of the mean residence time of A in the reactor, i.e. $k_e = t_{mr}^{-1}$ (cf. Section 4.1).

On pyrolysis the stationary concentration of compounds A, $[A]_T$, will be smaller than the corresponding value without pyrolysis, $[A]_o$, owing to the decomposition taking place. Applying a constant inlet flow of A to the reactor

$$F_A = k_e [A]_o = k_e [A]_T + k [A]_T \tag{5-12}$$

which may be rewritten into

$$k = k_e \frac{[A]_o - [A]_T}{[A]_T} \tag{5-13}$$

Applying mass spectrometry as a detection technique, the concentrations $[A]_o$ and $[A]_T$ are directly related to the ion intensities of the molecular ion, I_{amb} and I_T an ambient and pyrolysis temperature, respectively.

$$k = k_e \frac{I_{amb} - I_T}{I_T} \qquad (5-14)$$

5.2. The Effective Temperature Approach

As an alternative to the theoretical treatment of the low-pressure kinetics, we approached the problem from an empirical point of view (Egsgaard, Bo and Carlsen, 1985), by estimating the effective temperature for the molecules in the reactor. The effective temperature, T_{eff}, is defined as the temperature (i.e. actual energy distribution) that the molecules apparently reach in the reactor at a given operating (surface) temperature, i.e. in the reactor, based on the Curie-point principle the filament temperature, T_f. Hence, the reactor may be "calibrated" to give a correction term correlating the filament temperatures to the actual reaction temperatures, i.e. the effective temperatures.

Applying the equations given in Section 4.1. for the mean residence time, t_{mr}, for the molecules in the reactor (Eqn. 4-1) and the mean molecular rate, $\bar{c}$, (Eqn. 4-2) it is possible to derive rate constants, k, for given reactions by application of Eqn. 5-13 or, using mass spectrometry as detection system Eqn. 5-14. Hence, experimental determination of rate constants for a series of different filament temperatures, for reactions exhibiting known activation parameters (E_∞ and A_∞) permits an estimate to be made of the corresponding effective temperatures according to the rewritten Arrhenius Equation.

$$\ln\left[(I_{amb}-I_T)/I_T\right] + \ln k_e = \ln A_\infty - E_\infty/RT \qquad (5\text{-}15)$$

The correlation between the effective temperature and the surface temperature in the reactor, T_S, can be obtained based on the physically reasonable assumption that the increment in effective temperature per molecule-surface collision follows a linear law (Amorebleta and Colussi, 1982).

$$\frac{d\,T_{eff}}{dn} = \beta\,(T_s - T_{eff}) \qquad (5\text{-}16)$$

On applying the design of the Curie-point reactor design reactions are results of single collisions between the hot filament surface and the molecules (cf. Section 4.1.1.), i.e. dn ~ 1, and $dT_{eff} = T_{eff} - T_{amb}$. Thus, the following simple relationship between T_f and T_{eff} is obtained.

$$T_{eff} = T_{amb} + \beta\,(T_f - T_{amb}) \qquad (5\text{-}17)$$

Apart from depending on the filament temperature, β, which is a measure of the molecule-surface collision efficiency most probably also depends on the reactor geometry. Hence, a given reactor set-up has to be "calibrated" by a series of standard reactions to give the corresponding, reactor specific, $\beta(T_f)$, and hereby the $T_{eff}(T_f)$ relations.

In Fig. 5-1, the temperature correction factors, β, as a function of filament temperatures are shown for three reactions exhibiting a broad spectrum of activation parameters (Table 5-1).

Table 5-1 Reactions studied (activation energies in kcal/mol)

	E/ln A_∞
I: tert.-Bu-O-O-tert.-Bu → 2 tert.-Bu-O•	37.4/35.9
II: Me-N=N-Me → Me-N=N• + Me•	52.5/38.0
III: Et-N=N-Et → Et-N=N• + Et•	50.0/37.5

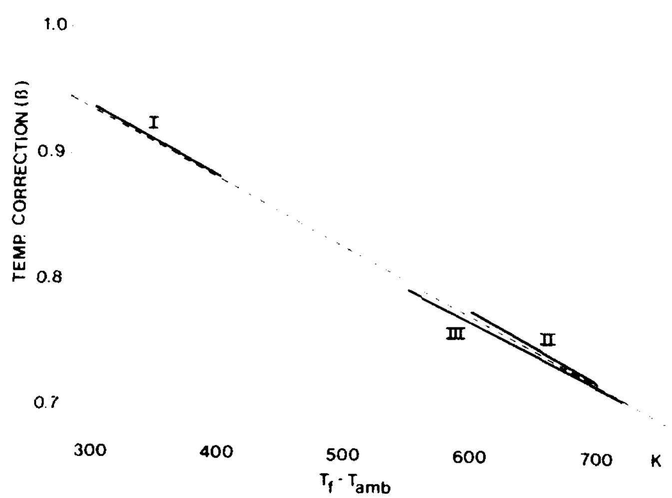

Fig. 5-1. Temperature correction factors, β, as a function of filament temperature.

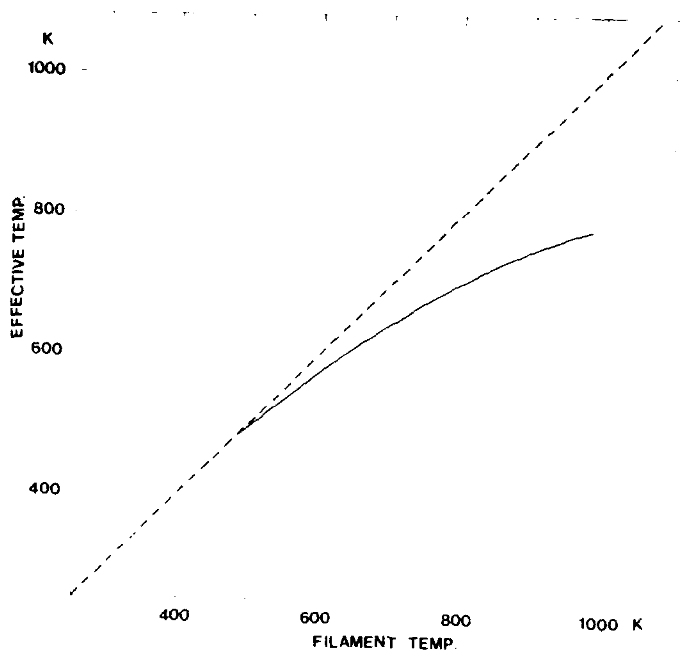

Fig. 5-2. Effective temperature as a function of filament temperature.

It is observed that the data fit rather well to a common "universal" $\beta(T_f)$ curve; this may seem somewhat surprising, since it could be expected that β would be molecule dependent (cf. Gilbert, 1982). However, based on the relatively small number of reactions included in the above figure we (Egsgaard, Bo, and Carlsen (1985) and Egsgaard and Carlsen (unpublished)) tentatively suggested a single $\beta(T_f)$ and hereby a single $T_{eff}(T_f)$ curve, the latter being visualized in Fig. 5-2.

The effect of variations in, or poorly determined values of β was also discussed (Egsgaard, Bo, and Carlsen, 1985). Introducing the expression for T_{eff} (Eqn. 5-17) in the rewritten Arrhenius equation (Eqn. 5-15) the following expression for the

$$\frac{\Delta E_\infty}{E_\infty} = \frac{\Delta\beta\,(T_f - T_{amb})}{T_{amb} + \beta\,(T_f - T_{amb})} \qquad (5\text{-}18)$$

relative variation in the activation energy was derived.

Hence, a 10% variation in β (e.g. = 0.8 ± 0.08, T_{amb} = 300K, and T_f around 850K) affords variations in the activation energy of less than ± 6%, which in the present context appears satisfactorily. The Arrhenius factor, log A_∞ is independent of β, however, since ln A_∞ values in practice are determined graphically, some limited variations may be expected.

6. SUMMARY

The present report describes, based on 18 previous papers published in the period 1980-1986, analysis of low-pressure gas-phase pyrolytic reactions by means of mass spectrometric techniques. The single chapters describe the different components in the pyrolysis - mass spectrometry system, i.e. the detection system, the sample/inlet system, and the pyrolysis reactor, the applicability being illustrated by selected examples. A separate chapter is devoted to gas-kinetic considerations.

Chapter 1 (Introduction)

A general introduction to the applicability of pyrolysis in different areas of chemical research, such as pure physical chemistry, physical organic/inorganic chemistry, preparative organic/inorganic chemistry, and a wide variety of analytical chemical subjects.

In low-pressure gas-phase pyrolysis the pyrolysis conditions are typically temperatures above 750K and pressures below 1 mtorr. The mean residence times of molecules in the pyrolysis reactor ranges from 1-100 ms. The strategies for carrying out low-pressure gas-phase pyrolyses - mass spectrometry are outlined.

Chapter 2 (The Detection System)

This chapter focuses on the applicability of mass spectrometric (MS) techniques in the study of low-pressure gas-phase pyrolytic processes as the more informative.

The introduction of the direct combination of a pyrolysis reactor and the ion source of a mass spectrometer, equipped with the

soft ionization mode, field ionization (FI) appears advantageous compared to the classical electron impact ionization (EI), since FI gives rise to molecular ions only, even of highly unstable molecules. The eventual interpretation of the spectra is highly facilitated as the spectra are not overshaddowed by EI induced fragmentation patterns of often unknown pyrolysis products.

To elucidate the nature of the single components further the introduction of MS/MS techniques as collision activation (CA) mass spectrometry appears as a highly effective tool. The utility of CA mass spectrometry in this context is illustrated by the study of the gas-phase pyrolysis of the hitherto unknown 1,2-oxathiolane.

The analysis of isomeric compounds may advantageously be carried out by application of CA mass spectrometry, possibly in combination with the use of isotopic substitution. Thus, the isomerization reactions in methyl acetate and the corresponding mono- and dithio analogues are illustrative in this connection. It appears that methyl acetate as well as methyl thionoacetate pyrolytically can be isomerized, whereas the corresponding dithio ester surprisingly appears stable towards a sulfur-to-sulfur migration of the methyl group.

Although analysis of low-pressure pyrolysis reactions in general is associated with pyrolysis in flow reactors, the reactions may in ertain cases advantageously be carried out in a static system, maintaining the FI and CA mass spectrometric options. The applicability of the static system pyrolysis is demonstrated by a mechanistic investigation of the thermal decomposition of 1,2-oxathiolane. Hereby the existence of an 1,2-oxathiolane - thietane-1-oxide equilibrium was established.

The final section in this chapter is devoted to a discussion of the utility of reference structures, e.g. generated by EI mass spectrometric fragmentations, as illustrated by the search for the aci-tautomer of nitromethane among the pyrolysis products generated by low-pressure pyrolysis of nitroalkanes.

Chapter 3 (Sample/Inlet System)

The choice of the inlet system is closely related to the nature of the sample. In order to introduce a continuous flow of reactant into the pyrolysis reactor, whereby the subsequent mass spectrometric analysis is strongly facilitated, a series of inlet systems was developed, dependent of the vapour pressure of the sample: a) gaseous or easily evaporable, b) liquids exhibiting a moderate to low vapour pressure at ambient temperature and c) solids. In cases a) and b) the necessary flow a reactant to the pyrolysis reactor were controlled by constrictors. The substance-requirement for the mass spectrometric analysis is as low as 0.1 μg/s.

Chapter 4 (The Pyrolysis Reactor)

The present report focuses on the introduction of the inductive heating principle, often named as Curie-point pyrolysis, for gas-phase pyrolytic studies. The more pronounced difference between conventional types of reactors and the equipment for Curie-point pyrolysis is the nature of the heated zone. In conventional reactors all internal surfaces are heated, whereas in the Curie-point pyrolyzer the walls of the reactor maintain ambient temperature, and only the ferromagnetic filament in the center of the reactor constitutes the heated zone.

A major advantage of the inductive heating technique is the very limited amount of reactor material, which has to be heated.

Hence, temperature rise times and subsequent cooling periods can be kept rather short. However, this technique also suffers from a series of disadvantages, especially the limited number of temperatures available.

In order to overcome the temperature problem, however, maintaining the advantages of the inductive heating, a "multi-temperature" filament was constructed. Thus, arbitrarily chosen temperatures in the range from ambient to the Curie-point of the filament were available, which is crucial in connection with gas-kinetic studies. For the latter purpose the principle of Pulse Pyrolysis is introduced, i.e. single ion monitoring in sequencies of pyrolyses and adequate cooling periods. The temperature control was based on extensive computerization of the pyrolysis - mass spectrometry system.

It is generally desirable that only unimolecular reactions take place. In low-pressure pyrolysis reactor, where the mean free paths for the molecules are larger than the diameter of the reactor, i.e. a so-called Knudsen reactor, this is generally fulfilled. An important consequence of the very low-pressure is that the mean residence times of the molecules in the pyrolysis reactor are independent of the internal pressure in the reactor, i.e. the mean residence time depends only of the reactor geometry and the temperature.

A theoretical study on the movement of molecules through low-pessure reactors clearly demonstrates that in the case of Curie-point pyrolyzers the thermal activation, and, hence, the occurrence of pyrolysis of the molecules is a result of single collisions between the molecules and the hot filament. Typically a series of collisions between the molecule and the reactor walls, maintaining ambient temperature, takes place between each molecule - filament collision.

An important factor in gas-phase pyrolytic studies is the interaction between the molecules and the hot surface during the thermal activation. Thus, certain compositions of hot surfaces may direct the pyrolysis towards certain products. These products are often due to extensive degradations promoted by active sites at the surface. In general these reactions are unwanted in connection with studies of pure thermally induced reactions. However, selective choice of surface coating may advantageously be applied in an attempt to direct pyrolysis in certain directions, i.e. heterogeneous catalysis.

Introduction of gold-coated filaments for gas-phase Curie-point pyrolysis apparently minimizes the degree of possible reactions induced by the presence of hot metal surfaces such as nickel and iron. The effect of gold-coating is illustrated by selected examples within the area of sulfur and nitrogen chemistry. The pyrolysis of methyl dithioacetate constitutes an illustrative example, as the pyrolysis on a gold-plated surface results in the expected products (thioketene and methanthiol), whereas by application of a nickel surface the compound is completely degraded even at temperatures as low as 350°C. It appears that gold-coating can suppress deoxygenations (apparent extrusion of atomic oxygen) from S-oxides as well as desulfurization of thiocarbonyl compounds. Analogously gold coating minimizes deoxygenation of nitro compounds.

Surface promoted deoxygenations can, on the other hand, be applied in order to generate new unstable species, as is illustrated by the pyrolytical formation of nitroso-ethene from the corresponding nitro compound.

In certain cases the surface may be directly involved in the reaction by donating additional atoms to primary generated reactive species. This is illustrated by the reaction of nitrenes, phenyl nitrene or imidogen, with elemental carbon leading to the corresponding nitriles, i.e. benzonitrile and hydrogen cyanide, respectively.

Chapter 5 (Gas Kinetic Consideration)

Typically gas-kinetic investigations of low-pressure pyrolysis reactions is associated with sophisticated mathematical operations. One of the problems in this context is that the molecules in low-pressure pyrolysis reactors do not reach the reactor temperature, i.e. the so-called fall-off problem. This chapter describes some very simple considerations of an empirical treatment of kinetic problems, based on an "Effective Temperature Approach", i.e. estimating the temperature, i.e. the actual energy distribution, that the molecules apparently reach in the reactor at a given operating temperature. Hence, the reactor may be "calibrated", based on reactions exhibiting known kinetics to give a correction term correlating the filament temperaturs to the actual reaction temperature, i.e. the effective temperature. The principle of calibrating the reator is illustrated by kinetic studies on some simple reactions exhibiting a broad spectrum of activation parameters. Finally the expected minor effects of possibly poorly determined correlation factors are discussed.

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AD-A207 457 ANALYSIS OF LOW-PRESSURE GAS-PHASE PYROLYTIC REACTIONS 2/3
BY MASS SPECTROMETRIC TECHNIQUES(U) RISOE NATIONAL LAB
ROSKILDE (DENMARK) L CARLSEN JAN 89 RISOE-R-545

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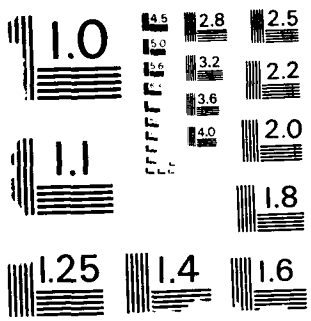
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Wherefore praise we famous men,
From whose bays we borrow -
They that put aside To-day -
All the joys of their To-day -
And with toil of their To-day,
Bought for us To-morrow
(R. Kipling)

DANSK RESUME

Nærværende rapport beskriver, på baggrund af 18 artikler publiceret i perioden 1980 - 1986, studier af gasfase pyrolytiske reaktioner ved lavt tryk under anvendelse af massespektrometriske teknikker. De enkelte kapitler beskriver de forskellige komponenter, der indgår i pyrolyse - massespektrometri systemet, dvs. detektorsystemet, inletsystemet samt pyrolysereaktoren. Anvendelsen af systemet bliver illustreret med udvalgte eksempler. I et afsluttende kapitel beskrives overvejelser i forbindelse med gaskinetiske undersøgelser.

Kapitel 1 (Introduktion)

Der gives en generel introduktion til anvendelsen af pyrolyseteknikken inden for forskellige områder af kemisk forskning som ren fysisk kemi, fysisk organisk/uorganisk kemi, præparativ organisk/uorganisk kemi, samt en lang række emner inden for analytisk kemi.

Lavtryks gasfase pyrolyse gennemføres typisk ved temperaturer over 750K og tryk under 1 mtorr. Middelopholdstiden for molekylerne i pyrolyse reaktoren spænder fra 1 til ca. 100 ms. Der afstikkes retningslinier for gennemførelsen af gasfase pyrolyse - massespektrometri undersøgelser.

Kapitel 2 (Detektorsystemet)

Dette kapitel fokuserer på anvendelsen af massespektrometriske (MS) teknikker til studier af lavtryks gasfase pyrolytiske processer.

Introduktionen af en direkte kombination mellem en pyrolyse reaktor og ionkilde på et massespektrometer, der er udstyret med "blød ionisering", feltionisation (FI), fremstår som fordelagtig sammenlignet med den klassiske 'electron impact' ionisering (EI), idet FI kun giver anledning til dannelse af molekylarioner, selv af særdeles ustabile molekyler. Fortolkningen af de resulterende massespektre bliver herigennem meget enklere, idet spektrene ikke fremstår som et overlap mellem en række EI inducerede fragmenteringsmønstre fra ofte ukendte pyrolyseprodukter.

Til et nærmere studie af de enkelte komponenter i pyrolysatet viser MS/MS teknikker, som fx kollisionsaktiverings (CA) massespektrometri, sig at være et særdeles effektivt værktøj. Anvendeligheden af CA massespektrometri illustreres i denne sammenhæng ved studiet af gasfase pyrolysen af den hidtil ukendte 1,2-oxathiolan.

Analyse af isomere forbindelser kan med stor fordel udføres under anvendelse af CA massespektrometri, eventuelt i forbindelse med isotopsubstitution. Således er isomeriseringen af methyl acetat samt de analoge mono- og dithioforbindelser undersøgt. I modsætning til methyl acetat og methyl thionoacetat, der begge pyrolytisk kan isomeriseres, viser den tilsvarende dithioester sig at være stabil m.h.t. svovl-til-svovl methylgruppe migration.

Selvom lavtryks pyrolyse normalt forbindes med pyrolyse i flow systemer, kan reaktioner i nogle tilfælde med fordel gennemføres i statiske systemer, idet man stadig opretholder FI og CA massespektrometri som detektionsmetode. Anvendeligheden af det statiske pyrolyse system er demonstreret med en mekanistisk undersøgelse over den termiske nedbrydning af 1,2-oxathiolan. Herigennem blev eksistensen af en 1,2-oxathiolan-thietan-1-oxid ligevægt fastslået.

En afsluttende del af dette kapitel helliger sig en diskussion af anvendelsen af referencestrukturer, fx genereret ved hjælp af EI massespektrometrisk fragmentering. Et studie, der havde til hensigt at fremstille den neutrale aci-tautomer af nitromethan ved pyrolytisk omlejring/fragmentering af nitroalkaner tjener som illustration heraf.

Kapitel 3 (Inletsystem)
Valget af inletsystem er tæt sammenknyttet med egenskaberne af den prøver, der ønskes pyrolyseret. Med henblik på at få et konstant flow af reaktant ind i pyrolyse reaktoren, hvorved den efterfølgende MS analyse lettes, er en række simple inletsystemer udviklet afhængig af prøvens damptryk: a) gasformige eller letfordampelige prøver, b) prøver med moderat til lavt damptryk samt c) faste prøver. I til fældene a) og b) styres det nødvendige flow ved brug af en konstriktor. Prøvemængden, der kræves til den massespektrometriske analyse, er særdeles beskedne, hvilket vil sige i størrelsesordenen 0.1 μg/s.

Kapaitel 4 (Pyrolyse reaktoren)
Nærværende rapport fokuserer på indførslen af induktiv opvarmning, kendt som Curie-punkts pyrolyse, til gasfase pyrolytiske studier. Den mest udtalte forskel på Curie-punkt reaktoren, sammenlignet med mere konventionelle reaktorer er udformningen af den varme zone. I konventionelle reaktorer er typisk alle indre overflader opvarmet til pyrolysetemperaturen, mens i Curie-punkts reaktoren bibeholder reaktorvæggen omgivelsernes temperatur, således at kun det ferromagnetiske filament i midten af reaktoren udgør den opvarmede zone.

En vigtig fordel ved anvendelse af den induktive opvarmning er den relativt begrænsede materialemængde, der skal opvarmes. Det vil sige temperaturændringer, både i op- og nedadgående retning kan gennemføres hurtigt. Imidlertid lider metoden også af ulemper. Her kan specielt nævnes det relativt begrænsede antal temperaturer, der er til rådighed.

For at afhjælpe dette temperaturproblem, men stadig bibeholde den induktive opvarmnings fordele er der konstrueret et "multitemperatur" filament. Dette giver mulighed for, med et og samme filament, at anvende temperaturer vilkårligt valgt i området fra stuetemperatur til filamentets Curie-punkt. Specielt i forbindelse med gennemførelse af gaskinetiske studier er dette af stor betydning. Til dette sidstnævnte område indføres begrebet Pulspyrolyse, dvs. enkeltion målinger i sekvenser af pyrolyser og passende nedkølingsperioder. Temperaturkontrollen til dette er baseret på extensiv brug af computerisering af pyrolyse - massespektrometri systemet.

Normalt er det ønskeligt, at kun unimolekylære reaktioner finder sted. I lavtryks reaktorer, hvor den middelfri vejlængde af molekylerne er større end reaktorens diameter, dvs. i såkaldte Knudsen reaktorer, er dette ønske normalt opfyldt. En vigtig konsekvens af de meget lave tryk er, at middelopholdstiden for molekylerne i reaktoren kun er afhængig af reaktorgeometri og -temperatur, men uafhængig af det indre tryk i reaktoren.

Et teoretisk studie af molekylbevægelser igennem lavtryks reaktorer viser, at i Curie-punkts reaktorer er den termiske aktivering, og hermed pyrolysen, af molekylerne et resultat af enkeltkollisioner mellem molekylerne og filamentoverfladen. En konsekvens heraf er, at der typisk foregår en række kollisioner mellem molekylerne og reaktorvæggen (stuetemperatur), dvs. en termisk deaktivering, mellem hvert molekyl - filament stød.

En vigtig faktor i gasfase pyrolytiske studier er vekselvirkningen mellem molekylerne og den varme overflade i forbindelse med den termiske aktivering. Således kan visse sammensætninger af overflade dirigere pyrolysen imod bestemte produkter. Ofte er disse produkter et resultat af en kraftig nedbrydning og hermed uønsket i studier af rene termiske reaktioner. Imidlertid må det ikke glemmes, at selektiv overfladebehandling kan anvendes til at styre reaktioner mod ønskede produkter, dvs. heterogen katalyse.

Introduktionen af guldbelagte filamenter til gasfase Curiepunkts pyrolyse minimiserer tilsyneladende reaktioner induceret af aktive metaloverflader som nikkel og jern. Effekten af guldbehandlingen illustreres med udvalgte eksempler inden for svovl og nitrogenkemien. Pyrolyse af methyl dithioacetat viser effekten tydeligt, idet pyrolyse på guldbelagte filamenter giver anledning til dannelse af de forventede produkter (thioketen og methanthiol), mens anvendelse af en nikkeloverflade resulterer i en fuldstædig dekomponering allerede ved temperaturer så lave som 350^{o}C. Guldbehandlingen kan tilsyneladende undertrykke deoxygenerering (formelt tab af atomart oxygen) fra S-oxider og desulfurisering af thiocarbonylforbindelser. Analogt minimiserer guldbehandling deoxygenereringen af nitroforbindelser.

Overfladeinduceret deoxygenerering kan imidlertid anvendes selektivt til generering af ellers vanskeligt tilgængelige forbindelser. Her tjener dannelsen af nitrosoethen fra den tilsvarende nitroforbindelse som et illustrativt eksempel.

I enkelte tilfælde kan overflader direkte indgå i reaktionsforløb ved at donere ekstra atomer til primært dannede reaktive specier. Dette er anskueliggjort ved studier af reaktionen mellem nitrener og elementart carbon, en reaktion, der fører til det tilsvarende nitriler.

Kapitel 5 (Gaskinetiske overvejelser)

Typisk involverer gaskinetiske studier af lavtryks pyrolytiske reaktioner temmelig kompliceret matematik. Et af problemerne i denne sammenhæng er, at molekylerne i lavtryks reaktorer ikke opnår reaktortemperaturen, det såkaldte "fall-off" problem. I dette kapitel gennemgås en række meget simple overvejelser i forbindelse med en empirisk behandling af gaskinetiske problemer, baseret på princippet om "Effektiv temperatur", dvs. en bestemmelse af den temperatur (aktuel energifordeling), molekylerne rent faktisk opnår i reaktoren ved en given reaktortemperatur. Dette betyder, at reaktoren "kalibreres" på baggrund af studier af en række reaktioner med kendte aktiveringsparametre, hvilket giver anledning til fastlæggelse af et korrektionsled, der giver sammenhængen mellem reaktortemperaturen og den temperatur, molekylerne opnår, dvs. den effektive temperatur. Princippet med at kalibrere reaktoren illustreres ved kinetiske studier på nogle simple reaktioner, der udviser et bredt spektrum af aktiveringsparametre. Til slut diskuteres de små effekter, der kan forventes at være resultatet af dårligt bestemte korrelationsfaktorer.

APPENDIX 1.

AN EFFECTIVE APPROACH TO FLASH VACUUM THERMOLYTIC STUDIES

LARS CARLSEN AND HELGE EGSGAARD

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AN EFFECTIVE APPROACH TO FLASH VACUUM THERMOLYTIC STUDIES

LARS CARLSEN and HELGE EGSGAARD

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

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ABSTRACT

Flash vacuum thermolysis in combination with field ionization mass spectrometry, supplementary with collision activated spectra of the single field ionized molecules, is shown to be a facile and highly informative method for studying even very complex mixtures of primarily formed products in the gas phase thermolysis of organic molecules. The method allows quantitative detection of substances with half lifes $t_{1/2} > 10^{-3}$ sec. A detailed description of the apparatus, which offers the possibility of studying gas phase thermolyses over a wide range of temperatures (300—1400 K), and the method is given, and possible applications discussed.

INTRODUCTION

In recent years the flash vacuum thermolysis (FVT) technique has become widespread in the study of highly reactive, and rather short-lived intermediates in the gas phase thermolytic decomposition reactions of organic molecules [1—3]. In general, the thermolyses are followed by rapid thermal quenching of the products on a liquid nitrogen cooled cold finger, possibly supplementary with spectroscopic detection systems such as IR [4—6] and/or UV—VIS spectrophotometers [4,5]. Direct combinations of FVT units and photoelectron spectroscopy (PES) [7], microwave spectroscopy (MWS) [6,8], and electron impact ionization mass spectroscopy (EI-MS) [1,6, 8—10] have been reported. However, these methods all have a somewhat limited applicability, since the spectroscopic assignment may be extremely complicated in cases where the thermolyses lead to a mixture of several, and often unknown, products.

In order to supply the need for an effective method of studying primarily formed products in gas phase thermolytic reactions, not necessarily unstable, we report here a simple FVT technique, which does not suffer from the above-mentioned failing. The method is based on the direct combination of a thermolysis unit and field ionization mass spectrometry (FI-MS) [11,12] complementary with collision activation mass spectrometry (CA-MS) [13] of the single field ionized molecules.

APPARATUS

In contrast to the often rather complicated glassware thermolyzers [2,7,14], we have constructed a simple and effective thermolysis unit as a modification of the Pye Unicam PV4000 pre-column-pyrolysis-system, which is based on the Curie-point pyrolysis technique [15], i.e. the high frequency inductive heating in ferromagnetic materials.

The thermolysis unit (Fig. 1) consists of three main parts: (a) injection block, (b) reactor (hot zone), and (c) line-of-sight inlet system as thermolysis unit—mass spectrometer interface. The injection block (brass) is connected directly to the Curie-point pyrolyzator, the latter being connected to the Varian line-of-sight inlet system by an adapter flange (Fig. 1H). Inside the thermolysis unit a quartz lining tube is placed (Fig. 1E) with an i.d. of 2 mm, which leads the thermolysis products directly into the ion source of a Varian MAT CH5 D instrument (the magnetic sector preceeding the electric sector) equipped with a combined electron impact ionization/field ionization/field desorption (EI/FI/FD) ion source. The field ion emitter was a 10 μm tungsten wire activated in benzonitrile vapour. The maintenance of the vacuum in the system is based on differential pumping (mercury diffusion pumps) of the ion source, analyzer tube, and the electric sector. Pumping speed was 3 × 150 l sec^{-1}. The total set-up is shown in Fig. 2.

The internal pressure in the thermolysis unit, especially in the reactor, is of importance for the possible exclusion of bimolecular reactions. In order to estimate the working pressure in the thermolysis unit we studied the possible recombination of *tert*-butoxy radicals to di-*tert*-butyl-peroxide. The radicals are generated thermally by thermolyzing di-*tert*-butyl-peroxide [16] at 1043 K, at which temperature the latter is completely cleaved into *tert*-butoxy radicals. We have not been able to detect the recombination product

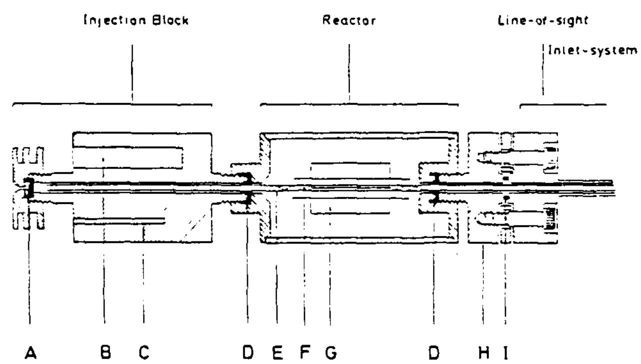


Fig. 1. Thermolysis unit. A, Septum; B, injection block heater; C, thermocouple for temperature readout; D, rubber washer; E, quartz lining tube; F, ferromagnetic wire; G, high frequency induction coil; H, adapter flange; I, gold wire sealing.

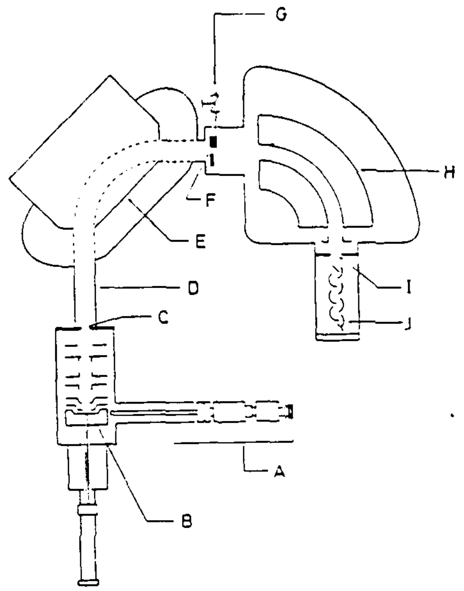


Fig. 2. Thermolysis unit — mass spectrometer set-up. A, Thermolysis unit; B, EI/FI/FD ion source; C, entrance slit; D, analyser tube; E, magnetic sector; F, intermediate focus slit; G, needle valve; H, electric sector; I, collector slit; J, detector (SEM).

by the FI-MS method, which means that it is formed in yields of less than 1%, leading us to the following expression [3,10]

$$\Delta[t\text{-BuO}\cdot]_r = t_{mr}k_r[t\text{-BuO}\cdot] < 0.01 \qquad (1)$$

where $\Delta[t\text{-BuO}\cdot]_r$ is the fraction of the radicals which have recombined in the time t_{mr} (mean residence time) with a rate constant k_r; the latter is in the present case reported to be $10^{8.8}$ sec^{-1} [17]. Taking the mean residence time, t_{mr}, arbitrarily to be 10^{-3} sec, it follows from eqn. (1) that $[t\text{-BuO}\cdot] < 10^{-7.8}$, which corresponds to an internal pressure, P_i, less than 5×10^{-4} torr, i.e. the mean free paths for the molecules are larger than the diameter of the reactor, and the intermolecular collision frequency is consequently very low, which means that bimolecular reactions can hardly be expected. Furthermore, based on the above estimate it is seen that the thermolysis unit, and as a part of the latter, the reactor, fulfils the requirements for a Knudsen reactor [3,10,18], i.e. the mean residence time t_{mr} depends only on the actual geometry of the latter (l 40 mm, i.d. 2 mm) and the temperature, and not the internal pressure. The mean residence time in the reactor (contact time in the hot zone) can then be calculated according to the Knudsen formula [10,18]

$$t_{mr} = 4V/\bar{c}A \text{ sec} \quad (2)$$

with V as the reactor volume and A as the area of the orifice (0.03 cm^2). The mean molecular rate, $\bar{c}$, can be estimated according to the kinetic gas theory

$$\bar{c} = 1.46 \times 10^4 (T/M)^{1/2} \text{ cm sec}^{-1} \quad (3)$$

where T is the reactor temperature and M is the molecular weight of the molecule under investigation, e.g. T = 800 K, M = 200 gives $\bar{c} = 2.92 \times 10^4$ cm sec^{-1}, and consequently $t^r_{mr} = 5.7 \times 10^{-4}$ sec. A similar estimate for the line-of-sight inlet system (l 25 cm) gives a mean residence time $t^i_{mr} = 3.6 \times 10^{-3}$ sec (T = 400 K, M = 100).

In spite of the above exclusion of bimolecular reactions, secondary processes, as are consecutive unimolecular decompositions of thermally labile primary formed reaction products, have to be considered. Firstly, a direct rethermolysis in the hot zone (reactor) has to be discussed. The simple first-order rate law $d[A]/dt = k[A]$ can, for small time intervals, be rewritten as

$$\Delta[A]/[A] = k_d \Delta t \quad (4)$$

k_d being the rate constant for the unimolecular decomposition, and $\Delta[A]/[A]$ the fraction of primarily generated A which has decomposed within the time Δt; the latter can, in the present case, be chosen as the mean residence time in the reactor t^r_{mr}. An estimate of the degree of rethermolysis of a compound exhibiting a rate constant k_d can then be directly obtained from eqn. (4), e.g. a degree of rethermolysis less than 1% can be expected for reactions with rate constants, at the appropriate temperature, $k_d < 10^2$ sec^{-1}. Secondly, the possible decomposition in the heated line-of-sight inlet system will be discussed; this is probably the major problem in cases where the primary generated compounds are highly thermally labile, since the mean residence time in this part of the system, t^i_{mr}, is ca. 10 times higher than t^r_{mr}. However, the temperature in the inlet system is in general much lower than the reactor temperature. Under normal conditions it is possible to observe products present in amounts down to 0.1—1.0% relative yield (molar fraction), depending on the FI sensitivities [12] of the compounds under investigation, which means the relation in eqn. (4) becomes

$$\Delta[A]/[A] = k_d t^i_{mr} < 0.99 \quad (5)$$

Using the above conditions for the line-of-sight inlet system (T = 400 K, M = 100, $t^i_{mr} = 3.6 \times 10^{-3}$ sec) gives $k_d < 2.9 \times 10^2$ sec^{-1}, corresponding to a half life $t_{1/2} > 2.4 \times 10^{-3}$ sec, i.e. labile compounds with half lifes greater than ca. 10^{-3} sec would in general be observable. It is, however, noteworthy that in special cases, compounds with even smaller half lifes may be observed. Thus the unimolecular thermal decomposition of *tert*-butoxy radicals into acetone and methyl radical proceed at 400 K with a rate constant $k_d \cong 10^{4.5}$ sec [19], corresponding to a $t_{1/2} \cong 2 \times 10^{-5}$ sec, and we are able to detect minor amounts of the radicals, approximately 0.2% assuming comparable FI sensitivities of the *tert*-butoxy radicals and acetone.

METHOD

In general, studies of the unimolecular gas phase thermolytic decompositions of organic molecules are carried out in the following way. Samples of ca. 50 μg of the pure compound are introduced (micro-syringes) into the reactor, equipped with the filament with the appropriate Curie temperature, via the heated injection block. To prevent condensation in the latter part of the system, the line-of-sight inlet system, connecting the reactor and the mass spectrometer ion source, is heated.

Owing to the relative fast evaporation of the samples in the injection block (ca. 5—10 sec) the FI-MS spectra must be recorded with a scan rate of 50—100 a.u. sec^{-1} (signal-to-noise > 1000).

Collision activated mass spectra [13] were obtained introducing helium as collision gas via a needle valve (Fig. 2G) into the second field free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focussed on the ion beam just behind the intermediate focus slit (Fig. 2F). Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The CA-MS spectra of the single ions are obtained by scanning the electrostatic field, and are recorded within 5 sec (signal-to-noise ca. 50).

It can be mentioned that in cases of samples with very low vapour pressures the injection block is disconnected and samples are placed directly onto the ferromagnetic wire by the dip-coating technique [9,15]. However, using this latter method the evidence of pure gas phase thermolysis is lost.

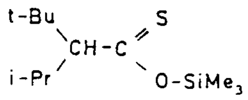
APPLICATIONS AND DISCUSSION

The paramount advantage of the combination of the thermolysis unit with field ionization mass spectrometry (FI-MS) as detection system reported here, is to be sought in the field ionization principle [11,12]. The detection system offers the possibility of analyzing even very complex reaction product mixtures, since FI takes place with no excess energy, excluding polarization by the high electric field, to the neutral molecule [11], i.e. FI gives rise to molecular ions — even of very unstable substances — accompanied only by a very few, if any, fragment ions, generally of low intensity (<1%) [12]. This is in contrast to EI, which may yield complicated electron impact induced fragmentation patterns, which leads to further confusion when they are to be described as superpositions of EI-MS spectra of several, and often unknown, reaction products.

It should in this connection be noted that another soft ionization method chemical ionization (CI) [20] does not reveal the same advantages although the sensitivity of CI-MS is comparable to that of EI-MS, since CI operates at pressures around 1 torr, i.e. bimolecular reactions cannot be excluded. Furthermore, it is to be expected that the bimolecular ionization mechanism [20] will mask the thermal formation of reactive species.

To illustrate the superiority of FI-MS relative to EI-MS as detection system in FVT experiments, we have studied FI-MS, 13 eV EI-MS, and 70 eV

EI-MS spectra following thermolysis of the trimethylsilyl-thionocarboxylate (I) at 1043 K, the thermolysis of I being studied as a part of our current investigations on gas phase thermolytic decompositions of thionocarboxylates [21].



I

We find that I fragments strongly under thermolytic conditions, whereas no FI induced fragmentation is observed. Based on the FI-MS spectrum obtained following thermolysis at 1043 K (Fig. 3a), the overall reaction may be rationalized in the following way

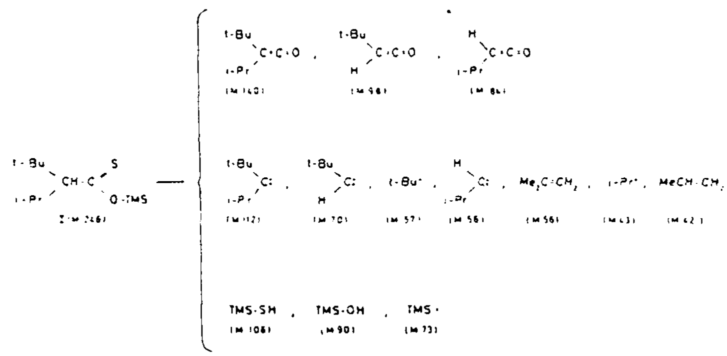


Figure 3b and c, depicting the 13 and 70 eV EI-MS spectra of following thermolysis at 1043 K, clearly illustrates the difficulties of using EI-MS as detection system. Compound I, as well as the reaction products, strongly fragmentate under 70 eV EI-MS conditions, and it is seen that several of the reaction products do not even exhibit molecular ions (Fig. 3c), a fact which is certainly not limited to these special compounds. A rationalization of the above reaction scheme, based on the spectrum shown in Fig. 3c, is obviously extremely difficult, if not impossible; neither does the low voltage 13 eV EI-MS spectrum (Fig. 3b) in the present case clarify the product composition, since decreasing the ionization energy gives rise to molecular ions without sufficient energy to be degraded by multiple pathways leading to fragment ions with lower m/z values. Thus the 13 eV EI-MS spectrum is characterized by more pronounced molecular ions together with fragment ions originating from the more energetically favoured fragmentation pathways. Hence, the latter spectrum is almost to be described as a superposition of the FI-MS and the 70 eV EI-MS spectra, i.e. the electron impact induced fragmentations are

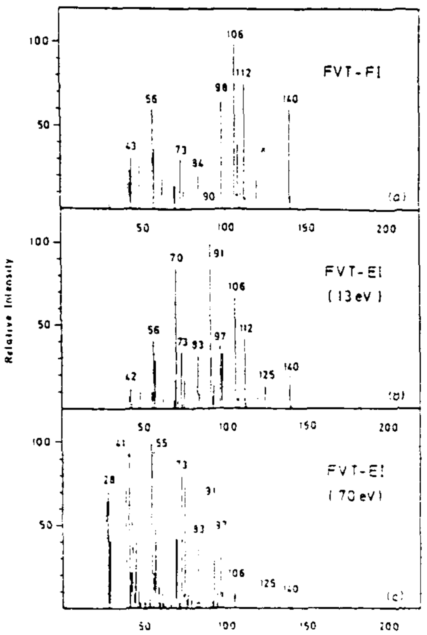


Fig. 3. FI-MS, 13 eV EI-MS, and 70 eV EI-MS spectra obtained following flash vacuum thermolysis of I at 1043 K. Since I is totally degraded at this temperature no molecular ion (M = 246) is observed.

still observed, but simultaneously the molecular ions have grown in.

Additionally it should be mentioned that in cases where the electron impact induced and the thermally induced fragmentations resemble each other, small changes in the spectrum due to the latter may well be drowned in the former. Furthermore, it is obvious in the present case that other conventional detection systems, such as IR-, UV/VIS-, PE-, or MW spectroscopy, would not leave any possibility of rationalizing a reaction scheme as shown above; neither would a simple isolation technique.

The FI-MS detection system enables us to detect all organic reaction products formed in relative yields (molar fractions), generally above 0.01. Small inorganic fragments, however, are not detectable using this technique, as these compounds have very low FI-weight sensitivities. Additionally, the geometry of the ion source of the mass spectrometer used may play an important role [12].

However, although the obtained FI-MS spectra of the thermolysates give extremely valuable primary information about the product compositions, the EI-MS spectra of the single species in the reaction product mixtures would be rather profitable in the search for further information on the structures, in cases of doubt, of the individual products, since it should be remembered that FI-MS spectra in general do not provide any structural information due to the lack of fragment ions. (Valuable information on the composition of the single compounds can, however, be obtained by intensive studies of the isotopic peaks in the FI-MS spectra.) The additional recording of the CA-MS spectra of the single field ionized molecules [13], however, supplies this want, as the collision of molecular ions of high kinetic energy (⩾3 keV) with neutral target atoms of low molecular weight, e.g. helium, is known to give rise to a large variety of fragments. In general, these types of fragments resemble those formed under normal 70 eV electron impact conditions [13]. No interference from even large quantities of other compounds can disturb the CA-MS spectra, as long as they do not have the same molecular weight as the compound under investigation. To illustrate the use of CA-MS, we studied the gas phase thermolysis of 5-phenyl-1,2,3,4-thiatriazole (II) at 1043 K. In Fig. 4 the FI-MS spectra of II without thermolysis and follow-

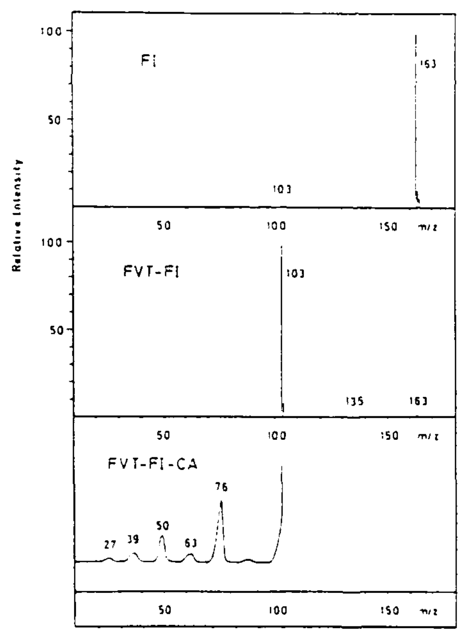
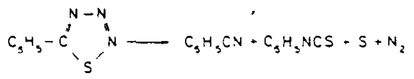


Fig. 4. FI-MS spectra of 5-phenyl-1,2,3,4-thiatriazole (II) without thermolysis [22] and following thermolysis at 1043 K, and CA-MS spectrum of the thermolysate with m/z = 103.

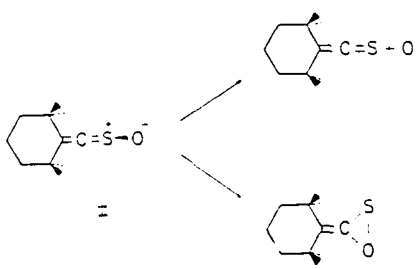
ing thermolysis at 1043 K are depicted together with the CA-MS spectra of the thermolysate with the molecular ion 103; the CA-MS spectrum of the latter is in complete accordance with the previously reported spectrum of benzonitrile [13], in agreement with the known thermal decomposition of II [22].



II

It is noteworthy in this connection that the very simple introduction of the collision gas (Fig. 2) used is profitable since it gives rise to rather intense CA-MS spectra, which enable us to record the complete spectra (0.1—1.0E) within a few sec (see above), i.e. even of rather unstable compounds, in contrast to the much slower recording reported by other authors [23]. (In cases of stable reaction products a direct comparison between the CA-MS spectra with those obtained from authentic samples is expedient.)

The method described here gives the possibility of a wide choice of stabilized, accurately controlled, and reproducible thermolysis temperatures [9,24], as a wide range of ferromagnetic materials with Curie-points from ca. 300—1400 K are readily available. It is obvious that by studying composite reaction mechanisms the mutual product ratios as a function of reaction temperatures may give valuable information on the single involved reactions. Thus, the gas phase thermolysis of 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclohexane *S*-oxide (III) has been rationalized in terms of two concurrent primary reactions that are extrusion of atomic oxygen and formation of the three-membered oxathiirane [25]. At 753 K the two reactions proceed to an almost equal extent *, whereas increasing the thermolysis temperature results in an increase in the thioketene formation, with a simultaneous decrease in



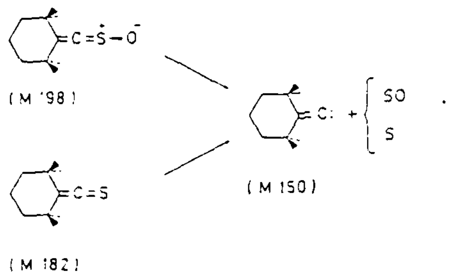
III

the oxathiirane yield, strongly indicating the thioketene formation to be the

* It is not possible to calculate the yields of the single species directly from the FI-MS spectra, as the single compounds may exhibit rather different FI-weight-sensitivities [12]. However, introducing mixtures of the available compounds among the reaction products, with varying mutual ratios, the individual relative sensitivities in general can be calculated directly or indirectly [25].

thermodynamically favourable pathway, whereas the electrocyclic ring closure to the oxathiirane is kinetically controlled.

The limiting factors of the present method, as is the case with all FVT studies, are (a) the contact time in the hot zone, and (b) the lower half life limit of the products which secure detection; account of the latter is given in the previous section. The very short contact time, 10^{-4}—10^{-3} sec, is extremely important to avoid secondary thermolytic reactions [3]. However, even using extremely short contact times, it might in several cases be difficult to distinguish between primary and secondary reaction products: e.g., by thermolyzing the thioketene *S*-oxide (III) at 1043 K, both this and the primary formed thioketene are able to form a vinylidene carbene (M = 150) by SO and S extrusions, respectively [25]. In the present case, with both the



thioketene and the *S*-oxide as stable compound, it was nevertheless possible to compare directly the two thermally induced fragmentation patterns (Fig. 5), whereby it can be demonstrated that less than 15% of the total amount of thioketene formed by thermolyzing the *S*-oxide could undergo rethermolysis [25].

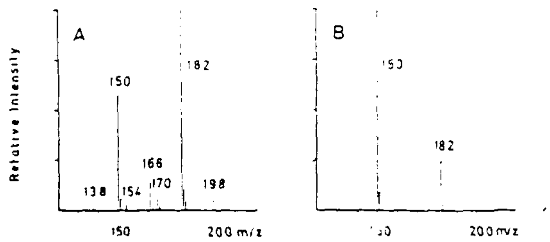


Fig. 5. FI-MS spectra of 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclohexane *S*-oxide (III) (A) and 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclohexane (B) following flash vacuum thermolysis at 1043 K.

CONCLUSION AND OUTLOOK

The above description of the facile and effective approach to FVT studies has demonstrated that this method, by FI-MS, rapidly gives primary information of even very complex product mixtures originating from gas phase thermolyses of organic molecules, as well as further structural information, by CA-MS, of the individual thermolytically formed species. Furthermore, quantitative information on the product compositions can be obtained by using the relative FI-weight sensitivities (see footnote on p. 55), and finally a mechanistic evaluation is achievable *.

Finally , the advantage of this method as a rapid technique for optimization of the reaction conditions should be remembered, e.g. before turning to more possible further spectroscopical characterization of thermally unstable thermolysates.

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* As with normal mass spectrometric investigations, it should be remembered that isotopic labelling of the starting materials may give important information.

58

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APPENDIX 2.

REAL-TIME COLLISION ACTIVATION MASS SPECTROMETRY OF PYROLYSIS PRODUCTS

HELGE EGGSGAARD, ELFINN LARSEN AND LARS CARLSEN

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TECHNIQUES IN GAS PHASE THERMOLYSES

PART 2 *. REAL-TIME COLLISION ACTIVATION MASS SPECTROMETRY OF PYROLYSIS PRODUCTS

HELGE EGSGAARD, ELFINN LARSEN and LARS CARLSEN *

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

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SUMMARY

Basic principles, capabilities and limitations of collision activation mass spectrometry are reported, with special reference to real-time analysis of flash vacuum thermolytically generated products. The analytical utility is demonstrated in terms of structure elucidation and isomerization studies. The potential feasibility of the combination pyrolysis—collision activation mass spectrometry in the study of otherwise non-accessible reference structures for gaseous ion investigations is discussed.

INTRODUCTION

Flash vacuum thermolysis is used in the study of thermally induced reactions of isolated gaseous molecules [1] and has found widespread use in the study of reactive and/or short-lived compounds [2—4]. The real-time analysis of such reactions is highly desirable. However, few analytical techniques are available at the very low pressures necessary to ensure unimolecular reactions only. So far mass spectrometry (MS) [1,5—8] and photoelectron spectroscopy [9] have been applied. Microwave spectroscopy has found widespread use in connection with gas phase thermolytic studies [10]; however, owing to the pressure necessary in this technique, bimolecular reactions cannot be excluded. In general, the methods have limited applicability as the spectral assignment may be complicated because thermolysis may lead to mixtures of several, often unknown, products. The potential applicability of collision activation (CA) supplementary to field ionization (FI) MS for multi-component mixture analysis has been reported previously [11—13]. Recently, the superiority of the direct combination of a flash vacuum thermolysis unit and a FI mass spectrometer complementary with CAMS analysis of the single field ionized products has been demonstrated [14]. We report

* For Part 1, see ref. 14.

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here on the general capabilities of real-time CAMS analysis applied to gas phase pyrolysis. The immediate characterization of pyrolytically generated products is elucidated by (a) the unimolecular thermolysis of 1,2-oxathiolane and (b) by thermal induced isomerizations of ethyl thionoacetate and ^{18}O-labelled ethyl acetate. The in situ generation of reference structures is illustrated by the formation of the parent N-phenylketenimine in connection with studies on the electron impact induced fragmentations of azoles [15].

BASIC PRINCIPLES

The required tandem mass analysis is typically achieved using a double-focusing instrument with reverse Nier-Johnson geometry, i.e., with the magnetic sector preceding the electric sector. Fragmentation of primary ions (m_0) in the second field-free region produces fragment ions (m_x) whose kinetic energy, compared with that of the primary ions, is directly related to the mass ratio (m_x/m_0), the electrostatic sector acting as the second mass analyser. Scanning the electric field produces a linear mass scan, which facilitates the interpretation of the data. It should be noted that using the electrostatic sector as the only second mass analyser, the resolutions of secondary mass spectra are in general low ($m/\Delta m \approx 200$). However, the total energetics of the fragmentations are retained in this spectrum. Improvement of the resolution is attainable using a linked B/E scan technique and hence monitoring the fragmentations occurring in the first field-free region [16].

Fragmentation of single ions

Application of ionization modes, such as electron impact (EI), leads to the formation of ions with considerable excess energy. Ions possessing half-lives of ca. 10^{-5} s may decompose in the second field-free region, giving rise to the metastable daughter ion spectrum [17]. These low-energy decompositions may in certain instances reveal a unique analytical utility, e.g., elucidation of isomeric differences [18]. However, a secondary mass spectrum, which will carry much more structural information, is obtained by collision activation of the single high-energy (>1 keV) ions. The fragmentations are initiated by vertical electron excitations in the ions [19], the energy demand being covered by conversion of a small fraction of the translational energy by the "near-miss" collision process [20,21]. The relative abundances of collision-induced fragments are independent of the energy distribution of the colliding ions [20—24]. Thus a CA mass spectrum reflects the ion structure. The apparent resemblance of CA mass spectra and the corresponding EI spectra is due to comparable internal energies of the fragmentating ions and residence times in the field-free regions and the ion source, respectively [22—24].

Finally, the recent development of quadrupole systems for CAMS analysis should be mentioned. The major benefits of these systems lie in the easy control of the quadrupole mass filters and an enhanced CA efficiency [25—27]. However, low-energy ion beams are employed, resulting in an entirely different collision process [25,26]. The energy transfer probably involves vibrational excitations in the ions [25,26]. Apparently, the quadrupole CAMS spectra are strongly dependent on the actual translational energy of the ions, complicating the interpretation of spectra arising from unknown compounds [28]. However, the method is most promising for the direct analysis of mixtures and hence may also be applicable to thermolytical studies [27].

CAPABILITIES AND LIMITATIONS

The eventual success of a real-time CAMS analysis of gas phase pyrolytic reactions is based on fulfilment of three key requirements: (a) specific ionization, (b) separation of the individual ionized compounds and (c) high CA efficiency.

Field ionization is a soft, unimolecular ionization mode [29]. The very low level of excitation of molecular ions is an important feature, as it greatly minimizes fragmentations of the latter. Hence, in general, FI gives rise to molecular ions accompanied by only few, if any, fragment ions [29,30]. However, FI has a considerably lower sensitivity than most other ionization modes; in particular, small inorganic molecules show extremely low FI sensitivities and will in general escape detection [14]. The apparent low sensitivity of these compounds may be due to a lower electrodynamic supply of neutral molecules along the emitter surface. Additionally, the relative high ionization potentials which these compounds exhibit, and also the actual geometry of the ion source, may play an important role [29]. It should be noted that another soft ionization method, chemical ionization (CI), does not have the same advantages as FI, although the sensitivity of CI-MS is comparable to that of EI-MS, as CI operates at around 1 Torr, i.e., bimolecular reactions cannot be excluded in the pyrolysis unit. Further, it is to be expected that the bimolecular ionization mechanism will mask the thermal formation of reactive species.

The requirements for the primary ion separation are lowered by application of FI. Interference is limited to cases where compounds exhibit identical integral molecular weights. In this study the resolution ($m/\Delta m$) of the magnetic sector, determined at the intermediate focus slit (0.4 mm ≈ 100% transmission) is 400—500 (10% valley) covering the mass range of interest in common pyrolysis experiments (*m/z* 1—500).

The collision efficiency is an important parameter, taking the relatively low ion currents obtainable by FI into account. The yield of fragment ions attainable by CA is typically of the order of a few per cent. Increasing the kinetic energy of the primary ions increases the abundance of high-energy fragmentations, as is predictable by the Massey adiabatic criterion [31]. The application of 3-keV ion beams results in ca. 1 eV as the most probable excitation energy (*m/z* 100) [31,32]. Superimposed CAMS spectra obtained from mixtures of, e.g., two compounds exhibiting equal integral molecular weights are complicated, especially in cases where one of the molecular ions exhibits high-energy fragmentations only [e.g., simple heterocumulenes such as thioketene (*m/z* 58)] whereas the other fragmentates via low-energy pathways [e.g., aliphatic ketones such as acetone (*m/z* 58)]. Attempts to identify the actual composition of such multiplets, based on the CAMS spectra only, may be erroneous as the CAMS spectrum will be dominated by the fragment ions formed via the low-energy fragmentation paths. To solve problems such as this, high-resolution FIMS has to be used.

Bearing this problem in mind, compounds are apparently characterized easily based on CAMS spectra by comparison with spectra of authentic samples. In very successful cases where application of the pyrolysis method leads to hitherto unknown compounds, structure elucidation may be achieved by applying the common mass spectrometric fragmentation rules, as the CA and EI induced fragmentations are fundamentally related, as mentioned above.

EXPERIMENTAL

The gas phase pyrolyses were carried out using the Py—FIMS technique, which has been described in detail previously [14]. The method is based on the direct combination of a Curie-point controlled pyrolysis unit [33], fulfilling the requirements for a Knudsen reactor, and a double-focusing Varian-MAT CH 5D mass spectrometer, equipped with a combined EI—FI—field desorption (FD) ion source. Samples were introduced to the pyrolysis unit either via a viscous gas inlet or using a solid inlet system [34]. The CAMS spectra were obtained by appropriate adjustment of the magnetic field to ensure passage of the desired ions only through the intermediate focus slit. Collision activation of the selected ions was performed, introducing helium as the collision gas as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. The spectra were recorded by scanning the electrostatic field and visualized directly on an X—Y recorder. The CAMS spectra are uncorrected for contributions from unimolecular metastable processes.

Ethyl thioloacetate was prepared by ethylation (C_2H_5I) of thioacetic acid; b.p.$_{760mm\ Hg}$ 115—116°C (lit. 116.4°C [35]). Ethyl thionoacetate [36] and S-phthalimido-3-mercaptopropan-1-ol [37] were synthesized as described previously. Ethyl [^{18}O]acetate was prepared similarly to methyl [^{18}O]acetate by hydrolysis ($H_2{}^{18}O$) of 1-ethoxyethylideneiminium chloride in pyridine [38].

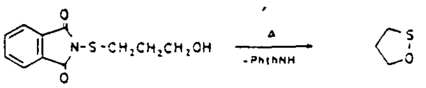
DISCUSSION

The first part of the discussion on real-time CAMS analysis will be devoted to two main areas of pyrolysis experiments, viz., unimolecular decompositions and rearrangements.

Product identification in unimolecular pyrolyses

The possibility of an instant characterization of single compounds in mixtures arising from gas phase reactions is probably the most striking feature of

FI—CAMS analyses. The pyrolysis of 1,2-oxathiolane (1) (M 90) illustrates well the capability of the method. This simple cyclic sulphenate has recently been synthesized by smooth cracking of S-phthalimido-3-mercaptopropan-1-ol in vacuo and characterized partly due to its thermal decomposition [37,39].



1 (M 90)

The FI spectrum of 1, generated at ca. 373 K, is shown in Fig. 1a. The FI spectrum recorded after pyrolysis of 1,2-oxathiolane, depicted in Fig. 1b, is dominated by peaks at m/z 56 and 58, corresponding to eliminations of hydrogen sulphide and sulphur, respectively, from 1 [39].

To obtain information on the identities of these compounds the CAMS spectra of the single field ionized molecules were recorded. The resulting spectra are shown in Fig. 2. The C_3H_4O compound (m/z 56) is readily identified as acrolein (2), the CAMS spectrum (Fig. 2a) being identical with that of an authentic sample. The alternative structure, HC ≡ C—CH_2OH, propargyl alcohol, is excluded on the basis of the FI spectrum alone, as it readily fragments under FI conditions, giving rise to an intense $[M-1]^+$ ion, which is not observed (cf. Fig. 1).

The identification of the C_3H_6O compound (m/z 58) appears more complicated, as six structures (3—8) a priori have to be considered.

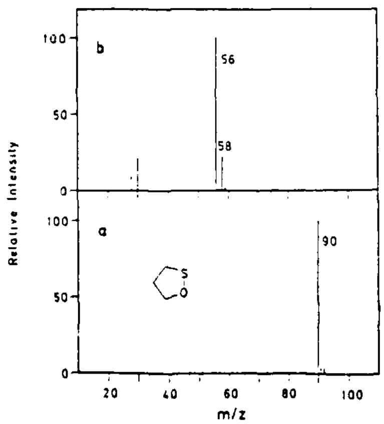


Fig. 1. Field ionization mass spectra of 1,2-oxathiolane (1), (a) without pyrolysis and (b) after pyrolysis at 1043 K.

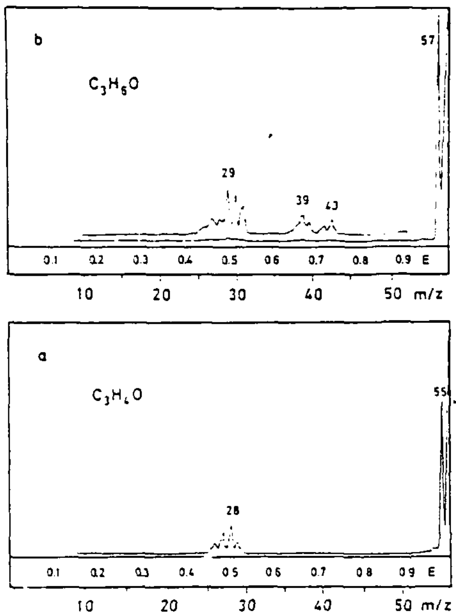
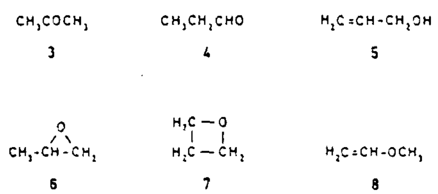


Fig. 2. Collision activation mass spectra of the field ionized (a) C_3H_4O and (b) C_3H_6O compounds of *m/z* 56 and *m/z* 58, respectively, formed by pyrolysis of 1,2-oxathiolane (1) at 1043 K.



However, large differences in the CAMS spectrum of the actual isomer and those of 3, 6 and 8 leave apparently propanal (4), allyl alcohol (5) and oxetane (7) only to be considered [40]. All three isomers seem to be plausible candidates, based on mechanistic considerations. In Fig. 3 the significant mass region *m/z* 25—35 of the FI—CAMS spectra of the isomers 4, 5 and 7 together with that of the thermally generated C_3H_6O isomer is shown. The resemblance of the CAMS spectra of allyl alcohol (5) and the unknown C_3H_6O isomer is striking. However, the presence of minor amounts of 4

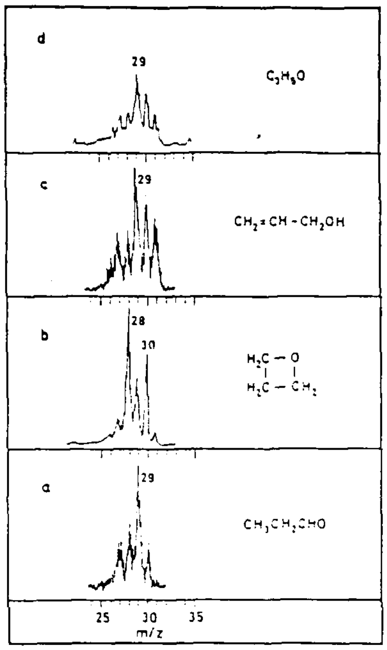
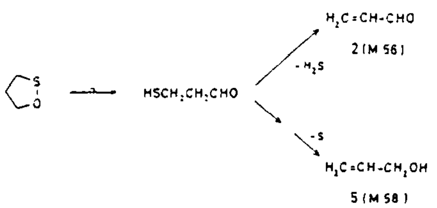


Fig. 3. Partial collision activation mass spectra of field induced molecular ions of (a) propanal (4), (b) oxetane (7), (c) allyl alcohol (5), and (d) the pyrolytically formed C_3H_6O isomer.

and/or 7 cannot be excluded. It should be added that the two low-intensity ion clusters around *m/z* 39 and 43 (Fig. 2b) are also observed, recording the complete CAMS spectrum of allyl alcohol. The formation of 2 by thermolysis of 1,2-oxathiolane has been discussed previously in terms of the initial formation of 3-mercaptopropanal, consecutively eliminating hydrogen sulphide [39,41].



At present, the formation of 5 is explained tentatively by removal of S from the cyclic hemimercaptal isomer of the mercaptoaldehyde, 2-hydroxythietane. Finally, it can be noted that a similar mechanism has been proposed recently for the thermal decomposition of the corresponding four-membered sulphenate, 1,2-oxathietane [42].

Rearrangement/isomerization reactions

The analyses of isomeric compounds present a common problem in pyrolysis experiments. Frequently appropriate crossover experiments have to be performed in order to ensure that apparent isomerizations do not arise from consecutive bimolecular reactions between initially formed products. Carrying out the reactions under pure unimolecular conditions the real-time CAMS analysis technique may be applied advantageously to rearrangement/isomerization reactions. In studies of isomerizations, both the starting material and the isomerized product of necessity exhibit the highest molecular

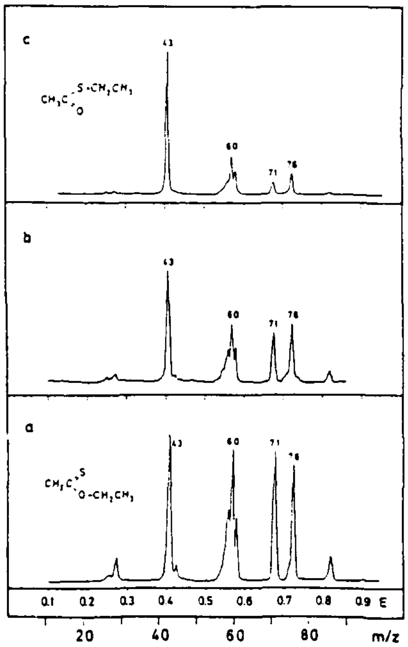
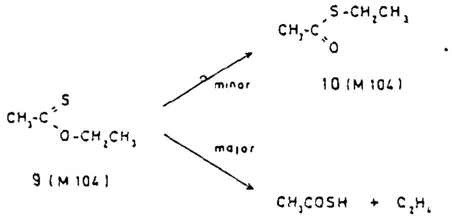


Fig. 4. Collision activation mass spectra of electron impact (70 eV) induced molecular ions (m/z 104) of ethyl thionoacetate (9), (a) without pyrolysis and (b) after pyrolysis at 1253 K, and (c) of ethyl thioloacetate without pyrolysis.

weights in the reaction mixture. Hence, the CAMS analysis can advantageously be carried out using EI ionization, leading to a higher sensitivity of the method.

The thiono—thioloacetate rearrangement has previously been reported by Oele et al. [43] and Bigley and Gabbott [44]. It was demonstrated that thiono esters rearrange to the thermodynamically more stable thiolo isomers, the reaction following first-order kinetics. However, on pyrolysing thiono esters that possess a β-hydrogen atom in the ester chain, the alkene elimination remains the predominant reaction [43,44]. In Fig. 4a and c the CAMS spectra of unthermolysed ethyl thionoacetate (9) and ethyl thioloacetate (10), respectively, are shown. Additionally, in Fig. 4b the CAMS spectrum recorded following the pyrolysis of ethyl thionoacetate at 1253 K is depicted. It is obvious that the mono-thioester apparently surviving the elevated temperature is a mixture of 9 and 10 (ratio 9/10 = 1.5; cf. ref. 38).



The reverse reaction, i.e., a thiolo—thiono rearrangement, is not observed on pyrolysing compound 10. It should be emphasized that the direct assay of the thiolo ester in the thermolysate is by no means straightforward, as pyrolysis of 9 at this temperature simultaneously leads to the formation of keten and ethanethiol [45], which may easily react to give the thiolo isomer.

In the thionoacetates the activation parameters for isomerization and elimination appear to be comparable [43,44]. The enhanced polarizability and nucleophilicity of the C=S bond relative to that of the C=O bond is assumed to play an important role in the isomerization reaction. However, with carboxylic acid esters the β-elimination is expected to be energetically much more favoured than the oxygen to oxygen alkyl group migration. Recently we have demonstrated by CAMS analysis the thermally induced intramolecular oxygen to oxygen methyl group migration in ^{18}O-labelled methyl acetate [38]. Methyl acetate was found to be thermally stable and the only concurrent reaction observed, a 1,2-elimination of methanol, proceeds to a very minor extent only. On this basis, it is of interest to know if oxygen to oxygen transfer of the ethyl group is detectable in the thermolysis of ^{18}O-labelled ethyl acetate (11). Previously Smith et al. observed very minor oxygen isomerization in ^{18}O-labelled ethyl acetate, but the phenomenon was not discussed [46].

The CAMS spectrum of electron impact ionized ethyl acetate is shown in Fig. 5. The dominating fragment (m/z 70) is a result of loss of H_2O from the molecular ion, a process demonstrated to involve mainly the carbonyl oxy-

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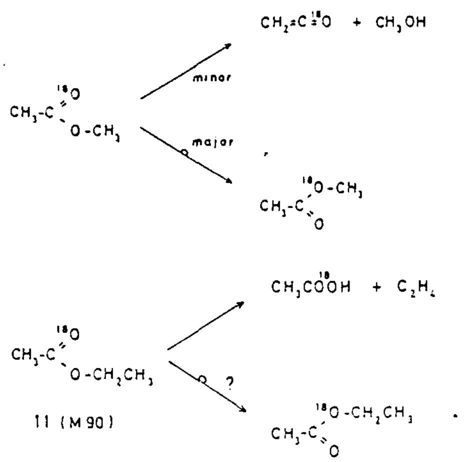


gen [47,48]. Fig. 6a shows the corresponding CAMS spectrum of ^{18}C-labelled ethyl acetate (11). It is emphasized that the CAMS spectrum of 11 reveals an apparent isomerization of the ionized molecule. It is noted that FI, which minimizes the risk of isomerization, leads to a comparable ion intensity ratio (*m/z* 70 : 72) (Table 1) in the FI—CAMS spectrum. Pyrolysis of 11 (Fig. 6b) affords a significant change in the *m/z* 70 : 72 ion intensity ratio (cf. Table 1) towards that expected for $CH_3C(O)^{18}OCH_2CH_3$. Simultaneously, the *m/z* 45 cluster changes in accordance with that predictable using the *m/z* 70 : 72 ion intensity ratio and the $CH_3CO^+ : CH_3CH_2O^+$ ratio (cf. Fig. 5), a thermally induced isomerization of ethyl acetate being unambiguously demonstrated. Hence, we tentatively propose an isomerization mechanism similar to that of methyl acetate, i.e., vibrational excitation of the OCO and COC in-plane bending modes of the ester group [38].

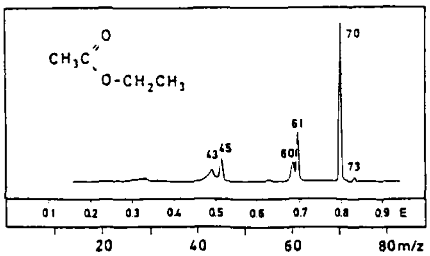


Fig. 5. Collision activation mass spectrum of the electron impact (70 eV) induced molecular ion (*m/z* 88) of ethyl acetate.

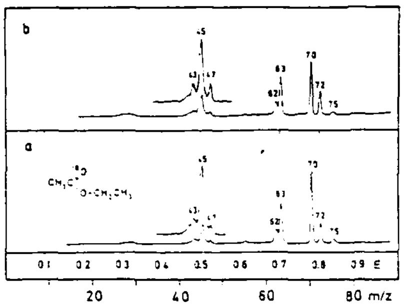
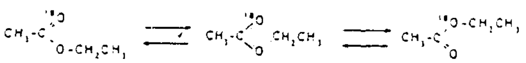


Fig. 6. Collision activation mass spectra of electron impact (70 eV) induced molecular ions (m/z 90) of ethyl [^{18}O]acetate (11), (a) without pyrolysis and (b) after pyrolysis at 1253 K.

TABLE 1

Intensity ratio of m/z 70 and 72 ions generated by collision activation of field ionization and electron impact induced molecular ions of ethyl [^{18}O]acetate (11)

	I_{72}/I_{70}
FI—CAMS	0.27
EI—CAMS	0.27
EI—CAMS after thermolysis at 1253 K	0.42



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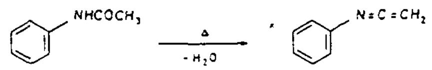
Generation of reference structures

The following discussion deals with the potential applicability of the pyrolysis method for in situ generation of otherwise inaccessible reference structures in connection with the study of gaseous ions. Knowledge on gaseous ion chemistry has increased rapidly during recent years owing to the development of powerful techniques for these specialized studies [17,49]. In most experiments (CA spectra, kinetic energy release, ΔH_f, etc.) the unknown ion structure is elucidated by comparison with reference ions [49]. Ion structures of odd-electron fragments are typically derived using molecular ions of authentic compounds assuming retention of the original geometry in the ionized state. However, when the required compounds may be too labile to be handled by ordinary mass spectrometric techniques, the pyrolysis method affords a unique opportunity for the in situ generation of such compounds. When the molecule contains heteroatoms, facilitating an estimate of possible charge localization in the ion, the pyrolysis generation may be especially advantageous. The possible formation of N-phenylketenimine (12) on pyrolysis of acetanilide (13) is chosen to illustrate this.



13 (M 135) 12 (M 117)

Substituted N-phenylketenimines are generally prepared by direct dehydration of the appropriate N-phenylamides [50]. However, the parent N-phenylketenimine (12) has only been prepared at low temperatures and polymerizes rapidly at room temperature [51]. In Fig. 7 the FIMS spectrum obtained after pyrolysis of 13 at 1043 K is depicted. Fig. 8 shows the EI—CAMS spectrum of the molecular ion of N-phenylketenimine (*m/z* 117). The application of EI is acceptable as acetanilide (13) eliminates H_2O under electron impact ionization to a very minor extent only [15,52]. Thus, the

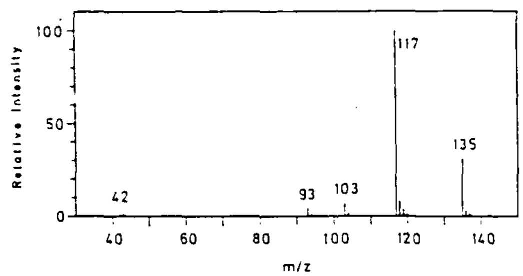


Fig. 7. Field ionization mass spectrum after pyrolysis of acetanilide (13) at 1043 K.

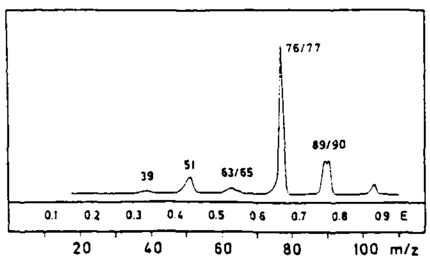
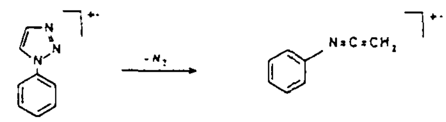


Fig. 8. Collision activation mass spectrum of the electron impact (70 eV) induced molecular ion of N-phenylketenimine (12) (*m/z* 117).

EI—CAMS spectrum (Fig. 8) represents a reference spectrum of N-phenylketenimine (12). The actual ion structure is of interest in connection with studies of *m/z* 117 ions commonly found in the EI spectra of phenylpyrazoles [53], *phenylimidazoles* [15] and *phenyltriazoles* [15]. The CAMS spectrum of 12 is found to resemble closely that of the *m/z* 117 ion arising from electron impact induced fragmentation of N-phenyl-1,2,3-triazole [15], which is strongly indicative of identical ion structures.



m/z 145 m/z 117

CONCLUSION

Real-time CAMS analysis has been found to be a useful method for studying primarily formed products in the gas phase pyrolysis of organic molecules, when ionized by field ionization, and for the study of thermally induced isomerizations using electron impact ionization. The applicability of in situ pyrolysis generation of labile compounds for gaseous ion studies has been demonstrated.

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APPENDIX 3.

GOLD-PLATED FILAMENTS FOR CURIE-POINT PYROLYSIS

HELGE EGSGAARD AND LARS CARLSEN

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TECHNIQUES IN GAS-PHASE THERMOLYSES

3 *. GOLD-PLATED FILAMENTS FOR CURIE-POINT PYROLYSIS

HELGE EGSGAARD and LARS CARLSEN *

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

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SUMMARY

The application of filaments exhibiting an inert surface, e.g., gold, for Curie-point pyrolysis is shown to minimize the degree of possible reactions induced by the presence of hot metal surfaces such as nickel and iron. The manufacture of gold-plated filaments is described and their utility in the study of pyrolytic reactions is illustrated.

INTRODUCTION

Since its introduction in the early 1960s [1–3], the induction heating technique, known as the Curie-point principle, has been demonstrated to be one of the most versatile means of studying pyrolytic decompositions of solids and non-volatile materials [4]. More recently the applicability of the technique to gas-phase pyrolytic studies has been reported [5–7].

The Curie-point pyrolysis technique, as generally applied, suffers, however, from several disadvantages: (a) the limited number of temperatures available, (b) the difference in composition of the single filaments available and (c) the possibility of reactions induced by collision between molecules and hot, reactive metal surfaces, e.g., nickel or iron. The former of these problems will be dealt with in a future paper [8], whereas this paper discusses the possible remedy of the latter two disadvantages.

We report here on the applicability of gold-plated filaments exhibiting identical, i.e., temperature-independent, and non-reactive surfaces for Curie-point pyrolysis studies.

* For Part 2, see ref. 6.

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EXPERIMENTAL

All pyrolyses were carried out by application of the flash vacuum thermolysis/field ionization mass spectrometry (FVT/FIMS) technique, which has been described in detail previously [5,6].

Manufacture of gold-plated filaments

The gold-plated Curie-point filaments were manufactured by electroplating. Ten to fifteen Curie-point filaments (wires) were mounted by soldering on a ca. 15 cm hook-up wire. The filaments were carefully burnished with fine-grade (400–600 grit) abrasive paper, followed by washing with acetone. Immediately before the electrolysis the filaments were placed for 5 min (at 20°C) in 1 *M* nitric acid. After thorough washing with distilled water the assembled filaments were gold plated by electrolysis, the filaments being the anode and pure metallic gold the cathode. The electrolysis bath contained 8 g of KCN, 4 g of Na_3PO_4, 4 g of NaOH and 2 g of $AuCl_3$ per litre. The electrolyses were carried out at 60°C with efficient stirring, the current being 5–10 mA.

Following the electroplating the assembled filaments were thoroughly cleaned with distilled water, separated and the single filaments polished with fine-grade abrasive paper as above.

The average thickness of the gold layer was estimated by weighing to be 10–15 μm.

RESULTS AND DISCUSSION

The greatest advantage of the application of filaments exhibiting identical surfaces in connection with pyrolysis studies is obvious, as temperature effects can be investigated without interference from possible concurrent catalytic reactions induced by the hot metal surfaces. Owing to its chemical inertness, gold appears preferable as the surface coating. However, before turning to the actual experimental verification, it is necessary to evaluate the extent to which a 10–15 μm gold coating may possibly change the thermal characteristics of the single filaments. The penetration depth, x, of the eddy currents in a conducting wire is given by the equation [9]

$$x = 5.03 \cdot 10^3 (\rho_t/\mu_r \cdot f)^{1/2}\ \mathrm{cm} \qquad (1)$$

where ρ_t is the resistivity ($\Omega \cdot$ cm) at temperature t (°C), μ_r is the relative magnetic permeability and f is the frequency (Hz) at which the induction coil is operated (for the actual device equal to $5.5 \cdot 10^5$ Hz). A relative magnetic permeability of 1.0 can be used for non-ferromagnetic materials such as

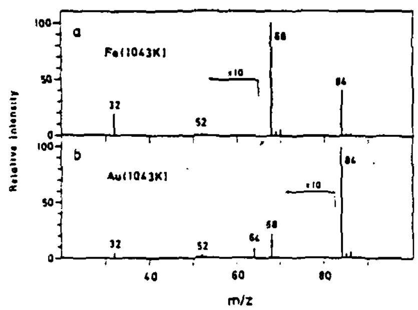


Fig. 1. Field ionization mass spectra after pyrolysis of dimethyl sulphoxide-d_6 at 1043 K using (a) an iron filament and (b) a gold-plated iron filament.

gold *. The temperature variation of ρ_t for gold is given by the equation [10]

$$\rho_t = 2.19(1 + 3.65 \cdot 10^{-3} \cdot t) \cdot 10^{-6}\ \Omega \cdot \text{cm} \qquad (2)$$

Eqn. 2 is valid in the temperature range −80 to 1000°C [10]. Based on these data the penetration depth of the eddy current in gold (f = 550 kHz) is estimated to vary from ca. 150 to ca. 225 μm in the temperature range 630–1275 K, which far exceeds the actual thickness of the gold coating, i.e., the surface gold coating will not change the thermal characteristics of the filaments.

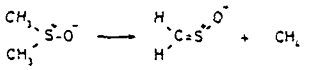
A series of gas-phase pyrolytic reactions recently studied by the FVT/FIMS technique is assumed to be influenced substantially by surface catalysis, e.g., the apparent extrusion of atomic oxygen from compounds containing a sulphoxide moiety such as dimethyl sulphoxide (DMSO) [11], thiiran 1-oxide [7], thietane 1-oxide [11], 1,2-oxathiolane 1-oxide [11] and thioketene S-oxides [12]. The rupture of the semipolar S–O bond requires around 90 kcal/mol [13], which exceeds the energy actually available by 20–30 kcal/mol. However, an interaction between the oxygen atom and a hot metal surface may lower the value significantly.

Fig. 1a shows the product composition following pyrolysis of dimethyl sulphoxide-d_6 (M 84) on a non-coated wire [Fe(1043)]. The reaction pattern is strongly dominated by the apparent extrusion of atomic oxygen leading to dimethyl sulphide-d_6 (M 68); minor amounts of formaldehyde-d_2 (M 32) and methanethiol-d_4 (M 52) are produced. The reaction mechanism has been discussed in detail previously [11]. The corresponding pyrolysis experiment carried out by application of a gold-plated filament [Au(1043)] resulted in

* $\mu_r \gg 1.0$ for ferromagnetic materials.

4

the product composition depicted in Fig. 1b. The pronounced decrease in the yield of dimethyl sulphide-d_6 is conspicuous; however, the apparent enhanced thermal stability of the sulphoxide under the latter conditions should be noted. Another interesting feature of DMSO pyrolysis under non-surface-catalytic conditions (Fig. 1b) is the formation of sulphine-d_6 (thioformaldehyde S-oxide), (M 64), a reaction which is totally suppressed when the pyrolysis is carried out using the iron filament. Block et al. [14] reported the pyrolytic formation of sulphine (2) from DMSO (1), the reaction being formulated to involve several consecutive steps; however, the present study clearly reveals a unimolecular pathway for sulphine formation from DMSO, tentatively formulated as a loss of methane. In this connection, it can be



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noted that the pyrolysis of thietane 1-oxide on a gold-plated filament afforded sulphine and ethylene as the major products, in agreement with the report of Block et al. [14].

Not only semi-polar sulphur–oxygen bonds appear to be labile under surface-catalytic conditions. A similar picture is developed with nitrogen–oxygen bonds, in the present context illustrated by the pyrolysis of nitrobenzene (3) (Fig. 2). In both cases depicted in Fig. 2, i.e., pyrolysis on iron and gold at 1043 K, two reactions apparently dominate the picture. These are the loss of atomic oxygen and nitrogen oxide, leading to formation of species with molecular weights of 107 and 93, assigned to nitrosobenzene (4) and phenoxy radicals (5), respectively, the latter probably being the result of

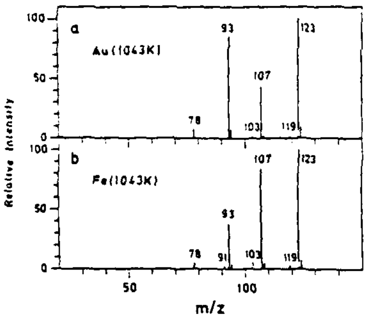
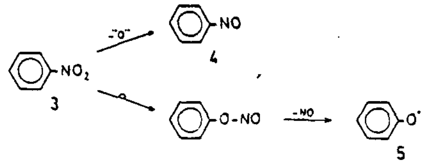


Fig. 2. Field ionization mass spectra after pyrolysis of nitrobenzene at 1043 K using (a) a gold-plated iron filament and (b) an iron filament.

a primary rearrangement of the nitrobenzene molecule into phenyl nitrite followed by NO elimination. This is an experimental verification of the



previously postulated intermediacy of phenoxy radicals in the pyrolysis of nitrobenzene [15,16]. In addition to phenoxy radicals the presence of phenyl radicals was expected [15,16]; however, only benzene, in minor amounts, was observed (Fig. 2), being formed by hydrogen abstraction, a reaction probably involving water bound to the surface of the inlet system. Surprisingly, no phenol, which would be the result of an analogous reaction of phenoxy radicals, was observed. The apparent discrepancy is explained by the different reactivities of the two radicals.

The most striking feature on changing from iron to a gold-plated filament is the variation in the phenoxy radical/nitrosobenzene ratio (*m/z* 93/107), changing significantly in favour of the former, which strongly suggests that the loss of atomic oxygen is facilitated by the presence of reactive surfaces (Fig. 2).

Apart from the above elimination of oxygen atoms, the presence of hot, reactive metal surfaces may be expected to influence the course of reaction severely, e.g., in pyrolyses of organosulphur compounds, which is illustrated below by examples from current thioketene research.

The pyrolytic sulphur extrusion from the thioketene 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane (Fig. 3a) observed previously [12] is unambigu-

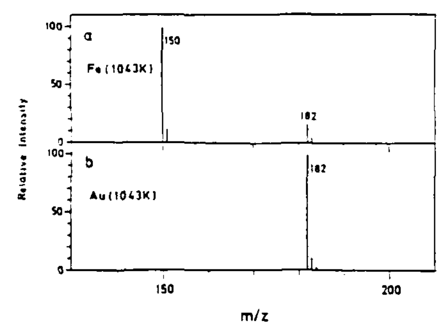
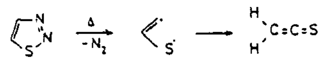


Fig. 3. Field ionization mass spectra after pyrolysis of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane at 1043 K using (a) an iron filament and (b) a gold-plated iron filament.

ously associated with the hot iron surface, as demonstrated by comparison with an experiment using a gold-plated filament [Au(1043)], under which conditions the thioketene is perfectly stable (Fig. 3b), in agreement with a C=S bond strength of about 125 kcal/mol [13]. Hence, by application of gold-coated filaments thioketenes apparently can be handled without decomposition.

Thioketenes can be generated by gas-phase pyrolysis of 1,2,3-thiadiazoles [18–20]. Very recently, a quantitative analysis by photoelectron spectroscopy (PES) of the gas-phase pyrolysis of the parent 1,2,3-thiadiazole (6) has been presented [21]. It was concluded that the reaction takes place via a 1,3-biradical (7) rearranging to thioketene (8), the latter being the sole product. It should be particularly noted that no acetylene was detected.



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Gas-phase pyrolysis of (6) at 1043 K using an iron filament caused extensive degradation, but only very small amounts of thioketene (8) were observed, the major product being acetylene. Pyrolysis of the thiadiazole using gold-plated filaments [Au(1043)] gave rise to the product composition shown in Fig. 4. Clearly thioketene (8) (M 58) is the major product, although minor amounts of acetylene (M 26) are seen. As the above experiment demonstrates our ability to handle thioketenes without decomposition, i.e., sulphur extrusion, we conclude that the apparent elimination of sulphur takes place unimolecularly from an intermediate species, probably the biradical (7).

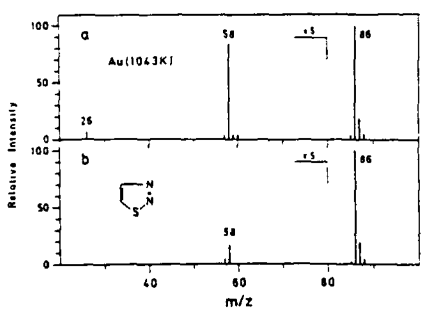

Fig. 4. Field ionization mass spectrum after pyrolysis of 1,2,3-thiadiazole at 1043 K (a) using a gold-plated filament and (b) without pyrolysis.

In order to explain the appearance of acetylene following pyrolysis using the technique described here [5,6], in contrast to the lack of the latter in the pyrolysis–PES experiments [21], it should be remembered that pyrolytically generated species are formed in vibrationally excited states. A relaxation of the excited species, in the present case the biradical (7), may be achieved by intermolecular collisions, molecule–wall collisions or intramolecularly, e.g., by fragmentation. As the pressure in the PES study [21] is ca. 10^2 times higher than that in the present study, it seems clear that a rapid intermolecular collisional quenching is achieved, apparently leading exclusively to (8), whereas in the latter case the excited biradical is "left alone" for approximately 1–5 μs, in which period of time a unimolecular relaxation by sulphur extrusion may take place, a mechanism which is tentatively suggested as being responsible for the acetylene formation observed in this study.

To summarize, we have demonstrated the applicability of gold-plated filaments for gas-phase Curie-point pyrolysis for studies of pure pyrolytic effects, eliminating possible catalytic effects induced by the presence of hot, reactive metal surfaces such as iron.

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APPENDIX 4.

HETEROGENEOUS CATALYSIS IN GAS-PHASE REACTIONS STUDIED BY CURIE-POINT PYROLYSIS. GAS-PHASE PYROLYSIS OF METHYL DITHIOACETAT

LARS CARLSEN AND HELGE EGSGAARD

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Note

Techniques in gas-phase thermolyses

Part 4 *. Heterogeneous catalysis in gas-phase reactions studied by Curie-point pyrolysis. Gas-phase pyrolysis of methyl dithioacetate

LARS CARLSEN * and HELGE EGSGAARD

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

(Received March 22nd, 1983; accepted March 28th, 1983)

In a recent study we reported the applicability of gold-plated filaments for gas-phase Curie-point pyrolysis [1], a technique which allows us to eliminate effects originating from the obvious differences in the surfaces for the single types of filaments for Curie-point pyrolysis (typically nickel, iron and cobalt), i.e., by applying gold-plated filaments we are able to study pure thermal effects.

However, selective surface coating of the filaments may, on the other hand, advantageously be used as an effective tool in studies of possible surface participation in gas-phase pyrolytic reactions, i.e., in the study of heterogeneous catalysis in gas-phase reactions. In this connection it is emphasized that gas-phase Curie-point analysis seems to be superior, as it can be demonstrated [2] that the reactions observed are the results of single collisions between the molecules and the hot metal surface, i.e., primary information is obtained, the picture not being eclipsed by the presence of possible secondary reactions.

In this paper, the utility of gas-phase Curie-point pyrolysis in studies on heterogeneous catalysis is illustrated by the gas-phase pyrolysis of methyl dithioacetate, as a part of our continuing interest in the pyrolytic behaviour of carboxylic acid derivatives [3–5]. The study was carried out by application of the flash vacuum pyrolysis/field ionization mass spectrometry (FVP/FIMS) technique, which has been described in detail previously [6,7].

In contrast to the thermal decompositions of methyl monothioacetates, which lead cleanly to ketene and methanethiol [5], a study of the dithio analogue, methyl dithioacetate (I), revealed at first sight a confusing picture.

* For Part 3, see ref. 1.

0165-2370/83/$03.00

Even at a temperature as low as 631 K (nickel surface) we found that I was degraded extensively (Fig. 1a). However, the products observed, C_3H_6S (*m/z* 74), dimethyl sulphide (C_2H_6S) (*m/z* 64), C_4H_6 (*m/z* 54) and methanethiol (*m/z* 48), are generally not to be associated with acetic acid ester thermolysis [3–5]. The first two of these products are apparently results of atomic sulphur and carbon monosulphide eliminations, respectively. The presence of the non-sulphur-containing compound (C_4H_6) seems surprising, as only three carbon atoms are available in I, i.e., only an interaction between the ester (I) and the hot nickel filament surface can account for the presence of C_4H_6 among the thermolysis products. Hence, it seems reasonable to assume that the thermal degradation of I is significantly influenced by reactions promoted by the presence of the hot, reactive nickel surface.

Experimental verification of the nickel surface involvement was obtained by thermolysing compound I at 631 K, but by application of a gold-plated filament [1]. It was observed (Fig. 1b) that under these conditions methyl dithioacetate, as expected, was perfectly stable. At higher temperatures

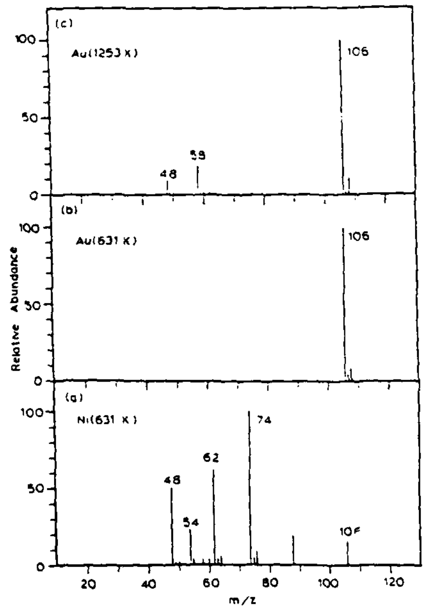
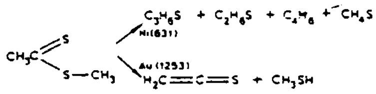


Fig. 1. Field ionization mass spectra of methyl dithioacetate following gas-phase thermolyses at 631 K (nickel), 631 K (gold) and 1253 K (gold).

(1253 K), however, still applying gold-plated filaments, we found that the ester (I) decomposed smoothly into the expected products, i.e., thioketene (*m/z* 58) and methanethiol (*m/z* 48) (Fig. 1c). Without gold-plating qualitatively the same picture as shown in Fig. 1a was seen.



I

A deeper mechanistic insight into the surface-promoted reactions of methyl dithioacetate (I), wich is outside the scope of this paper, requires isotopic labelling experiments in order to identify the sulphur atoms actually lost in the reactions leading to C_3H_6S and C_2H_6S, respectively. Parallel studies on the gas-phase pyrolysis of ^{34}S-labelled I are in progress.

This study has revealed the potential of the gas-phase Curie-point pyrolysis technique for investigations of heterogeneous catalysis, e.g., reactions involving hot nickel surfaces. The rapidity and facility with which these investigations can be carried out should be especially enphasized. The technique appears to be a highly informative method giving valuable information on primary reactions before one needs to turn to more costly and time-consuming preparative studies, e.g., in attempts to optimize certain desirable processes.

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APPENDIX 5.

CONTINUOUS-FLOW INLET SYSTEMS FOR LOW PRESSURE CURIE-POINT PYROLYSIS. INTRODUCTION OF PULSE-PYROLYSIS.

HELGE EGSGAARD AND LARS CARLSEN

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TECHNIQUES IN GAS-PHASE THERMOLYSES

PART 5 *. CONTINUOUS-FLOW INLET SYSTEMS FOR LOW PRESSURE CURIE-POINT PYROLYSIS. INTRODUCTION OF PULSE-PYROLYSIS

HELGE EGSGAARD and LARS CARLSEN *

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

(Received March 6th, 1984; accepted March 13th, 1984)

SUMMARY

With emphasis on a constant reactant flow, a series of inlet systems for gas-phase Curie-point pyrolysis-mass spectrometry experiments have been studied. Inlet systems for the handling of gaseous, liquid and oligomeric (solid) samples have been designed and their performances evaluated. The principle of pulse-pyrolysis is introduced and its applicability to kinetic studies outlined.

INTRODUCTION

Recently the applicability of the direct combination of a Curie-point controlled pyrolysis unit and a mass spectrometer/mass spectrometer system to gas-phase studies has been reported [1]. The use of field ionization in combination with collision activation mass spectrometry has been found to be a particularly superior method for real-time analysis of gas-phase reactions carried out under flash vacuum conditions [2]. In the original approach the compound under investigation was introduced by means of micro-syringes via a heatable injection block system. However, it appears that this method reduces the number of compounds that can be studied to those which exhibit an appropriate vapour pressure, i.e. that evaporate within few seconds on injection. Thus, a continuous reactant flow into the reactor would greatly facilitate the mass spectrometric analysis, as a constant flow of pyrolysis products would consequently be achievable.

* For Part 4, see L. Carlsen and H. Egsgaard, J. Anal. Appl. Pyrol., 5 (1983) 257.

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2

As a result of our continuing interest in flash vacuum pyrolytic studies, we report here on inlet systems that have been designed with the purpose of delivering a continuous flow of reactant in timescales from minutes to hours. In addition, the possibility of changing the Curie-point filaments without disconnecting the pyrolysis unit from the mass spectrometric system is emphasized. The performance is illustrated with examples from current research areas such as the gas-phase pyrolysis of di-*tert.*-butyl peroxide and nitrobenzene and the generation of 1,2-oxathiolane and 1,2-dithiolane from solid precursors. Finally, as a consequence of the presence of a continuous flow through the pyrolysis reactor, we introduce the principle of pulse-pyrolysis, a technique by which gas-phase Curie-point pyrolysis can be advantageously applied to kinetic studies.

EXPERIMENTAL

Low-pressure pyrolyses were carried out using the pyrolysis–mass spectrometry technique previously described in detail [1,2].

The pyrolysis unit consists of three main parts: (1) inlet system, (2) reactor (Pye-Unicam PV4000) and (3) pyrolysis unit–mass spectrometer interface [1]. The mass spectrometric real-time analyses were performed on a Varian-MAT CH 5D instrument [2].

S-Phthalimido-3-mercaptopropan-1-ol [3] and the 1,2-dithiolane oligomer [4] were synthesized as reported previously (although ref. 4 states that the dimer of 1,2-dithiolane is formed, the synthesis afforded the oligomeric material).

Sample handling

The problem of sample introduction is sub-divided according to whether the sample is (a) gaseous or easily evaporable, (b) a liquid exhibiting a moderate to low vapour pressure at ambient temperature or (c) a solid, e.g., oligomeric species, whereby the monomeric substance can be generated by gentle heating.

Case (a) is solved by adoption of the technique commonly used in mass spectrometric gas analysis. The inlet system consists of a glass reservoir (ca. 100 mL) connected to the reactor via a glass capillary constrictor (Fig. 1A). Owing to the relatively high vapour pressure in the reservoir (10–100 Torr) the flow into the reactor becomes viscous *. The glass leaks were made by

* In a viscous flow the amount of material transferred depends on the square of the pressure difference and also on the viscosity coefficient. Hence, when the reactant is a mixture of two or more components, the flow-rate of the single components is a function of the actual overall composition in the reservoir. This is in contrast to the molecular flow situation, where the flow-rate of a single component depends only on the pressure difference and is virtually independent of the possible accompanying components.

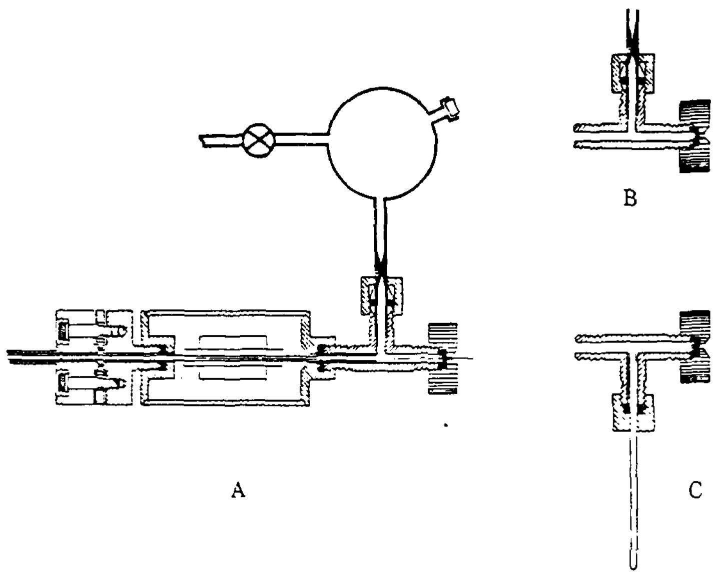

Fig. 1. Inlet systems for low-pressure Curie-point pyrolysis: (A) continuous gas inlet system assembled with the PV4000 pyrolysis unit, (B) the continuous "liquid" inlet system, and (C) the "solid" inlet system.

constricting a Pyrex tube (6 mm O.D.) by judicious heating and blowing in a C_3H_6/O_2 flame. The leak-rates of the individual capillaries were determined by means of the gas inlet systems of the mass spectrometer. In flash vacuum pyrolysis (FVP) experiments, were field ionization was used as the detection method, leak-rates of ca. $5 \cdot 10^{-3}$ Torr l s^{-1}, corresponding to a mass flow of ca. 0.1 $\mu g\ s^{-1}$ to the ion source were found preferable.

Samples with moderate to low vapour pressures [case (b)] could in principle be handled using a heatable version of the above-described gas inlet system. However, such compounds frequently appear to be adherent and extensive flushing may be necessary in order to avoid interference from preceding experiments. In order to handle such compounds a system consisting of a capillary leak only has been tested (Fig. 1B). The liquid sample is placed directly into the leak cavity, the desirable amount of material (ca. 0.1 $\mu g\ s^{-1}$) evaporating continuously through the leak into the FVP reactor. As the mass flow under these conditions is considerably higher than with gaseous samples, leaks possessing leak-rates of the order of $5 \cdot 10^{-5}$ Torr l s^{-1} have been found suitable for obtaining a ca. 0.1 $\mu g\ s^{-1}$ mass flow.

4

Finally, an inlet system has been designed for pyrolytic studies of gaseous products primarily generated from solids, e.g., oligomers (Fig. 1C). The gaseous species are obtained continuously by *smooth thermal decomposition* (oil or air bath) of the solid placed in an external quartz tube. In principle, this type of inlet system could be used to evaporate solids in general. However, such experiments are hampered by the thermal non-uniformity of the reactor, i.e., the temperature of the reactor wall is close to ambient, giving rise to loss of compounds due to adsorption on to the cold surfaces. This is a clear disadvantage of Curie-point pyrolysis in its present form. However, as an interesting consequence, it appears that the pyrolytic reactions become the result of single collisions between the reactant molecules and the hot filament [5].

APPLICATIONS AND DISCUSSION

Inlet systems

The continuous flow of reactants and pyrolysis products facilitates the optimal operation of the mass spectrometer. This is especially important when field ionization is applied, as field ionization, even though it is the ionization mode of choice for the determination of product distributions in complex organic mixtures, in general exhibits a low sensitivity compared with, e.g., electron impact ionization. The utility of the glass-inlet system (Fig. 1A) for the determination of low-intensity pyrolysis products is illustrated by the pyrolysis of di-*tert.*-butyl peroxide (DTBP). This compound is known to undergo homolytic cleavage of the O–O bond to form *tert.*-butoxy radicals, which decompose consecutively into acetone and methyl radicals [6,7]:

$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2(CH_3)_3C\text{-}O^{\cdot}$$

$$(CH_3)_3C\text{-}O^{\cdot} \overset{k_3}{\rightarrow} CH_3\text{-}CO\text{-}CH_3 + \dot{C}H_3$$

In Fig. 2 the field ionization mass spectra of di-*tert.*-butyl peroxide without (Fig. 2a) and following pyrolysis at 1043 K (Fig. 2b) are shown. After pyrolysis the formation of a compound exhibiting a molecular ion of m/z 73 is apparent and it seems reasonable to suggest that this ion is due to the *tert.*-butoxy radical ($C_4H_9O^{\cdot}$; $M = 73$).

The mean transfer time from the reactor to the ion source of the mass spectrometer has been estimated to be ca. $4 \cdot 10^{-1}$ s ($M = 100$). Based on the the rate constant for the unimolecular decomposition of *tert.*-butoxy radicals into acetone and methyl radicals ($k_3 = 10^{4.5}$, corresponding to a half-life $t_{1/2} = 2 \cdot 10^{-5}$ s [8]) only very small amounts of the *tert.*-butoxy radicals

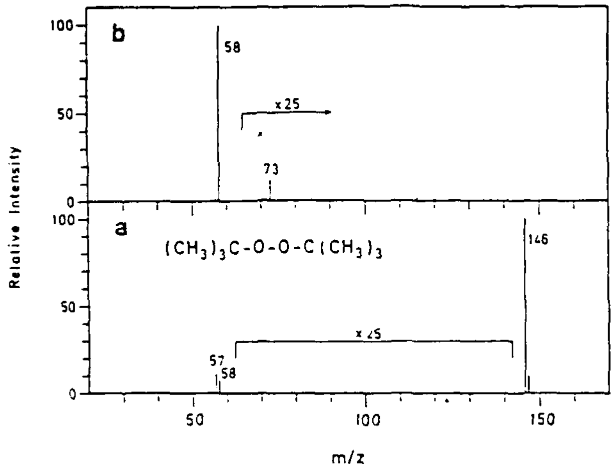

Fig. 2. Field ionization mass spectra of di-*tert.*-butyl peroxide (DTBP), (a) before pyrolysis and (b) following pyrolysis at 1043 K (gold-plated filament).

should enter the ion source. However, the line-of-sight inlet system allows a limited number of radicals to reach the ion source in a few paths, i.e., the population corresponding to the lower bound of the function defining the transfer time from the reactor to the ion source, which may account for the detection of the species.

It is noteworthy in this connection that in a pyrolytic study on aliphatic nitrites [9] the primary generated alkoxy radicals escape detection in all instances, clearly demonstrating the performance of the present system.

The application of collision activation mass spectrometry plays an important role in the characterization of single pyrolytically generated compounds. In order to obtain collision activation mass spectra of high quality, a stable primary ion beam is required and hence a stable and sufficient flow to the ion source. In particular, studies on isomerization reactions require a high reproducibility of the relative ion intensities in order to obtain an unambiguous verification of the isomerized species. The glass-inlet system is most useful for ensuring a stable flow into the reactor with gases or low-boiling liquids, but is inadequate in studies on compounds that exhibit moderate to low vapour pressures. Nitrobenzene is a relatively polar compound with a modest vapour pressure [$P(85\,°C) = 10$ Torr]. The unimolecular pyrolysis of nitrobenzene by application of the liquid-capillary-inlet system (Fig. 1B) has been reported previously [10]. The product distribution determined by field ionization (Fig. 3) reveals an intense ion of m/z 93,

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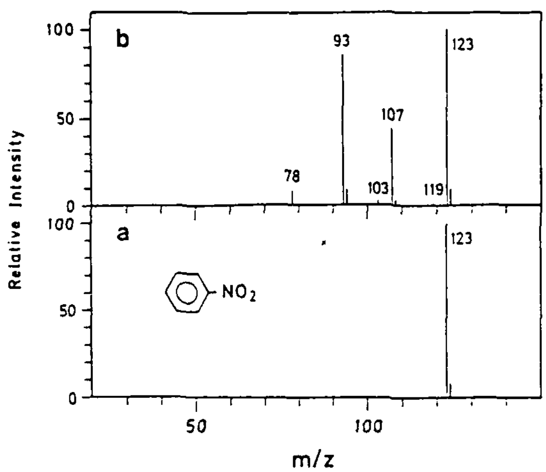


Fig. 3. Field ionization mass spectra of nitrobenzene. (a) before pyrolysis and (b) following pyrolysis at 1043 K (gold-plated filament).

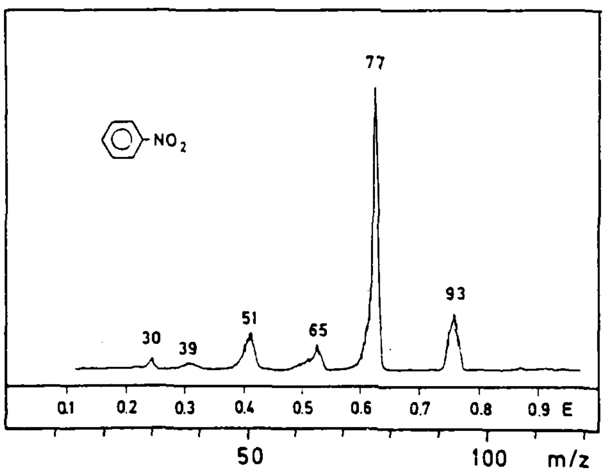


Fig. 4. Collision activation mass spectrum of the electron impact-induced molecular ion of nitrobenzene (m/z 123).

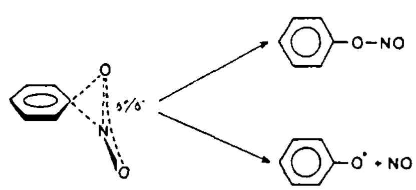
assigned to the phenoxy radical, which a priori can be expected to be generated by removal of NO from an intermediate phenyl nitrite [11,12]. In an attempt to obtain an experimental verification of this reaction the electron impact-induced molecular ion (m/z 123) was investigated by collision activation without and following pyrolysis (1043 K). Fig. 4 shows the collision activation mass spectrum of unpyrolyzed nitrobenzene, the spectrum being virtually unchanged following pyrolysis. The electron impact spectra of nitro compounds are in general different from those of the corresponding nitrites [13] and therefore significant differences between the collision activation mass spectra of nitrobenzene and phenyl nitrite should also be expected [2]. With this background, we conclude that phenyl nitrite is not present in the pyrolysate entering the ion source (< 2% relative to nitrobenzene).

The intermediacy of nitrites in the pyrolysis of nitro compounds is generally formulated as a sequence of radical reactions [14]:

$$Ph{-}NO_2 \rightarrow Ph^{\cdot} + NO_2$$

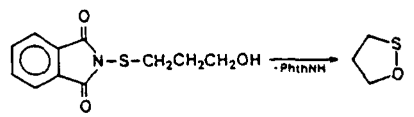
$$Ph^{\cdot} + NO_2 \rightarrow Ph{-}O{-}NO$$

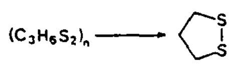
As bimolecular reactions can be regarded as absent under the present conditions, the observed products have to be rationalized in terms of unimolecular reactions only. The formation of the necessary C–O bond most probably involves a three-centred transition state:



The activated complex may possess two distinct resonance structures, which are expected to lead to phenyl nitrite, by ring opening, and the phenoxy radical, by direct expulsion of NO. The apparent absence of phenyl nitrite in the pyrolysate is in agreement with the latter mechanism. However, taking the thermal lability of nitrites into account, we are unable to rule out definitely the possible intermediacy of phenyl nitrite in the low-pressure pyrolysis of nitrobenzene.

Solids, owing to the thermally non-uniform reactor design, can only be handled with difficultly, as mentioned in the Introduction. However, a solid-inlet system has been used successfully to generate desired compounds from polymers or by specific thermally induced reactions; subsequently the liberated gaseous species may be subjected to pyrolytic studies. The latter is well illustrated by the generation of the cyclic sulphenic ester 1,2-oxathiolane by smooth cracking of the phthalimido derivative [2,15]. An investigation of the gaseous product by field ionization (Fig. 5a) reveals only a single product, 1,2-oxathiolane. The byproduct phthalimide remains in the reaction tube. The related disulphide, 1,2-dithiolane, at ordinary temperatures and pressures known only as a polymeric substance, is similarly obtained in high purity by heating the polymer to its melting point (105–110 °C) [4] (cf. Fig. 5b).





In summary, we have demonstrated that the inlet systems described here are capable of handling even compounds with very different physical properties, i.e., from gaseous to polymeric materials.

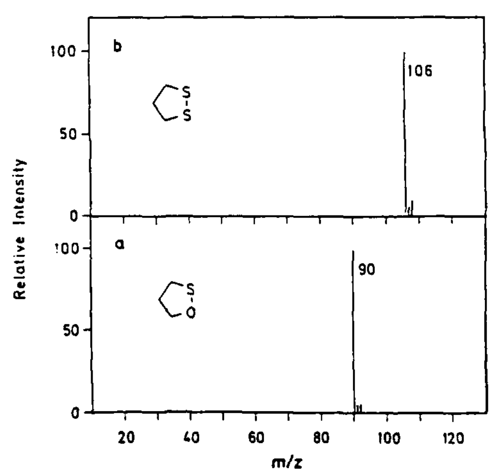


Fig. 5. Field ionization mass spectra of (a) 1,2-oxathiolane and (b) 1,2-dithiolane.

Pulse-pyrolysis

Kinetic studies of pyrolytic reactions are often troublesome * owing to the possible interference from consecutive bimolecular reactions involving primary generated pyrolysis products. However, the very low pressure pyrolysis (VLPP) technique, described e.g., by Golden et al. [17], reduces this problem, whereas the kinetic evaluation turns out to be complicated [18–22].

The very low pressure ensures that only unimolecular reactions appear and the appearance of consecutive unimolecular reactions is diminished by careful reactor design. The use of inductive heating in connection with low-pressure gas-phase pyrolysis is well established [23], and in contrast to the traditional Knudsen reactor design the Curie-point pyrolyzer benefits from very fast heating rates and extremely well defined pyrolysis temperatures. The introduction of continuous inlet systems opens up the opportunity of carrying out kinetic studies by low-pressure Curie-point pyrolysis, the potential being illustrated with examples from di-*tert.*-butyl peroxide (DTBP) pyrolysis. The pyrolysis of the peroxide is virtually irreversible under the given conditions owing to the low reactor pressure. Hence the process will follow first-order kinetics. Introduction of the term specific flux [17] of the peroxide, F_{DTBP}, entering the reactor leads to the following expression:

$$F_{DTBP} = k_e[DTBP] + k[DTBP] \qquad (1)$$

For $k = 0$, $F_{DTBP} = k_e[DTBP]_0$; k_e is the unimolecular escape rate constant [17], which is equal to the reciprocal of the mean residence time, t_{mr}, in the present instance being approximated by the Knudsen formula (eqn. 2),

$$t_{mr}\,(s) = 4V/\bar{c}AK \qquad (2)$$

where V is the reactor volume (0.13 cm^3), A the area of the orifice (0.03 cm^2) and K a constant **. The mean molecular rate, $\bar{c}$, is determined according to the kinetic gas theory (eqn. 3), T being the temperature and M the molecular weight of the molecule under investigation, i.e., in the present case $M = 146$.

$$\bar{c}\,(cm\ s^{-1}) = 1.46 \cdot 10^4\sqrt{(T/M)} \qquad (3)$$

On pyrolysis, the stationary concentration of the peroxide, $[DBTP]_T$, is

* Actually, the pyrolysis of a single compound becomes equivalent to the decomposition and interactions of often complex mixtures of primary products, e.g., the simulation of the ethane-propane pyrolyses requires an estimate of ca. 400 main reactions [16].

** The constant K is a correction factor, which has to be included, because in the present set-up the pyrolyzate leaves the reactor zone through a tube (length 24 cm, radius r 0.1 cm) [24]. In the present case K, which is a dimensionless function of l/r, equals 0.011 [5]. It should be noted that in our previous studies this "tube effect" was neglected [1], which caused a pronounced underestimate of mean residence and transfer times.

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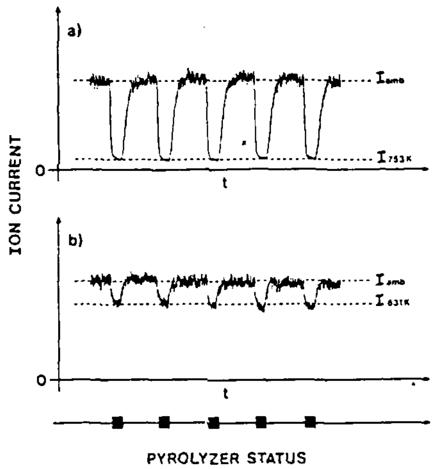

Fig. 6. Pulse-pyrolysis of di-*tert*.-butyl peroxide (DTBP) (m/z 146) at 753 K (a) and 631 K (b) (gold-plated filaments), the ion current as function of time being monitored by field ionization mass spectrometry. Pyrolysis pulse length: 15 s (denoted by -■-).

smaller than the corresponding values without pyrolysis $[DTBP]_0$, owing to the decomposition that takes place.

$$F_{DTBP} = k_e[DTBP]_0 = k_e[DTBP]_T + k(T)[DTBP]_T \quad (4)$$

Rewriting eqn. 4 leads to the expression 5, where the stationary concentrations $[DTBP]_0$ and $[DTBP]_T$ are directly related to the ion intensities of the molecular ion (m/z 146).

$$\frac{[DTBP]_0 - [DTBP]_T}{[DTBP]_T} = \frac{k(T)}{k_e} = \frac{I_{amb} - I_T}{I_T} \quad (5)$$

Fig. 6 shows a sequence of pyrolyses with adequate cooling periods, i.e., pulse-pyrolysis, of di-*tert*.-butyl peroxide at 631 and 753 K. A high reproducibility of the stationary concentrations, $[DTBP]_0$ and $[DTBP]_T$, is apparent. Also noteworthy are the relatively long cooling periods, which increase considerably with increasing pyrolysis temperature (cf. Figs. 6 and 7). The relevant data derived from Fig. 6 and the calculated rate constants are given in Table 1. It is emphasized that the calculated rate constants $[k(T)]$ are low-pressure values, which by means of the RRKM theory [18] in

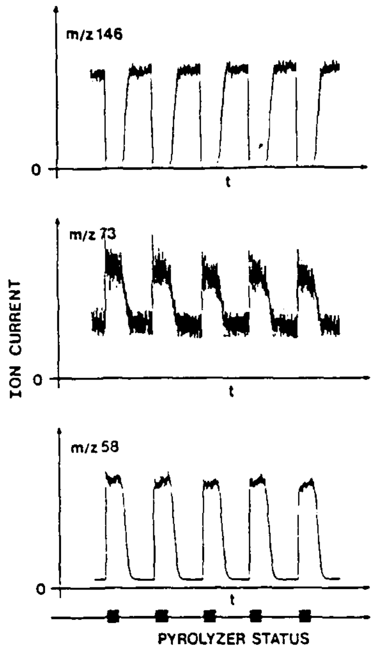

Fig. 7. Pulse-pyrolysis of di-*tert*.-butyl peroxide (DTBP) at 1043 K (gold-plated filament), the ion current as function of time being monitored by field ionization mass spectrometry: (top) the precursor DTBP (m/z 146), (middle) the primary product ($C_4H_9O^{\cdot}$) (m/z 73) and (bottom) the eventual product (acetone) (m/z 58). Pyrolysis pulse length: 15 s (denoted by -■-).

principle may be converted into the corresponding high-pressure values $k_{\infty}(T)$ *. However, on the basis of the limited number of data presented here, this will not be achievable. A method for conversion of $k(T)$ to $k_{\infty}(T)$ and subsequent evaluation of high-pressure Arrhenius parameters, especially designed for low-pressure Curie-point pyrolysis studies, based on an effective temperature approach, is being developed [5].

* The high-pressure values $k_{\infty}(T)$ are given by $\log k_{\infty}(T) = 15.6 - 37.4/\theta$ ($\theta = 2.303RT$) (ref. 8, p. 430), i.e., the rate constants for 631 and 753 K are calculated to 444 and 55735 s^{-1}, respectively. The rate constants determined here (Table 1), on the other hand, correspond to effective temperatures of 546.9 and 604.2 K, respectively, i.e., the molecules obtain an internal energy corresponding to 75 and 67%, respectively, of that theoretically achievable.

TABLE I

Low-pressure rate constants for the decomposition of di-*tert.*-butyl peroxide (DTBP)

T (K)	I_{amb}	I_T	t_{mr} (ms)*	k_e (s^{-1})*	$k(T)$ (s^{-1})
631	100	76	70	14.3	4.5
753	100	10.8	70	14.3	118.1

* Owing to the "single-collision nature" of the pyrolyses in the present set-up [5], the molecules will probably leave the reactor with a temperature close to ambient. Hence, t_{mr}, and consequently k_e, applied here correspond to 300 K.

Finally, it should be noted that the principle of pulse-pyrolysis may also be useful for the detection of minor pyrolysis products as shown in Fig. 7, where the appearance of the ion at m/z 73 (*tert.*-butoxy radical) is synchronous with the appearance of the major product acetone (m/z 58) and the disappearance of the precursor DTBP (m/z 146), unambiguously demonstrating that the formation of m/z 73 is pyrolytically induced.

CONCLUSION

We have described inlet systems for *low-pressure Curie-point pyrolysis*, with emphasis on a constant, continuous flow, which appears of importance in connection both with identification studies (collision activation mass spectrometry) and with kinetic investigations. The potential of low-pressure Curie-point pyrolysis in kinetic studies leading to low-pressure rate constants has been demonstrated. However, to derive high-pressure Arrhenius parameters investigations of the energy-transfer process with special reference to the effective collision frequency in the reactor are necessary.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Carsten Christoffersen (University of Copenhagen) for providing a sample of 1,2-dithiolane oligomer.

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APPENDIX 6.

PULSE PYROLYSIS: GAS KINETIC STUDIES IN AN INDUCTIVELY HEATED FLOW REACTOR

HELGE EGSGAARD, PETER BO AND LARS CARLSEN

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TECHNIQUES IN GAS-PHASE THERMOLYSES

PART 6*. PULSE PYROLYSIS: GAS KINETIC STUDIES IN AN INDUCTIVELY HEATED FLOW REACTOR

HELGE EGSGAARD, PETER BO and LARS CARLSEN *

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

SUMMARY

A prototype of an inductively heated flow reactor for gas kinetic studies is presented. The applicability of the system, which is based on a direct coupling between the reactor and the ion source of a mass spectrometer, is illustrated by investigations of a series of simple bond fission reactions. The method permits the direct determination of low-pressure rate constants, the transformation to high-pressure values, and correspondingly evaluation of activation parameters, being derived by means of an empirical "effective temperature approach".

INTRODUCTION

In recent years we have reported in a series of papers on the applicability of Curie-point pyrolysis to gas-phase pyrolytic studies [1–6], the system being based on a direct combination of the Curie-point pyrolyser and the ion source of a mass spectrometer. As stated previously [3], one of the major disadvantages of the Curie-point technique, as generally applied, is the limited number of pyrolysis temperatures available. Especially from a kinetic point of view, the availablity of only 5–10 temperatures in the range 358–1131°C is highly unsatisfactory. Further, varying the temperature, by changing the filament, may be expected to create undesirable geometric changes in the reactor owing to possible alteration of the flow conditions.

In order to overcome these disadvantages while maintaining the advantages of the inductive heating principle, e.g., rapid heating, we describe here a prototype of an inductively heated flow reactor for gas kinetic studies, where arbitrarily chosen temperatures in the range from ambient to the Curie-point of the filament can be reached within less than 1 min, the

* For Part 5, see ref. 6.

0165-2370/85/$03.30

stabilization of the temperatures being generally within ±1%. In combination with the recently introduced continuous flow inlet systems and the principle of pulse pyrolysis [6], the latter term being defined as a sequence of pyrolyses separated by adequate cooling periods, an effective tool for gas kinetic studies is obtained.

A complete kinetic investigation, including the determination of 20 rate constants over a filament temperature range of 100–150°C, may be achieved within ca. 60 min. This is at least one order of magnitude faster than conventional heating techniques. The utility of the technique is illustrated by studies on a series of well investigated reactions.

EXPERIMENTAL

The filament

The construction of the "multi-temperature" filament is based on a chromel–alumel thermocouple (0.5 mm O.D.). The thermocouple was connected to the internal surface of a gold-plated iron tube (length 35 mm, O.D. 1 mm, I.D. 0.8 mm) by Au soldering, the necessary heating being carried out inductively by application of a small length of cobalt wire to ensure a high temperature (1131°C). To ensure a stable, non-catalytic surface, the assembled filament was gold-plated as described previously [3]. The multi-temperature filament is shown schematically in Fig. 1.

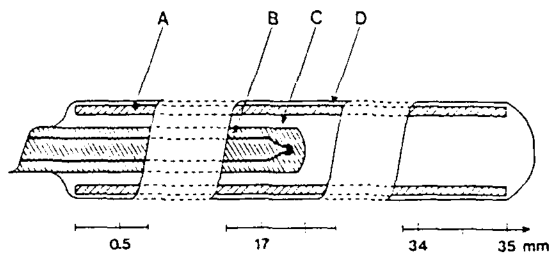

Fig. 1. "Multi-temperature filament" design. A, Ferromagnetic (e.g., Fe) tube, B, thermocouple; C, gold matrix; D, gold plating.

Temperature control

Not surprisingly, the techniques outlined here, i.e., temperature control and data collection and handling (see below), rely heavily on computerization of the pyrolysis–mass spectrometry system. Fig. 2 shows the experimental set-up. The mass spectrometer and pyrolysis unit consist of a Varian-MAT

CH 5D and a modified Pye Unicam PV4000 pyrolyser, respectively (cf., ref. 1). The computer facility is centred around a Hewlet-Packard HP9836 desk-top computer. The system is shown in Fig. 2.

In contrast to the conventional Curie-point technique, where the high-frequency (HF) unit is operated continuously throughout the duration of the pyrolysis, the multi-temperature inductive heating method is based on a pulse-mode operated HF unit. Hence the temperature control is the result of an interplay between the following three HF parameters: (1) pulse length (the time periods where HF is applied), (2) delay time (the time periods between the HF pulses) and (3) amplitude. The first two are controlled interactively via the HP9836 unit, typical values being 25 and 200 ms, respectively. The amplitude, on the other hand, is controlled manually. Owing to the relatively low power (30 W) delivered by the PV4000 unit, lowering of the amplitude is only of interest at low filament temperatures ($T_f < 500$°C).

Obviously, a given pulse length/delay ratio is, in principle, the optimal choice for a narrow temperature range only. However, in practice it can be used over a T_f range of 100–150°C without any significant decrease in quality.

Attainment of a given arbitrary temperature appears as a three-parameter process: (a) a rapid sequence of HF pulses to obtain the temperature required, (b) a simple on/off procedure to gain thermal equilibrium in the filament and (c) a final control based on HF pulses delivered only if the temperature profile is decreasing and if the temperature is below the chosen value (Fig. 3).

In Fig. 4 temperature variations with time for $T_f = 400$, 500, 600 and 700°C are shown. Fig. 5 illustrates the actual temperature stabilization for $T_f = 500$°C. In general, the temperature control achieved is better than ± 1%.

For kinetic studies, a series of filament temperatures, typically over a

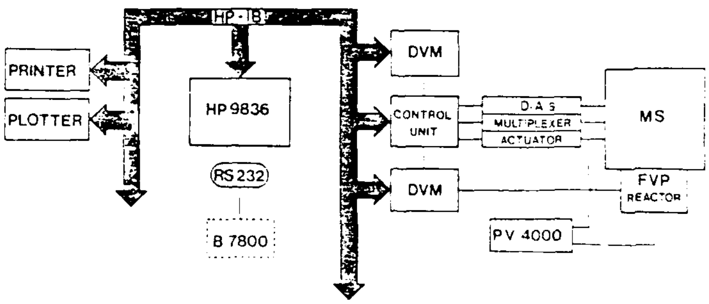

Fig. 2. Computerized pulse pyrolysis–mass spectrometry configuration.

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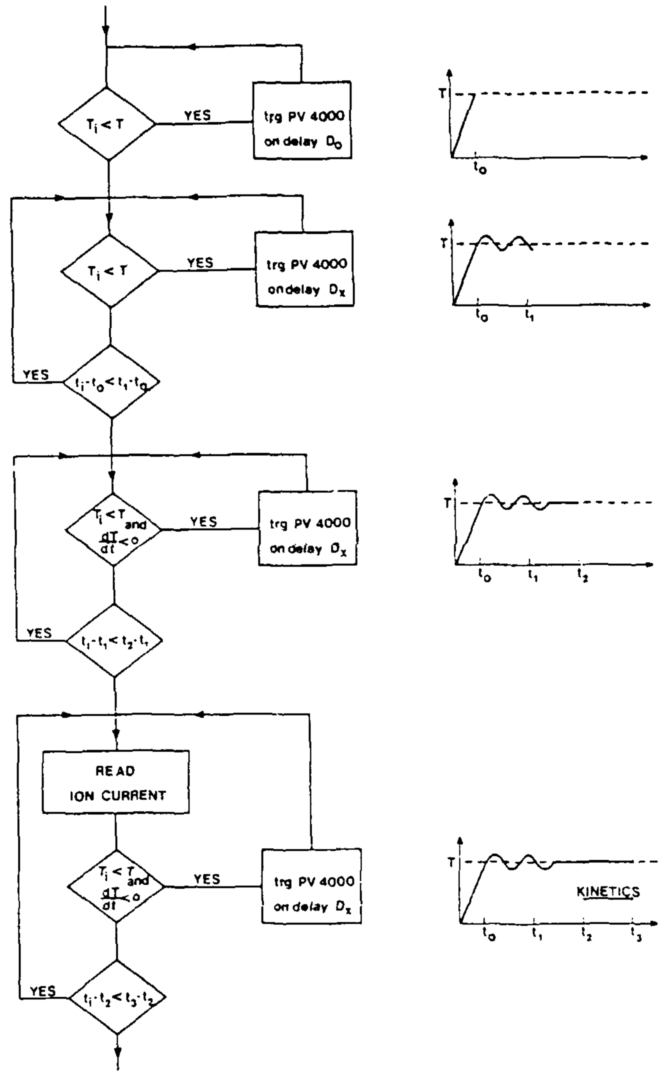


Fig. 3. Temperature control flow chart.

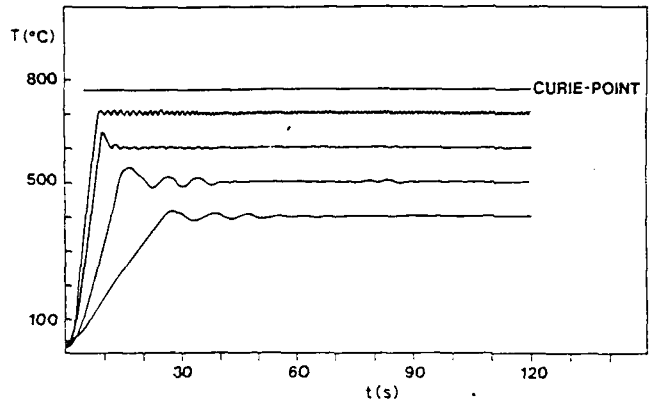


Fig. 4. Arbitrary temperature selection by "multi-temperature filament" (T_f = 400, 500, 600 and 700°C).

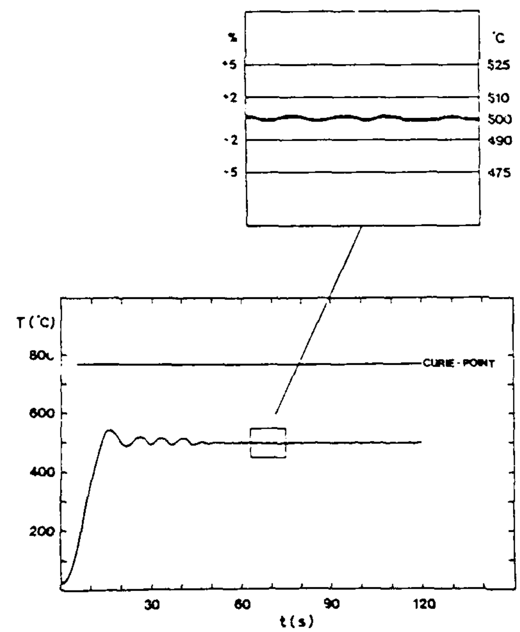


Fig. 5. Temperature stability of "multi-temperature filament" at T_f = 500°C.

range of 100–150°C, are needed, with adequate cooling periods, i.e., pulse pyrolysis. In Fig. 6 a pulse pyrolysis sequence is shown, the filament temperature ranging from 400 to 525°C in steps of 25°C.

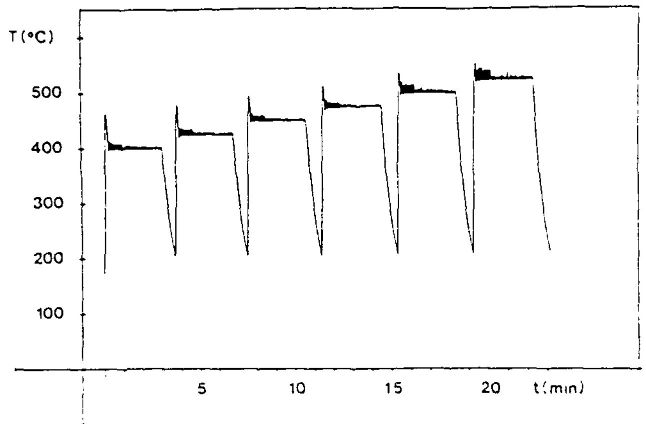


Fig. 6. Pulse pyrolysis sequence for kinetic studies.

Data collection and handling

As the inductive heating procedure gives rise to high rates of temperature increase, rapid control of the HF unit is crucial, which can only be achieved by a relatively large number of temperature measurements (ca. 50 measurements per second). The temperature measurements are conducted via an HP3497A data acquisition/control unit and an HP3456A digital voltmeter. The corresponding digitized ion currents (see below) are compiled in parallel by a HP3478 digital voltmeter.

The collected data are evaluated by the HP9836 computer facility in order to obtain low-pressure rate constants, as well as to obtain the low- to high-pressure correction and eventually the Arrhenius parameters.

Kinetic analysis

Kinetic studies of pyrolytic reactions, e.g., within the field of combustion, are often troublesome, owing to the possible appearance of several consecutive uni- and bimolecular reactions involving primary generated pyrolysis products [7]. However, carrying out the pyrolysis at very low pressures, as described by Golden et al. [8], diminishes this problem, as only unimolecular reactions will appear. Unfortunately, the subsequent kinetic analysis turns out from a theoretical point of view to be complicated [9–13]. Briefly, it can be said that the problem arises as the reacting molecules in a very low pressure pyrolysis flow reactor do not reach thermal equilibrium, owing to an insufficient number of molecule–wall collisions, before they leave the reactor. Hence the statistical energy distribution in the molecules does not correspond directly to the reactor temperature. This effect, the so-called fall-off, becomes increasingly pronounced at higher pyrolysis temperatures. Theoretically, the unimolecular behaviour of reacting molecules at low pressures can be described by the RRKM theory [9], which is inadequate in many instances, however, owing to the lack of required thermodymanic data for the molecules under investigation.

By the technique here described we approach the problem from an empirical point of view, namely by determining the "effective temperature" for the molecules in the reactor, i.e., the temperature (actual energy distribution) which the molecules apparently achieve in the reactor at a given filament temperature. Hence, a correction term may be derived, which enables us to correlated experimentally determined rate constants with actual reaction temperatures (the "effective temperatures").

Experimentally, rate constants (k) are determined according to eqn. 1, where I_T and I_{amb} correspond to the ion current of the selected ion entering the mass spectrometer following pyrolysis and at ambient temperature, respectively [6,8]; k_e is the unimolecular escape constant, which equals the inverse mean residence time, t_{mr}, of the molecules in the reactor (cf., eqns. 2 and 3) [6,8].

$$k = k_e(I_{amb} - I_T)/I_T \quad s^{-1} \tag{1}$$

$$k_e = t_{mr}^{-1} = \bar{c}AK/4V \quad s^{-1} \tag{2}$$

$$\bar{c} = 1.46 \cdot 10^4\sqrt{(T/M)} \quad cm\ s^{-1} \tag{3}$$

where A is the area of the orifice of the reactor (0.0384 cm^2), V is the reactor volume (0.114 cm^3) and K is a constant, the tube factor [6]. Owing to the "single-collision nature" of the pyrolysis in the present reactor set-up [14], both the unreacted molecules and the pyrolysis products will probably leave the reactor with a rate corresponding to a temperature close to ambient. Hence, the k_e applied here correspond to 300 K.

However, it should be noted that even variations in k_e due to temperature effects (cf., eqns. 2 and 3) will have very little effect on the activation parameters derived from the Arrhenius equation:

$$k = A_\infty \exp(-E/RT) \tag{4a}$$

$$\ln[(I_{amb} - I_T)/I_T] + \ln k_e = \ln A_\infty - E/RT \tag{4b}$$

Neglecting the temperature effect on k_e completely, as in this study, may lead to an underestimation of the activation energy by less than 1 kcal mol^{-1}

over a temperature range from 300 to 900 K (E determined as the slope of the Arrhenius plot). Accordingly, the corresponding underestimation of ln A_∞ will be less than 0.5.

Experimental determination of a series of rate constants at different filament temperatures, T_f (eqn. 1), permits an estimate of the effective temperatures, T (actually corresponding to the single rate constants) by including known activation parameters (E and A_∞) in the Arrhenius equation (eqn. 4).

It seems physically reasonable to assume that the effective temperature increment per collision between the molecule and the hot filament surface follows a linear law [15]:

$$dT/dn = \beta(T_f - T) \quad (5)$$

However, in the present set-up, where reactions are results of single collisions between molecules and the filament ($dn = 1$ and $dT = T - T_{amb}$), the following relationship between the filament temperature and the effective temperature is obtained:

$$T = T_{amb} + \beta(T_f - T_{amb}) \quad (6)$$

It should be noted that the temperature correction factor, β, which is a measure of the molecule–wall collision efficiency, is not necessarily a "universal" constant, depending only on the reactor geometry and the filament temperature. In addition, it is highly likely that the β-values are "molecule-dependent". Thus, Gilbert recently suggested an empirical relationship between the β-values and the boiling point of the molecules [16]. Nevertheless, it appears (see below) that the molecule-dependent variations for the limited number of reactions described below are minor. Hence, as a first assumption, we tentatively suggest a single $\beta(T_f)$ curve and, accordingly, a single $T(T_f)$ curve.

RESULTS AND DISCUSSION

In this preliminary study of the application of an inductively heated flow reactor for gas kinetic investigations, five reactions have been included, as summarized in Table 1. All the reactions have been kinetically investigated previously [17–19], i.e., well documented activation parameters are available.

Investigations of the unimolecular decomposition kinetics of these five reactions, as described in the previous section, gave rise to five series of temperature correction factors, β. Fig. 7 shows the dependence of β as function of the filament temperature. It can be seen that the data for the first three reactions (I–III, Table 1) are well described by a single "universal" $\beta(T_f)$ curve (Fig. 7, dotted line), whereas the data for the decompositions of tetramethyllead (Me_4Pb, IV) and diethyl carbonate (Et_2CO_3, V) do not fit this curve.

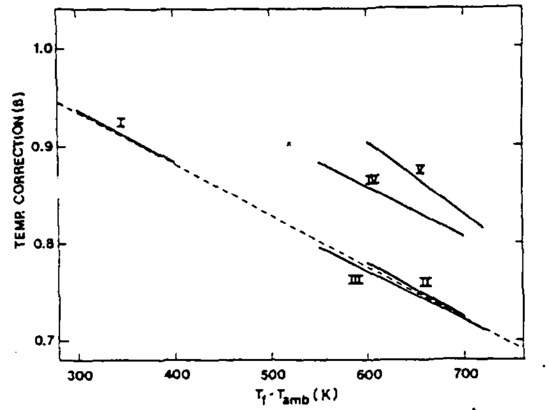
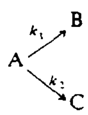


Fig. 7. Temperature correction factors, β, as a function of filament temperature.

With tetramethyllead, some kind of auto-catalysis probably takes place, the eventual product being lead. This became evident by visual inspection of the filament surface following the investigation of reaction IV. In this case the gold surface was covered by a dark coating, apparently lead, i.e., the "non-catalytic" gold surface was lacking.

More surprising was the $\beta(T_f)$ relationship for diethyl carbonate (reaction V), the estimated correction factors being considerably smaller than would be expected if the data fitted the "universal" $\beta(T_f)$ relationship. The estimated $\beta(T_f)$ relationship (Fig. 7), which is based on the activation parameters given in ref. 18, strongly indicates that the decomposition of diethyl carbonate, at least in the present experimental set-up, is not described by a single reaction [18], but more reasonably by at least two parallel reactions:



$$\ln k_1 k_2 = \ln A_{\infty 1} A_{\infty 2} - (E_1 + E_2)/RT$$

In the latter case the estimated rate constants (eqn. 1) are in fact a combination of k_1 and k_2. However, as the $\beta(T_f)$ fit is based on E_1 alone, this leads to an underestimation of the temperature correction. Experimentally, the presence of a second reaction path for the decomposition of diethyl carbonate was verified by analysing the product composition following pyrolysis of the latter, as previously described [1]. In addition to ethanol and

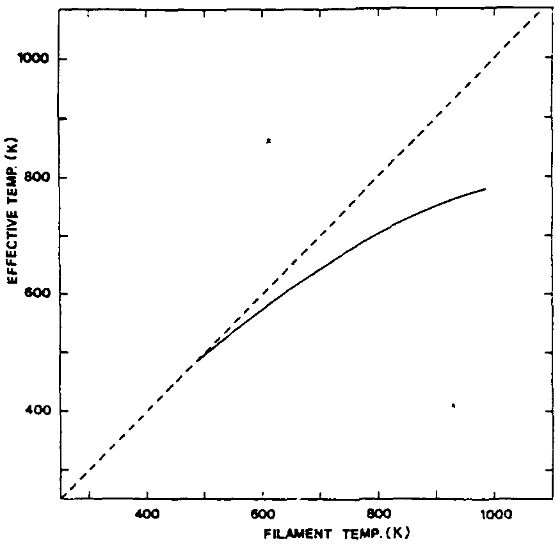


Fig. 8. Effective temperature as a function of filament temperature.

ethylene [18], we found considerable amounts of acetaldehyde, which is probably formed via a five-membered transition state as described for ethyl acetate [20].

Taking the above discussions into account, it seems reasonable to construct a $T(T_f)$ curve based on the data obtained from reactions I–III (Table 1). The $T(T_f)$ relationship is shown in Fig. 8, and corresponds well with the results reported by Amorebleta and Colussi [15].

Finally, the possible effect of a poorly determined temperature correction should be mentioned. Introducing the expression for the effective temperature (eqn. 6) into the Arrhenius equation (eqn. 4a) gives the following

TABLE 1

Reactions studied

	$E/\ln A_\infty$ *	Ref.
I: *tert.*-Bu–O–O–*tert.*-Bu → 2 *tert.*-Bu–O$^{\cdot}$	37.4/35.9	17, p. 430
II: Me–N=N–Me → Me–N=N$^{\cdot}$ + Me$^{\cdot}$	52.5/38.0	17, p. 448
III: Et–N=N–Et → Et–N=N$^{\cdot}$ + Et$^{\cdot}$	50.0/37.5	17, p. 451
IV: Me_4Pb → Me$^{\cdot}$ + $Me_3Pb^{\cdot}$	49.4/33.9	18
V: EtO–CO–OEt → $C_2H_5OH + C_2H_4 + CO_2$	46.4/30.3	19

* Activation energies in kcal mol^{-1}.

expression for variations in activation energy as function of variations in β:

$$\Delta E = R\Delta\beta(T_f - T_{amb})(\ln A_\infty - \ln k) \quad (7)$$

with the relative variation in the activation energy being given by

$$\Delta E/E = \Delta\beta(T_f - T_{amb})/[T_{amb} + \beta(T_f - T_{amb})] \quad (8)$$

For filament temperatures around 850 K we find $\beta = 0.8$ (cf., Fig. 7). Hence, a 10% variation in β, corresponding to ± 0.08, affords variations in activation energies (eqn. 8, $T_{amb} = 300$ K) of less than $\pm 6\%$. In theory, $\ln A_\infty$ is independent of β. However, in practice one may expect some limited variations of $\ln A_\infty$, based on a graphical estimation.

It is strongly emphasized that the system here described is a prototype of an inductively heated flow reactor for gas kinetic studies, and only simple bond-fission reactions have been applied to estimate the $T(T_f)$ relationship. Attempts to study other types of reactions, e.g., elimination of ethylene from ethyl acetate [21], were surprisingly unsuccessful, which we ascribe to unfavourable reactor design. Roughly, reactions proceeding through transition states with a high degree of organization, (e.g., the six-membered cyclic transition state for the above mentioned elimination of ethylene from ethyl acetate) will be strongly impeded by thermal quenching of the activated molecules at the cold reactor wall before they reach the organized transition state, a phenomenon that will be of minor importance in instances of simple bond-fission reactions, the latter exhibiting transition states of more random structure. The effect is recognized in mass spectrometry as the "kinetic shift" phenomenon [22]. It is expected that more careful reactor design will eliminate the kinetic shift phenomenon; this will be the subject of further studies.

CONCLUSION

A prototype of an inductively heated flow reactor for gas kinetic studies, with the reactor directly coupled to the ion source of a mass spectrometer, has been described. The applicability of the system was elucidated by investigations of the unimolecular decomposition of a series of simple bond-fission reactions. A "universal" relationship between the filament temperature, T_f, and the effective temperature, T, has been derived. Obviously the system, in its present state, is less favourable for the study of reactions with highly organized transition states. This shortcoming, however, is expected to be remedied by more careful reactor design.

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APPENDIX 7.

DIRECT SURFACE PARTICIPATION IN GAS-PHASE CURIE-POINT PYROLYSIS: THE PYROLYSIS OF PHENYL AZIDE

HELGE EGGSGAARD AND LARS CARLSEN

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TECHNIQUES IN GAS-PHASE THERMOLYSES

PART 7*. DIRECT SURFACE PARTICIPATION IN GAS-PHASE CURIE-POINT PYROLYSIS: THE PYROLYSIS OF PHENYL AZIDE

HELGE EGSGAARD and LARS CARLSEN*

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde (Denmark)

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SUMMARY

The possible direct participation of the hot reactor surface in the formation of pyrolysis products was elucidated through the pyrolytic decomposition of phenyl azide. It is demonstrated that the intermediate phenyl nitrene generated reacts with elemental carbon at the filament surface, leading eventually to benzonitrile. The importance of well defined surfaces is discussed.

INTRODUCTION

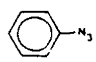
The importance of the procedure used for cleaning wires for Curie-point pyrolysis has been reported by Windig et al. [1] and recently we reported on the applicability of gold-plated filaments for gas-phase Curie-point pyrolysis in an attempt to surpress, or even eliminate, reactions induced by the presence of hot, reactive metal surfaces such as nickel, iron or cobalt [2,3]. The effect of gold coating was elucidated by, e.g., the apparent loss of atomic oxygen from compounds containing semi-polar $X^{+}-O^{-}$ bonds (X=S or N) [2].

This paper describes the direct participation of the surface in the formation of products in gas-phase Curie-point pyrolysis, exemplified by the pyrolytic decomposition of phenyl azide (1). Thus, observation of products. the formation of which seems unlikely, or even impossible, at first sight may be considered in terms of a direct surface participation, i.e., a gas–solid reaction.

In a previous paper [2] we discussed the gas-phase pyrolysis of nitrobenzene (2), which, on applying an iron filament (770 °C) surprisingly gave

* For Part 6, see H. Egsgaard, P. Bo and L. Carlsen, J. Anal. Appl. Pyrol., 8 (1985) 3.

minor amounts of benzonitrile (3). The formation of relatively large amounts (5.3%) of 3 on pyrolysis of 2 has previously been reported by McCarthy and O'Brien [4], but the presence of 3 among the pyrolysis products was not discussed.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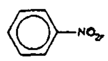
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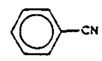
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The nitrile 3 unambiguously contains an additional carbon atom compared with the starting nitrobenzene 2. An obvious, but unusual, explanation would be a reaction between phenyl nitrene (4), generated by consecutive deoxygenation of 2 [2], and elemental carbon present at the Curie-point filament. It should be noted that with the application of uncoated wires, e.g., iron, carbonaceous deposits are typically formed, which can easily be observed by visual inspection of the wires following use in pyrolyses experiments.

To verify the above assumption we studied the gas-phase pyrolysis of phenyl azide (1) as the ideal precursor for the nitrene 4. The studies were carried out using the low-pressure gas-phase Curie-point pyrolysis technique, which has been described in previous papers [5,6], the products being analysed by field ionization (FI) and collision activation (CA) mass spectrometry (MS).

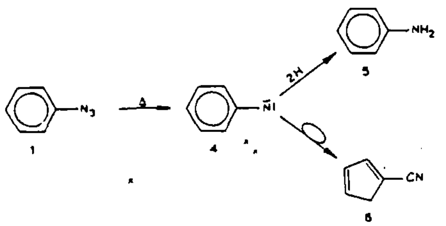
EXPERIMENTAL

Gas-phase pyrolysis–FI–CAMS experiments were carried out as described previously [5,6], applying a continuous-flow inlet system [7].

Gold-plated filaments were produced as described in a previous paper [2]. The carbon coatings were obtained by treatment of the appropriate gold-plated filament with a thin paste of activated carbon (Norit W20) in water followed by drying in vacuo. Prior to use the filaments were repeatedly heated to the Curie point.

RESULTS AND DISCUSSION

Pyrolysis of 1 at 770°C applying a gold-plated [2] iron filament afforded the expected products only (Fig. 1b), as aniline (5) (m/z 93) and 1-cyano-1,3-cyclopentadiene (6) (m/z 91) were observed. Both products result from the presence of an intermediate nitrene, picking up two hydrogens from the reactor surface (4 → 5) and rearranging (4 → 6) [8,9], respectively.



Application of a gold-coated iron filament, further coated with a layer of amorphous carbon, led to the formation of an additional product, exhibiting a molecular weight of 103 on pyrolysis of 1 (Fig. 1c). Based on CAMS [6] and comparison with authentic samples, this product was identified as benzonitrile (3)/phenyl isocyanide (7). Hence, we conclude that the nitrene 4 apparently can react with elemental carbon, leading to 3/7.

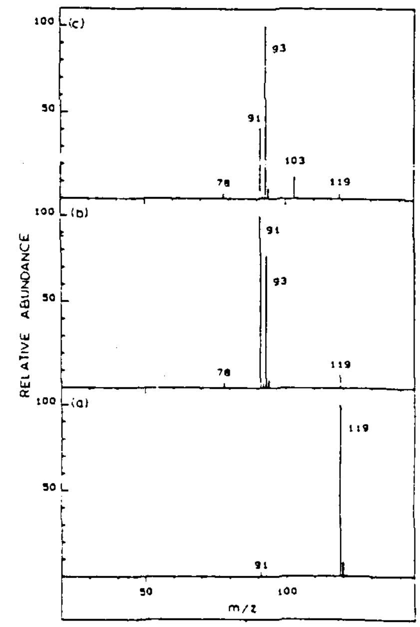
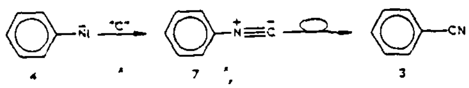


Fig. 1. Field ionization mass spectra of (a) unpyrolysed phenyl azide and after pyrolysis of phenyl azide at 770°C at (b) gold and (c) gold/carbon surfaces.

Obviously, the reaction between a nitrene and elemental carbon must afford primarily an isocyanide. However, phenyl isocyanide (7) rapidly rearranges into the corresponding nitrile 3 [10]. Further, it appears not to be possible to distinguish between 7 and 3 by CAMS.



The presence of benzonitrile among the pyrolysis products from phenyl azide has previously been discussed by Crow and co-workers [11,12]. They proposed a mechanism involving the loss of an $N_3^{\cdot}$ radical from the azide, the remaining phenyl radical subsequently combining with a $CN^{\cdot}$ radical, arising from a consecutive decomposition of 1-cyano-1,3-cyclopentadiene (6), leading to the nitrile (3). Based on the above, this mechanism can obviously be ruled out under the prevailing conditions, as the study of the pure unimolecular decomposition of 1 (Fig. 1b) did not lead to 3.

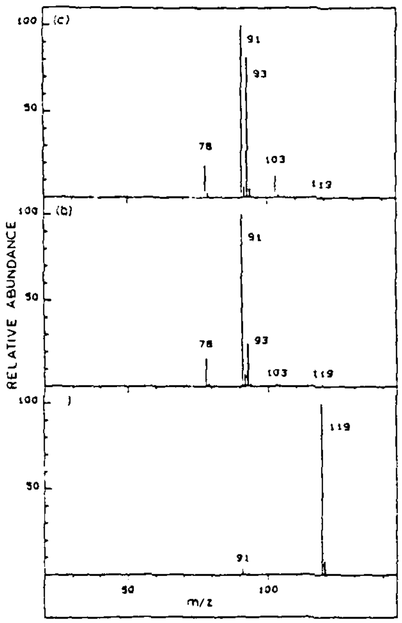


Fig. 2. Field ionization mass spectra of (a) unpyrolysed phenyl azide and after pyrolysis of phenyl azide at 980°C at (b) gold and (c) gold/carbon surfaces.

It can be mentioned that minor amounts of the low-volatile azobenzene were also observed. Control experiments on the pyrolysis of azobenzene under the above conditions did not show any formation of 3.

Increasing the pyrolysis temperature to 980°C resulted in a significant change in the composition of the pyrolysis products, as shown in Fig. 2. The relative amounts of the single products were shifted in favour of the unimolecularly formed product 6, reflecting a decreased lifetime of 4, as a consequence of the increased pyrolysis temperature.

The above results unambiguously demonstrate the possibility of direct participation of the surface in the formation of pyrolysis products. Therefore, it is strongly emphasized that the actual nature of the hot reactor surface must be known in order to rationalize pyrolysis results properly. Especially when pyrolysis results obtained with different pyrolysis equipment are to be compared, it should be taken into account that even minor differences in surface composition may lead to an apparent irreproducibility.

ACKNOWLEDGEMENT

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APPENDIX 8.

GAS-PHASE THERMOLYSIS OF A THIOKETENE-S-OXIDE

LARS CARLSEN, HELGE EGSGAARD AND ERNST SCHAUMANN

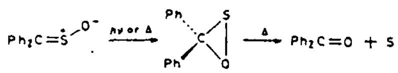
J.CHEM.SOC. PERKIN TRANS. 2 (1980) 1206-1211

Gas-phase Thermolysis of a Thioketen-*S*-Oxide [1,2]

By Lars Carlsen * and Helge Egsgaard, Risø National Laboratory, DK–4000 Roskilde, Denmark
Ernst Schaumann, Institut für Organische Chemie und Biochemie, der Universitat Hamburg, D–2000 Hamburg, 13, Martin-Luther-King-Platz 6, Federal Republic of Germany

The unimolecular gas-phase thermolytic decomposition of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide (3) has been studied as a function of temperature by a flash vacuum thermolysis (f.v.t.) technique. The products detected are the carbenes (4) and (5), the ketone (6), the keten (7), the thioketone (8), and the thioketen (9). The product ratio is highly dependent on the thermolysis temperature. The thermolysis of (3) is mechanistically rationalized by assuming the existence of only two concurrent primary processes, which are (a) extrusion of atomic oxygen, leading to the thioketen (9), and (b) electrocyclic ring closure into the corresponding three-membered oxathiiran (10). The latter is dominant at lower temperatures, whereas higher thermolysis temperatures favour atomic oxygen extrusion. At further elevated temperatures additional concurrent primary reactions, *i.e.* extrusions of SO and CSO leading to the carbenes (5) and (4), respectively, are observed. Owing to an apparently very short half-life of the oxathiiran (10), only the decomposition products of the three-membered ring compound have been detected. These are the thioketone (8), formed by rearrangement of (10) into the α-thiololactone (11) followed by loss of CO, minor amounts of the ketone (6), formed analogously, and the keten (7), as a result of simple sulphur extrusion.

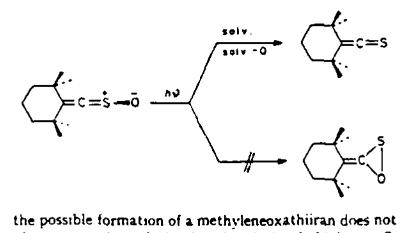
IN connection with our continuing interest in the thermal and photolytical transformations of thiocarbonyl *S*-oxides (sulphines), we previously reported the electrocyclic ring closure of thiobenzophenone *S*-oxides (1) into



(1) (2)

the corresponding 3,3-diaryloxathiirans (2), as a thermally [3] as well as a photolytically [4-6] induced reaction. However, we found oxathiirans to be thermally highly labile compounds,[3-6] which at room temperature rapidly decompose into the corresponding ketones and elemental sulphur.

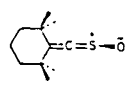
In contrast to this we found that thioketen *S*-oxides are deoxygenized photolytically, presumably by reaction between the excited thioketen *S*-oxide molecule and the solvent.[7] The resulting thioketen was detected in 95% yield together with only vanishingly small amounts (<3%) of the keten. On this basis we concluded that



the possible formation of a methyleneoxathiiran does not play any major role in the photolysis of thioketen *S*-oxides.

In this paper we report results on the gas-phase thermolysis of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide (3),[1,8] which at room temperature is a thermally stable thioketen *S*-oxide. We have investigated the thermal decomposition of (3) in an attempt to study possible ring closure to the methyleneoxathiiran and/or thioketen formation as a result of extrusion of atomic oxygen, analogous to the above mentioned photodeoxygenation.[7]

The thermolysis of (3) was studied by a flash vacuum thermolytic (f.v.t) procedure,[9] which secures detection of



(3)

unimolecularly formed products alone and predominantly, only primary thermolysis products.

EXPERIMENTAL

The thioketen *S*-oxide (3) was prepared by peracid oxidation of the corresponding thioketen, as described previously.[8]

Flash Vacuum Thermolysis Technique.[9]—The f.v.t. technique is based on the direct combination of a thermolysis unit with a double focusing mass spectrometer with a field ion source. The thermolysis unit is constructed as a modification of the Pye–Unicam PV4000 pre-column-pyrolysis system, which is based on the Curie point principle, *i.e.* high frequency inductive heating in ferromagnetic materials. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heated line-of-sight inlet system.

Samples (*ca.* 50 μg) of the pure compound were introduced (microsyringe) into the reactor *via* a heated injection block. The contact time in the hot zone has been estimated to be *ca.* 10^{-3}—10^{-4} s,[9] fullfilling the contact time requirement for f.v.t. equipment.[10] Because of the geometry of the system thermolysis products with half-lives < *ca.* 10^{-3} s are assumed to escape detection.[9] The internal geometry of the reactor (*l* 40 mm, i.d. 2 mm) combined with the low pressure (*ca.* 10^{-4} Torr) assure a very low frequency of intermolecular collisions relative to the molecule-hot surface collision frequency, *i.e.* only unimolecular reactions take place.

The mass spectra were recorded on a Varian MAT CH 5D instrument (the magnetic sector preceeding the electric sector) equipped with a combined electron impact ionization–field ionization–field desorption ion source. The field ion emitter was a 10 μm tungsten wire activated in benzonitrile vapour. The maintenance of the vacuum in the

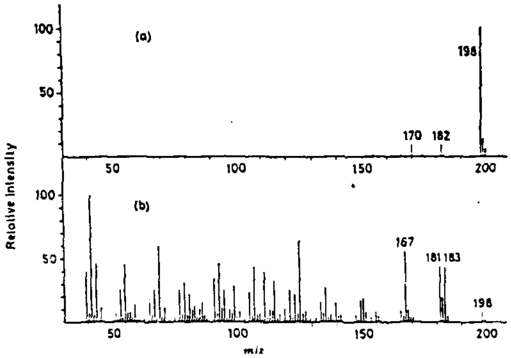


FIGURE 1 Field ionization (a) and electron impact ionization (b) mass spectra of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane *S*-oxide

system is based on differential pumping of the ion source, analyser tube, and the electric sector. Pumping speed was 3 × 150 l s^{-1}.

Collision activation (c.a.) spectra were obtained by introducing helium as the collision gas *via* a needle valve into the second field free region between the magnetic and electric sector of the mass spectrometer. The collision gas was admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The c.a. spectra of the single ions were then obtained by scanning the electric field.

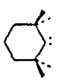
Owing to the relatively fast evaporation of the samples in the injection block (5—10 s) the mass spectra were recorded with a scan rate of 50—100 a.u. s^{-1} (signal : noise > 1 000), and the c.a. spectra within 5 s (signal : noise *ca.* 50).

The paramount advantage of the use of field ionization mass spectrometry as a detection system is to be sought for in the field ionization principle.[11] Since field ionization takes place with no excess energy, excluding polarization by the electric field, to the neutral molecule,[11a] it gives rise to molecular ions, even of very unstable substances, accompanied only by few, if any, fragment ions, in general of low intensity (< 1%).[11b] In contrast electron impact mass spectrometry may produce very complicated electron impact-induced fragmentation patterns; this may be further confusing in cases where they are to be described as superpositions of electron impact mass spectra of several, often unknown, thermolysis products. This difference is clearly elucidated in Figure 1, depicting the field ionization and 70 eV electron impact mass spectra of the thioketen *S*-oxide (3).

Further structural information on the reaction products may be obtained by the additional recording of the c.a. spectra of the single field ionized molecules,[13] as the collision of field ionized molecules of high kinetic energy with neutral target atoms (*e.g.* He) is known to give rise to a large variety of fragments. In general these types of fragmentations resemble those formed under normal 70 eV electron impact conditions.[14] Furthermore, in cases of stable reaction products a direct comparison of the c.a. spectra with those of authentic samples can be carried out.

RESULTS

A priori, a variety of products can be expected by thermolytic decomposition of (3): the carbenes (4) and (5), with molecular ions of 138 and 150, respectively, the ketone (6) (*M* 154), the keten (7) (*M* 166), the thioketone (8) (*M* 170), the thioketen (9) (*M* 182), and the oxathiiran (10) (*M* 198), together with unchanged starting material (3) (*M* 198).



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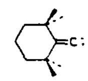

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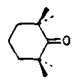

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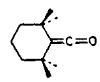

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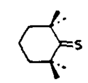

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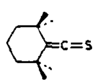

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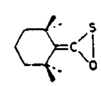


(10)

A wide range of ferromagnetic materials with Curie points from room temperature to *ca.* 1 400 K are readily available. We have studied the thermolytic decomposition of (3) at six temperatures in the 423—1 043 K range. The field ionization mass spectra obtained following thermolysis at these six temperatures are depicted in Figure 2.

The spectra can be assigned to mixtures of compounds (4)—(9). It should be noted that the isotopic patterns may give valuable information, *e.g.* compounds (5)—(7) have evidently eliminated sulphur, since only iostopic clusters corresponding to ^{13}C and ^{18}O are seen, whereas the characteristic ^{34}S isotopic peaks are lacking. Furthermore, the identity of (8) and (9) was confirmed by comparison of the c.a. spectra of the single field ionized molecules with those obtained from authentic samples.[13] Unfortunately, it is not possible to detect small inorganic fragments, owing to the very low field ionization weight sensitivity of these compounds.*

It is not possible to calculate the yields of the single species directly from the field ionization mass spectra, as the individual compounds may exhibit rather different sensitivities.[11] However, by scanning mixtures of compounds (6)—(9) using varying mutual ratios, the individual relative weight sensitivities were calculated (see Table). The sensitivity of the vinylidene carbene (5) was calculated indirectly as 1.11, based on the partial decomposition of the thioketen (9) at 1 043 K (Figure 3b). We further assumed the sensitivity of the carbene (4) to be equal to that of (5).

Relative yields, expressed as mole fractions, of compounds (3)—(9) as a function of thermolysis temperature [a]

Compound	F [b]	Thermolysis temperature (K) 423	631	753	783	883	1 043
(3)	0.80 ± 0.13	1.00	1.00	0.11 ± 0.02	0.03 ± 0.005	0.04 ± 0.005	0.01 ± 0.002
(4)	0.90 ± 0.17 [c]	<0.01	<0.01	<0.01	<0.01	0.01 ± 0.002	0.03 ± 0.006
(5)	0.90 ± 0.17 [d]	<0.01	<0.01	<0.01	<0.01	0.03 ± 0.006	0.42 ± 0.08
(6)	1.13 ± 0.13	<0.01	<0.01	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	<0.01
(7)	2.65 ± 0.54	<0.01	<0.01	0.18 ± 0.04	0.15 ± 0.03	0.13 ± 0.03	0.17 ± 0.03
(8)	1.35 ± 0.14	<0.01	<0.01	0.27 ± 0.03	0.16 ± 0.02	<0.01	<0.01
(9)	0.67 ± 0.08	<0.01	<0.01	0.42 ± 0.04	0.64 ± 0.06	0.78 ± 0.07	0.37 ± 0.03

[a] Yields are corrected for the amount of impurities present in the starting material. [b] The F factor (reciprocal field ionization weight sensitivity) is the value by which the actual observed peak height must be multiplied to give the amount of substance corresponding to the signal. [c] $F(4)$ assumed to be equal to $F(5)$. [d] $F(5)$ calculated indirectly from the partial thermal decomposition of (9) (see Figure 3).

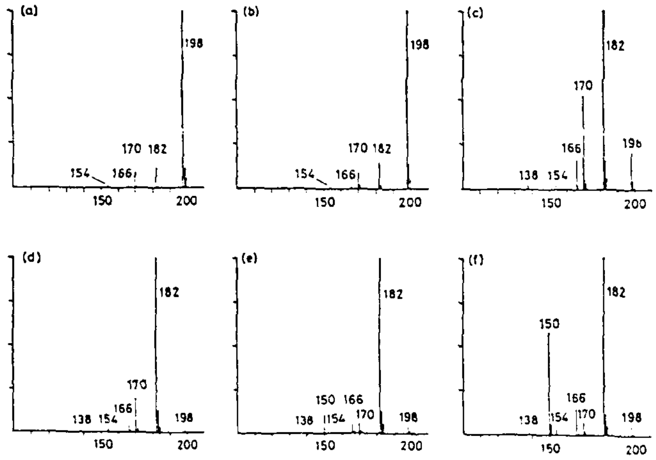


FIGURE 2 Field ionization mass spectra of 1,1,3,3-tetramethyl 2-thiocarbonylcyclohexane S-oxide following thermolysis at (a) 423, (b) 631, (c) 753, (d) 783, (e) 883, and (f) 1 043 K

As seen from Figure 1a the thioketen S-oxide (3) contained minor amounts of (7)—(9) as impurities. Equal amounts of these compounds are detected upon thermolysis at 423 and 631 K (Figures 2a and b) indicating that no decomposition takes place at these temperatures. Using the relative field ionization weight sensitivities we calculated the relative yields of the individual compounds formed at

* Furthermore, the geometry of the ion source may play an important role (see ref. 11b).

higher temperatures, expressed as mole fractions, corrected for the initial content of impurities in the starting material. The results are given in the Table.

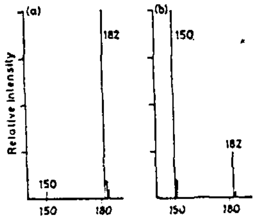
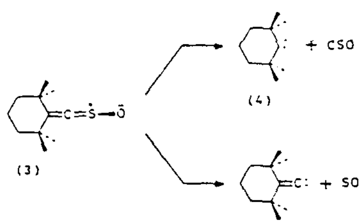


FIGURE 3 Field ionization mass spectra of 1,1,3,3-tetramethyl-2-thiocarbonylcyclohexane following thermolysis at (a) 883 and (b) 1 043 K

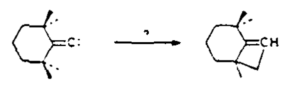
DISCUSSION

Easiest to explain is the formation of the carbenes (4) and (5), which apparently are generated by simple ruptures of the C=C and C=S bonds, respectively. Unfortunately, as mentioned above, field ionization suffers by the inability to detect small inorganic fragments, e.g. CSO and SO.



The formation of the vinylidene carbene (5) takes place at a markedly lower temperature than that of (4) in agreement with a lower C=S bond energy relative to that of the C=C bond.* Furthermore, it should be noted that the high yield of the carbene (5) found by thermolysing (3) at 1 043 K (Table) may originate from two sources, as the thioketen (9) at 1 043 K extrudes sulphur in high yield (Figure 3b). However, almost no sulphur extrusion from (9) was observed for thermolysis at 883 K (Figure 3a). Based on the field ionization mass spectra depicted in Figures 2f and 3b we have estimated the extent of further thermolysis of (9) to be <1.5% On the other hand, it is generally believed [10,14] that the very short contact times (*ca.* 10^{-3}—10^{-4} s) assure detection only of the primary products. Thus, we tentatively suggest that the major part of (5) originates directly from the *S*-oxide (3). Finally, it should be mentioned that the thioketen (9) is the only product found to undergo further thermolysis within the temperature range studied.

It should be noted that although we describe the products (4) and (5) as carbenes here they may well be isomeric structures, as *e.g.* (5) can undergo an easy intramolecular insertion reaction.[15] Nevertheless, we find support for the carbene structure by studying the relative field ionization weight sensitivities (Table), which are found to be comparable for the ketone (6) and the carbenes, since compounds with non-bonding electrons in general exhibit much higher weight sensitivities than pure hydrocarbons.[13b]



(5)

Additionally, it can be noted that the carbene (5) when generated in solution, does not undergo intramolecular insertion.[13b]

Surprisingly the major product from the gas-phase thermolysis of (3) in the temperature range 733—883 K is

the corresponding thioketen (9), apparently formed by simple extrusion of atomic oxygen. Some reports on atomic oxygen extrusion have appeared, *e.g.* it is well known that pyridine *N*-oxide in the gas phase is photolytically deoxygenized.[16] Several other thermal and photolytic reactions, in the gas phase as well as in solution, could also be explained by atomic oxygen extrusion.[?,17] However, in these cases the reactions were carried out under circumstances where it was not possible to exclude bimolecular reactions. To our knowledge the reaction reported here is the first example of a thermally induced unimolecular atomic oxygen extrusion from an organic *S*-oxide.[1] The apparently large decrease in the yield of (9) by changing the thermolysis temperature from 883 to 1 043 K (Table) is explained by the occurrence of the concurrent SO extrusion reaction, leading to the carbene (5).

Since none of the products (6)—(8) can be formed by simple bond rupture mechanisms, we formulate, by analogy with the thermal decomposition of thioketone *S*-oxides,[3,18] a primary ring closure into the methylene-oxathiiran (10). However, oxathiirans are, as mentioned previously, thermally highly labile compounds,[3-6] *e.g.* the decomposition of 3,3-diphenyloxathiiran has been studied by a flash photolytic study of diarylsulphines,[6]

* E_{bond}(C=C) 611.2 kJ mol^{-1} (*cis*-but-2-ene R. W. Alder, R. Baker, and J. M. Brown, 'Mechanism in Organic Chemistry,' Wiley, London, 1971, p. 7; E_{bond}(C=S) 540.0 kJ mol^{-1} ('Thioformaldehyde,' S. W. Benson, *Chem. Rev.*, 1978, 78, 23).

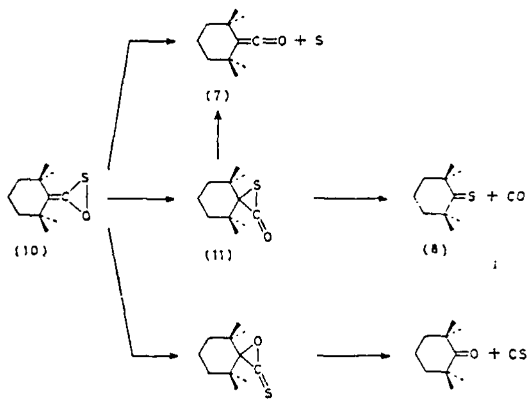
the half-life being estimated to 1.3×10^{-3} s (in acetonitrile at room temperature). The diaryloxathiirans decompose quantitatively into the corresponding ketones and elemental sulphur upon thermolysis.[3-6] With this


(3) (10)

background the formation of the keten (7) is easily explained by sulphur extrusion from the oxathiiran (10). On the other hand, it has also been reported that oxathiirans may rearrange into the corresponding structure (12) have, to our knowledge, appeared, but by analogy with the decomposition of (11) we tentatively assume that (12) either spontaneously rearranges into (11) or extrudes carbon monosulphide to form the ketone (6).‡ In recent reports on oxathiiran rearrangements[4,15] migration to sulphur is found to be predominant relative to migration to oxygen, in excellent agreement with the very low yield of the ketone (6) and the much higher yield of the corresponding thioketone (8), the former tentatively being described as a result of migration to oxygen.

In summary we rationalize the oxathiiran decomposition as in the Scheme.

Taking the sum of the yields of (6)—(8) (see Table) as an expression of the total amount of primarily formed



SCHEME

thio-esters.[4,15] In the present case, with a methylene-oxathiiran such as (10), this rearrangement would cause formation of cyclic esters, α-thiololactones, and/or α-thionolactones. Recently Schaumann and Behrens[13a] reported the α-thiololactone (11) as the product from the *nitrone oxidation of the thioketen (9). The compound* was found to be thermally unstable, decomposing at 348 K (tetrachloromethane) entirely to the thioketone (8) and carbon monoxide.[13a] We have studied the gas-phase thermolysis of (11) at different temperatures. The compound was highly labile under these conditions, decomposing even at the lowest possible thermolysis temperature, 423 K, completely into a mixture of the thioketone (8), formed by CO extrusion, and the keten (7), apparently generated by loss of elemental sulphur.*,† However, no reports on the isomeric α-thionolactone oxathiiran (10), it can be seen that the two concurrent primary reactions, atomic oxygen extrusion and oxathiiran formation, both proceed to an almost equal extent at 753 K. An increase of the thermolysis temperature results in an increase in atomic oxygen extrusion *with an equivalent simultaneous decrease* in oxathiiran formation. However, the formation of the vinylidene carbene (5) at 1 043 K should be taken into account in order to maintain the overall (9) : (10) ratio (Figure 4). These variations may be described as a reflection of the concurrence of kinetically controlled oxathiiran formation and thermodynamically controlled extrusion of atomic oxygen.

Similarly the decomposition of the oxathiiran (10)

* 423 K corresponds to the temperature of the heated line-of-sight inlet system, *i.e.* complete thermal decomposition of possible formed α-thiololactone (11) can be expected.

† Some temperature effects on the thioketone keten ratio are found the overall result, however, is independent *of the thermolysis temperature.*

‡ A theoretical investigation on the potential energy surface of the possible α-thiololactone—α-thionolactone interconversion is in progress (L. Carlsen, to be published).

may be expressed in terms of kinetically *versus* thermodynamically controlled processes, the former leading to (8) [found to be present only for thermolysis at 753 and 783 K (Table)] *via* the strained three-membered ring

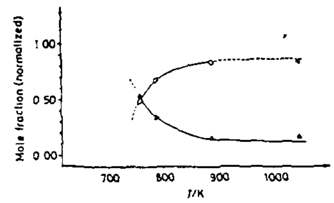


FIGURE 4 Molar fractions (normalized) of oxathiiran (10) (Δ) and thioketen (9) (○) as a function of thermolysis temperature. The point X corresponds to the theoretical amount of thioketen taking the amount of carbene (5) into account

(11), the latter to the sulphur-extrusion product, the keten (7).

Conclusions.—The gas-phase thermolytic decomposition of the thioketen *S*-oxide (3) affords a variety of products. The product ratios, which are highly dependent on the thermolysis temperature, can, however, be rationalized by the existence of only two concurrent primary processes (a) extrusion of atomic oxygen, whereby the thioketen (9) is formed, and (b) electrocyclic ring closure to the methyleneoxathiiran (10), the latter being followed by several consecutive concurrent reactions leading to the compounds (6)—(8). At higher temperatures further concurrent primary reactions must be taken into account, *i.e.* the formation of the carbenes (4) and (5) by simple bond rupture mechanisms.

We are indebted to Mrs. J. Funck for her careful preparation of the drawings.

[9/1166 *Received, 23rd July, 1979*]

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APPENDIX 9.

GAS-PHASE THERMOLYSIS OF SILYLATED THIONOCARBOXYLIC ACID DERIVATIVES: A ROUTE TO THIOKETENES?

LARS CARLSEN, HELGE EGSGAARD, ERNST SCHAUMANN, HERBERT MROTZEK AND WOLF-RUDIGER KLEIN

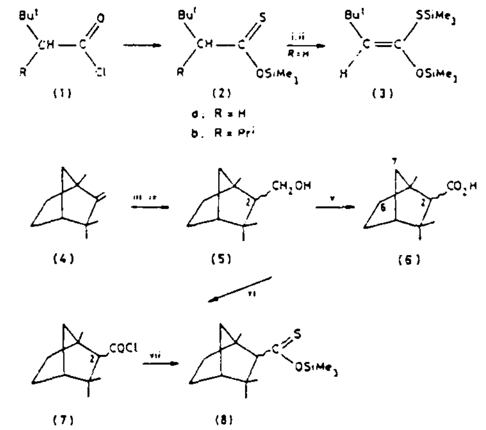
J.CHEM.SOC. PERKIN TRANS. 2 (1980) 1557-1562

Gas-phase Thermolyses. Part 3.[1] Gas-phase Thermolysis of Silylated Thionocarboxylic Acid Derivatives: a Route to Thioketens?

By Lars Carlsen * and Helge Egsgaard, Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark
Ernst Schaumann,* Herbert Mrotzek, and Wolf-Rüdiger Klein, Institut für Organische Chemie und Biochemie der Universität Hamburg, D-2000 Hamburg 13, Martin-Luther-King-Platz 6, Federal Republic of Germany

The unimolecular gas-phase thermolytic decomposition of three silylated thionocarboxylic acid derivatives (2b), (3), and (8) have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range from 783 to 1 404 K in order to elucidate its possible applicability as a route to thioketens. Only very minor amounts of the expected thioketens were found, whereas the corresponding ketens were obtained as the major products. A possible mechanism for keten formation is discussed.

THE β-elimination of hydrogen chloride from acyl chlorides containing an α-hydrogen atom is perhaps the most important synthetic pathway to ketens.[2] The possible corresponding formation of thioketens from thioacyl chlorides can, however, be applied only in exceptional cases.[3,4] Alternatively, thionocarboxylic carboxylic acid *silyl* esters are found to be *ca.* 62 kJ mol^{-1} more stable than the corresponding thiolo compounds.[7] Hence, the thermodynamically unfavourable thiono to thiolo rearrangement together with the known ready elimination of silyl ethers from silylated carboxylic acid derivatives,[8] suggest the use of silylated



SCHEME 1 *Reagents*. i, Pr^i_2NLi; ii, Me_3SiCl; iii, B_2H_6; iv, H_2O_2; v, Cr^{VI} or Mn^{VII}; vi, $SOCl_2$; vii, $MeC(S^-)=NSiMe_3$

esters may be expected to yield thioketens upon thermolysis. However, this method may be of limited value, since a competing reaction analogous to the Chapman rearrangement is expected to lead to thiolocarboxylate esters[5] rather than alcohol elimination. Thus, to our knowledge only one example of thioketen formation from a thionoester has been reported,[6] the thioketen being isolated as its dimer.

In contrast to *alkyl* thionocarboxylates thionocarboxylic acid derivatives as thioketen precursors. In this paper we report on the gas-phase thermolyses of three silylated thionocarboxylic acid derivatives in order to study the possible formation of thioketens. The starting materials (2b), (3), and (8) (see Scheme 1) have been chosen so as to provide sterically stabilized products, which would facilitate subsequent preparative operations.

The thionoester (2a) was synthesized by reaction of the acyl chloride (1a) with a dithiocarbamidate followed by silylation of the intermediate by chlorotrimethylsilane as reported by Kricheldorf and Leppert.[9] The sterically highly hindered ester (2b) was prepared by a reaction of (1b) with the anion of *N*-trimethylsilylthioacetamide, adopting the method of Luke.[10] The thionoester (2a)

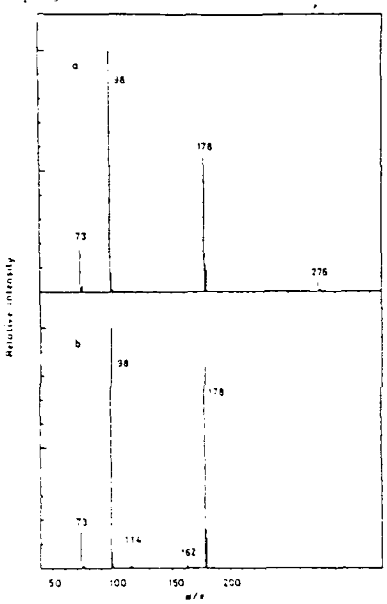


FIGURE 1 Field ionization mass spectra obtained after thermolysis of (3) at 1 043 K (a) and 1 404 K (b)

could be reacted further with lithium di-isopropylamine and chlorotrimethylsilane to the keten *OS*-acetal (3). A similar conversion was not observed in the case of (2b).

The precursor (7) to the thionoester (8) was prepared from homofenchene (4) by a procedure similar to that reported for the synthesis of 2-t-butyl-3,3-dimethylbutyryl chloride.[11] By using $KMnO_4$ in the presence of tetra-n-butylammonium bromide[12] in the oxidation of (5) to (6) instead of chromium trioxide the yield could be raised from 43 to 75%. The final silylation of (7) into (8) was performed as mentioned above using the metallated *N*-trimethylsilylthioacetamide reagent.

Compounds (5)—(8) can exist as *exo*- and/or *endo*-conformers. The primary alcohol (5) exhibits two sets of three methyl ^1H n.m.r. signals, which strongly suggests the presence of both possible configurations at C-2. Similarly, more than three methyl signals and two signals for 2-H are observed for compounds (7) and (8). The carboxylic acid (6) apparently exists exclusively as a single conformer. However, the very small difference expected in the ^4J coupling between *exo*-2-H and *exo*-6-H, and *endo*-2-H and *anti*-7-H, respectively (see *exo*- and *endo*-2-fenchol[13]), unfortunately affords no possibilities for the determination of the actual configuration.

Gas-phase Thermolyses of (2b), (3), *and* (8).—The unimolecular gas-phase thermolytic decomposition of the silylated thionocarboxylic acid derivatives (2b), (3), and (8) were studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) technique[14,15] (see Experimental section) in the temperature range from 783 to 1 404 K. Field ionization is known to give intense molecular ions and little fragmentation.[14]

In Figures 1a and 2a the f.i.m.s. spectra obtained from the thermolysis at 1 043 K of compounds (3) and (8), respectively, are shown. At this temperature the compounds are almost completely decomposed. Lowering the thermolysis temperature to 783 K did not change

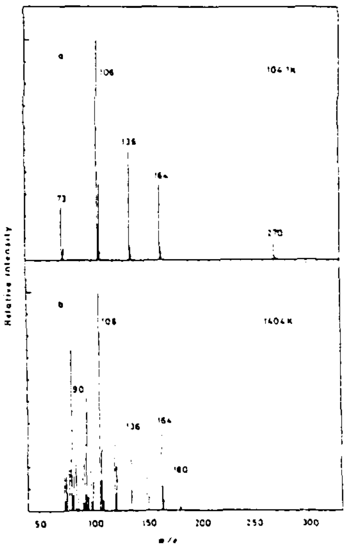
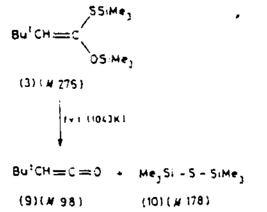


FIGURE 2 Field-ionization mass spectra obtained after thermolysis of (8) at 1 043 K (a) and 1 404 K (b)

the composition of the product mixture, but only the relative yields. Also the absolute yields are changed, as *ca.* 95% of the starting materials were recovered.

The spectrum depicted in Figure 1a exhibits two peaks at *m/e* 178 and 98. The compound responsible for the latter peak evidently does not contain sulphur, since only an isotopic cluster corresponding to ^{13}C and ^{18}O is seen, whereas the characteristic ^{34}S isotopic peak is lacking. The isotopic cluster surrounding the peak



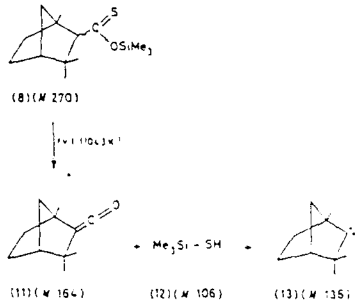
SCHEME 2

of *m/e* 178 is consistent with the presence of two trimethylsilyl groups and one sulphur atom, as the relative intensities of the peaks of *m/e* 178/179/180/181 were found and calculated to be 1.00/0.19/0.12/0.02 and 1.00/0.18/0.13/0.02, respectively. On this basis the thermolysis of (3) is then formulated as in Scheme 2.

An analogous analysis of the spectrum depicted in Figure 2a leads to the conclusion that compound (8) upon thermolysis decomposes into the keten (11) and trimethylsilanethiol (12). Additionally a product exhibiting a molecular ion at *m/e* 136, which may be assigned to carbene (13) or an isomeric species, is formed (Scheme 3).

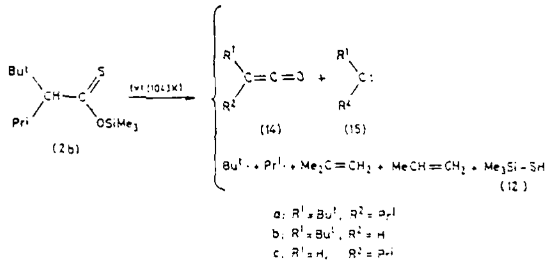
In contrast to these very simple fragmentation reactions compound (2b) exhibits a rather complicated decomposition pattern. The product mixture consists of the three possible ketens (14) and the three possible carbenes (15) together with t-butyl and s-propyl radicals, methylpropene and propene as products of consecutive radical decomposition, and the thiol (12). However, no indication of any thioketen formation was found (Scheme 4).

Changing the thermolysis temperature to 1 404 K, in the case of (2b), did not give rise to any new product formation, but caused only a change in the relative composition of the product mixture. For compounds (3) and (8), however, small changes are observed by elevating the thermolysis temperature, as new sets of peaks are developed in the f.i.m.s. spectra obtained following thermolysis at 1 404 K (Figures 1b and 2b). In both cases appearance of the new peaks can be rationalized as the result of competing thioketen formation. In the case of (8) the higher temperature also



SCHEME 3

resulted in the appearance of a variety of new peaks of low intensity, caused by more pronounced degradation of the carbon skeleton, probably similar to the thermolytic pathways observed for (2b) (Scheme 5).



SCHEME 4

It should be noted that it is not possible to calculate the yields of the single species directly from the f.i.m.s. spectra, as the single compounds may exhibit rather different field ionization sensitivities.[14] However, as the ketens and thioketens probably exhibit comparable sensitivities,[15] it is obvious that only very minor amounts of the thioketens are formed.

AD-A207 457 ANALYSIS OF LOW-PRESSURE GAS-PHASE PYROLYTIC REACTIONS BY MASS SPECTROMETRIC TECHNIQUES(U) RISOE NATIONAL LAB ROSKILDE (DENMARK) L CARLSEN JAN 89 RISOE-R-545 3/3

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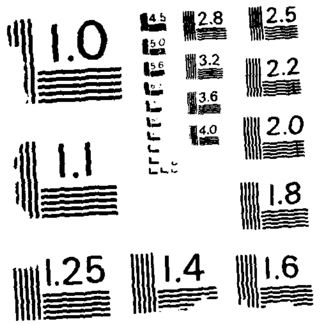
1.0
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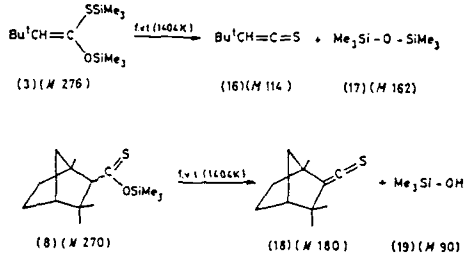
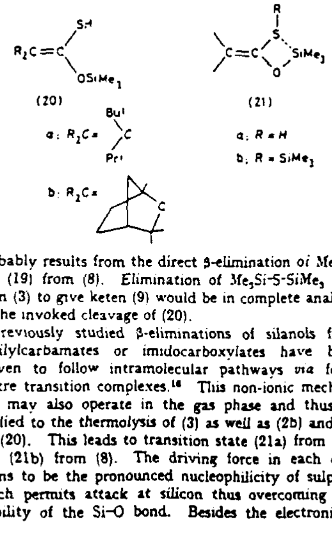
1.25
1.4
1.6

DISCUSSION

The elimination of trimethylsilanethiol (12) *from* (2b) or (8) and of bistrimethylsilyl sulphide (10) from (3) to give ketens is in apparent contrast to the relative strengths of Si–S and Si–O bonds.[7] Moreover, (2b) and (8) obviously cannot furnish ketens *via* a simple one-step process. A rationale for keten formation in these examples can be made by assuming primary enthiolization to give (20a and b), respectively, followed by β-elimination of Me_3Si–SH (12), whereas formation of thioketen (18) at the more elevated temperature probably results from the direct β-elimination of Me_3Si–OH (19) from (8). *Elimination of* Me_3Si–S–$SiMe_3$ *(10)* from (3) to give keten (9) would be in complete analogy to the invoked cleavage of (20).

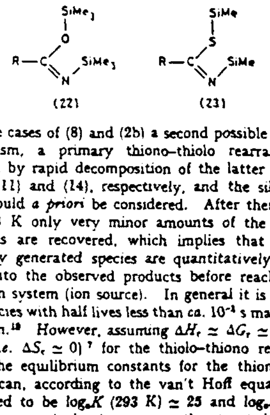


SCHEME 5



Previously studied β-eliminations of silanols from *N*-silylcarbamates or imidocarboxylates have been proven to follow intramolecular pathways *via* four-centre transition complexes.[16] This non-ionic mechanism may also operate in the gas phase and thus be applied to the thermolysis of (3) as well as (2b) and (8) *via* (20). This leads to transition state (21a) from (20) and (21b) from (8). The driving force in each case seems to be the pronounced nucleophilicity of sulphur which permits attack at silicon thus overcoming the stability of the Si–O bond. Besides the electronic a steric effect may also favour transition states like (21) *incorporating sulphur, as the larger size of sulphur* compared with oxygen will diminish strain in the four-membered ring.

The reactivity of sulphur in four-centre transition states involving silicon is also obvious from the relative stabilities of bis-silylated amides (22) and thioamides (23). Thus compound (22; R = Ph) is gradually cleaved to give benzonitrile only at reflux temperature (*ca.* 470 K),[17] whereas the corresponding thio-compound (23; R = Ph) eliminates Me_3Si–S–$SiMe_3$ (10) *in situ* on silylation of *N*-trimethylsilylthiobenzamide at 253 K.[10]



In the cases of (8) and (2b) a second possible reaction mechanism, a primary thiono–thiolo rearrangement followed by rapid decomposition of the latter into the ketens (11) and (14), respectively, and the silanethiol (12), should *a priori* be considered. After thermolyses at 1 043 K only very minor amounts of the starting materials are recovered, which implies that possible primarily *generated species are quantitatively* decomposed into the observed products before reaching the detection system (ion source). In general it is believed that species with half lives less than *ca.* 10^{-3} s may escape detection.[18] However, assuming $\Delta H_r \simeq \Delta G_r \simeq -62$ kJ mol^{-1} (*i.e.* $\Delta S_r \simeq 0$)[7] for the thiolo–thiono rearrangement, the equilibrium constants for the thiono–thiolo system can, according to the van't Hoff equation, be calculated to be $\log_e K$ (293 K) $\simeq 25$ and $\log_e K$ (1 043 K) $\simeq 7$, respectively, *i.e.* even at the elevated temperature the thiolo–thiono rearrangement will be rather favourable. In the present case the latter rearrangement should compete with the possible rethermolytic β-elimination of silanethiol (12) from the thiolo-species, the latter totally suppressing the former, corresponding to quantitative rethermolysis. Based on the above figures and the fact that rethermolyses in general may be expected to occur to only a small extent [18] it seems unlikely that a primary thiono–thiolo rearrangement should be expected to play any major role in the thermolyses of (8) and (2b).

In conclusion, it appears that because of the electronic and possibly also steric effect of neighbouring sulphur the Si–O bond is readily cleaved in the silylated thiocarboxylic acid derivatives (2b), (3), and (8) to give ketens, thus excluding this method as a suitable route to thioketens.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrograph, and the ^{1}H n.m.r. spectra ($CDCl_3$) on Varian T60, Varian EM360, and Perkin-Elmer R32 instruments.

Flash Vacuum Thermolysis Technique [18]—The f.v.t. technique used is based on the direct combination of a thermolysis unit with a double focusing mass spectrometer with a field ion source. The thermolysis unit is constructed as a modification of the Pye–Unicam PV4000 pre-column pyrolysis system, which is based on the Curie-point principle, *i.e.* the high frequency inductive heating in ferromagnetic materials. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heated line-of-sight inlet system.

Samples (*ca.* 50 µg) of the pure compound were introduced (micro-syringe) into the reactor *via* a heated injection block. The contact time in the hot zone has been estimated to be *ca.* 10^{-3}—10^{-4} s,[18] fulfilling the contact time requirement for f.v.t. equipment. According to the geometry of the system, thermolysis products with half-lives < *ca.* 10^{-3} s are assumed to escape detection.[18] The internal geometry of the reactor (length 40 mm, internal diameter 2 mm) combined with a low actual pressure (*P ca.* 10^{-4} Torr) assure a very low frequency of intermolecular collisions relative to the molecular–hot surface collison frequency, *i.e.* only unimolecular reactions take place.

The mass spectra were recorded on a Varian *MAT CH* 5D instrument equipped with a combined electron impact ionization–field ionization–field desorption ion source. The field ion emitter was a 10 µm tungsten wire activated in benzonitrile vapour.

Compounds (1a),[19] (1b),[20] (4),[11] and *N*-trimethylsilylthioacetamide (from thioacetamide and hexamethyldisilazane) [12] were prepared according to reported procedures.

3,3-*Dimethyl(thiobutanoic) Acid O-Trimethylsilyl Ester* (2a).—Compound (2a) was prepared by reaction of (1a) with 2-phenylethylamine–carbon disulphide–triethylamine followed by silylation with chlorotrimethylsilane–triethylamine,[9] yield 49%; b.p. 341—343 K at 11 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.35 (9 H, $SiMe_3$), 0.98 (9 H, Bu^t), and 2.64 (2 H, CH_2).

3,3-*Dimethyl-2-isopropyl(thiobutanoic) Acid O-Trimethylsilyl Ester* (2b).—*N*-Trimethylsilylthioacetamide (12.5 g, 0.086 mol) in hexane (15 ml) was slowly added to BuLi (0.086 mol) in hexane at 195 K. After 1 h (1b) (14.5 g, 0.082 mol) in hexane (20 ml) was slowly added and the solution was allowed to warm to room temperature. The precipitate was removed by filtration (with exclusion of moisture). The filtrate was concentrated *in vacuo* and the product was isolated by distillation, yield 54%; b.p. 356—358 K at 2 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.40 (9 H, $SiMe_3$), 0.97 and 1.09 (6 H, d, *J ca.* 7 Hz, diastereotopic Me of Pr^i), 1.02 (9 H, s, Bu^t), 2.00 (1 H, m, CH of Pr^i), and 2.77 (1 H, d, *J* 5 Hz, 2-H).

3,3-*Dimethyl-1-trimethylsilioxy-1-trimethylsilylthiobut-1-ene* (3).—Compound (2a) (9.4 g, 46 mmol) in dry THF (20 ml) was slowly added to a stirred solution of lithium di-isopropylamine (50 mmol) [prepared from di-isopropylamine (50 mmol) and an equimolar amount of BuLi in hexane] at 195 K. The stirring was continued for 3 h followed by dropwise addition of chlorotrimethylsilane (5.4 g, 50 mmol) in dry hexane (10 ml). The mixture was allowed to heat up to room temperature and the precipitated LiCl was removed by filtration after 20 h (exclusion of moisture). The *solvent was removed in vacuo* and the product isolated by distillation, yield 9.0 g (72%); b.p. 348—350 K (at 0.9 mbar); $\nu_{max.}$ 1 640 cm^{-1} (C=C); δ 0.23 and δ 0.27 (both 9 H, $SiMe_3$), 1.03 (9 H, Bu^t), and 4.70 (1 H, =CH) (Found: C, 52.65; H, 10.35; S, 11.1. $C_{12}H_{28}OSSi_2$ requires C, 52.15; H, 10.15; S, 11.6%).

1,3,3-*Trimethylbicyclo[2.2.1]heptan-2-ylmethanol* (5).—*Compound* (5) was prepared from (4) by reaction with diborane followed by oxidation of the resulting borane with H_2O_2,[11] yield 89%; m.p. 334 K; $\nu_{max.}$ (KBr) 3 340 cm^{-1} (OH); $[\alpha]_D^{20}$ −37.7° ($CDCl_3$); δ 0.8—1.8 [m, containing δ 0.83, 0.88, 0.96, 1.00, 1.03, and 1.12 (Me)] and 3.68 (d, *J* 7 Hz, CH_2O) (Found: C, 78.25; H, 12.15. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%).

1,3,3-*Trimethylbicyclo[2.2.1]heptane-2-carboxylic Acid* (6).—*Compound* (6) was preferentially prepared by oxidizing (5) according to ref. 12, yield 75%, m.p. 379 K; $[\alpha]_D^{20}$ −4.4° ($CDCl_3$); $\nu_{max.}$ (KBr) *ca.* 3 000br (OH) and 1 700 cm^{-1} (C=O); δ 0.9—2.3 [m, containing δ 1.02, 1.14, and 1.17 (Me)], 2.16 (d, *J ca.* 2 Hz, H-2), and 10.7br (OH) (Found: C, 72.5; H, 10.0. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95%).

1,3,3-*Trimethylbicyclo[2.2.1]heptane-2-carbonyl Chloride* (7).—*Compound* (7) was prepared by reaction between (6) and thionyl chloride, yield 60%, b.p. 347 K at 0.95 mbar; $\nu_{max.}$ (film) 1 805 cm^{-1} (C=O); δ 0.9—2.3 [m, containing δ 1.00, 1.09, 1.14, 1.17, and 1.25 (Me)] and 2.61 and 2.70 (both d, *J ca.* 2 Hz, *endo-* and *exo-*2-H) (Found: C, 65.85; H, 8.65. $C_{11}H_{17}ClO$ requires C, 65.8; H, 8.55%).

O-*Trimethylsilyl 1,3,3-Trimethylbicyclo[2.2.1]heptane-2-thiocarboxylate* (8).—The reaction was analogous to the above preparation of (2b) from (1b), yield 25%; b.p. 383 K at 1.1 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.41 (9 H, $SiMe_3$), 0.8—2.2 [m, containing δ 0.98, 1.00, 1.14, and 1.16 (Me)], and 2.76 and 2.87 (both d, *J ca.* 2 Hz, *endo-* and *exo-*2-H).

Compounds (2a), (2b), and (8) did not give satisfactory elemental analyses due to their highly hygroscopic nature.

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APPENDIX 10.

GAS PHASE THERMOLYSES OF THIETAN 1-OXIDE AND 1,2-OXATHIOLANE 2-OXIDE. EVIDENCE FOR THE INTERMEDIACY OF 1,2-OXATHIOLANE

LARS CARLSEN, HELGE EGSGAARD AND DAVID N. HARPP

J.CHEM.SOC. PERKIN TRANS. 2 (1981) 1166-1170

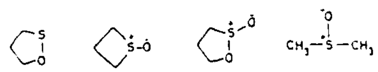
Gas Phase Thermolyses. Part 4.[1a] Gas Phase Thermolyses of Thietan 1-Oxide and 1,2-Oxathiolan 2-Oxide. Evidence for the Intermediacy of 1,2-Oxathiolan

By **Lars Carlsen** * and **Helge Egsgaard**, Chemistry Department, Risø National Laboratory, DK—4000 Roskilde Denmark
David N. Harpp, Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A2K6

The unimolecular gas phase thermolyses of thietan 1-oxide, 1,2-oxathiolan 2-oxide, and dimethyl sulphoxide have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range 783—1 404 K. The reactions are rationalized in terms of atomic oxygen extrusions and sulphoxide–sulphenate rearrangements. Evidence is presented for the common intermediacy of 1,2-oxathiolan from the thermolyses of both thietan 1-oxide and 1,2-oxathiolan 2-oxide.

We have previously reported on the thermal[2,3] and photolytic[4] generation of the simplest cyclic sulphenates, the three-membered oxathiirans, which are found to be thermally highly labile compounds. The corresponding four- and five-membered cyclic sulphenates, 1,2-oxathietans, and 1,2-oxathiolans, respectively, are not known. The former has, however, been studied theoretically within the CNDO/B and CNDO/S frameworks.[5] To our knowledge only one example of a stable cyclic sulphenate has been reported,[6] the compound being highly substituted. Attempts to synthesize the parent five-membered sulphenate, 1,2-oxathiolan (1), by deoxygenation of the corresponding stable *S*-oxide employing a series of reagents commonly used for reduction of sulphoxides were unsuccessful.[7] However, evidence has been obtained for the isolation of (1) by cyclization of *S*-phthalimido-3-mercaptopropan-1-ol. Compound (1) exhibits a half-life of *ca.* 3 h at room temperature.[8]

As a part of our current interest in the unimolecular gas phase thermolytic decompositions of organic sulphur compounds,[1] we now report our results on the unimolecular gas phase thermolyses of thietan 1-oxide (2) and 1,2-oxathiolan 2-oxide (3) as possible precursors to the unknown 1,2-oxathiolan (1). The thermolyses of (2) and (3) were studied since sulphoxides are known thermally to rearrange to the corresponding sulphenates,[9] and organic *S*-oxides have been shown to extrude atomic oxygen under pure unimolecular gas phase thermolytic conditions.[3] To elucidate the presence of these two reactions we also studied the unimolecular gas phase thermolysis of dimethyl sulphoxide (4).



(1) (2) (3) (4)

The thermolyses were studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) method,[10] which secures detection of unimolecularly formed products only.

EXPERIMENTAL

Compounds (2)[11] and (3)[12] were synthesised according to published procedures

Flash Vacuum Thermolysis Technique.—The f.v.t. technique, described in detail elsewhere,[10] is based on the direct combination of a thermolysis unit with a double focusing Varian MAT CH 5D mass spectrometer, equipped with a combined electron impact ionization–field ionization–field desorption (e.i.–f.i.–f.d.) ion source. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heatable line-of-sight inlet system. Samples (*ca.* 50 μg) of the pure compounds were introduced (microsyringe) into the hot zone (reactor) *via* a heated injection block. The contact time in the reactor has been estimated to be *ca.* 10^{-3}—10^{-4} s. The internal geometry of the reactor (length 40 mm, internal diameter 2 mm) combined with a low actual pressure (*P ca.* 10^{-4} Torr) assures a very low frequency of intermolecular collisions relative to the molecule–hot surface collision frequency, *i.e.* only unimolecular reactions take place. However, it should be remembered that surface catalytic effects may operate.

The thermolysis products are detected by recording the field ionization mass spectra immediately after the thermolyses. F.i. gives rise to molecular ions (even of very unstable substances) accompanied only by few, if any, fragment ions.[13]

Further identification of the single compounds formed by the gas phase thermolyses are obtained by recording the collision activation (c.a.) mass spectra[14] of the corresponding molecular ions.[10]

RESULTS

Several authors have recently reported on the gas phase thermolysis of dimethyl sulphoxide (4).[15-17] From this work a rather complicated decomposition pattern could be expected upon thermolysis of (4). Two papers by Block and his co-workers caught our attention as they reported the formation of sulphine (thioformaldehyde *S*-oxide)[16] and methanesulphenic acid.[17] However, these studies do not report on the unimolecular decomposition of (4). The same is true in a study by Thyrion[18] who rationalized a complete degradation of (4) in terms of a series of speculative radical reactions. The f.i.-m.s. spectrum of (4) following thermolysis (1 404 K), is however very simple, as only three reaction products, dimethyl sulphide (5) (*M* 62), methanethiol (6) (*M* 48), and formaldehyde (7) (*M* 30), are observed (Figure 1). The identity of these compounds was

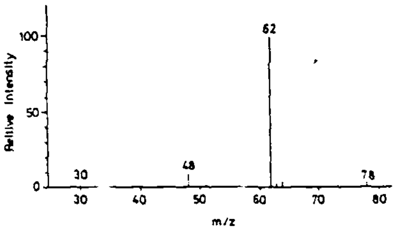


FIGURE 1 Field ionization mass spectrum of dimethyl sulphoxide following unimolecular gas phase thermolysis at 1 404 K

verified by studying the corresponding thermolysis of dimethyl [$^2H_6$]sulphoxide, which resulted in the formation of products with molecular weights of 68, 52, and 32, respectively. No peak corresponding to [$^2H_2$]sulphine (*M* 64) was observed. Thermolysis of (4) at lower temperatures did not afford new products, as only the above three reaction products were observed, albeit, in lower overall yield.

In the case of thietan 1-oxide (2) (*M* 90) we found that the product composition is somewhat dependent on the thermolysis temperature. Figure 2 depicts the f.i.-m.s. spectra following thermolyses of (2) at 883, 1 043, and 1 404 K, respectively. On the basis of these spectra, complementary with collision activation mass spectra of authentic samples, a product assignment of thietan (8) (*M* 74), acrolein (11) (*M* 56), sulphine (9) (*M* 62), and products with the molecular

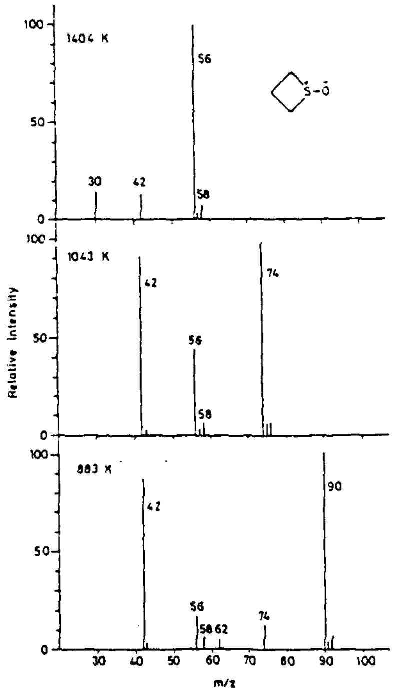


FIGURE 2 Field ionization mass spectra of thietan 1-oxide following unimolecular gas phase thermolyses at 883, 1 043, and 1 404 K, respectively

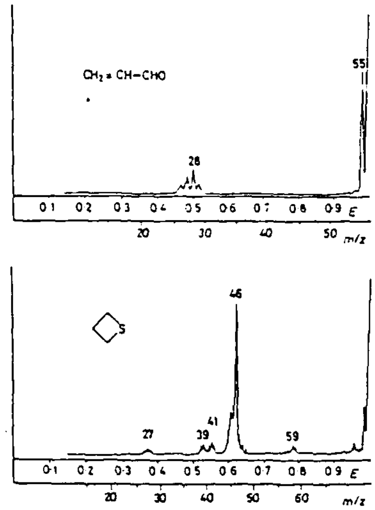


FIGURE 3 Collision activation spectra of field ionized thietan and acrolein obtained after thermolysis of thietan 1-oxide at 1 043 K

compositions C_3H_6O (10) (*M* 58) and C_3H_6 (12) (*M* 42), respectively are observed. Due to the low intensity of the peak with *m/z* 58 it has, unfortunately, not been possible to obtain satisfactory c.a.-m.s. spectra for a conclusive identification.* Neither has it, by the c.a. method applied here, been possible to distinguish between propene and cyclopropane (12) (*M* 42). Figure 3 depicts the f.i.-c.a. spectra of thietan and acrolein obtained after thermolysis of (2) at 1 043 K. The spectra are identical to those recorded from authentic samples.

In Figure 4, the product composition following thermo-

* C.a.-m.s. spectra of authentic samples only exhibit minor quantitative differences.

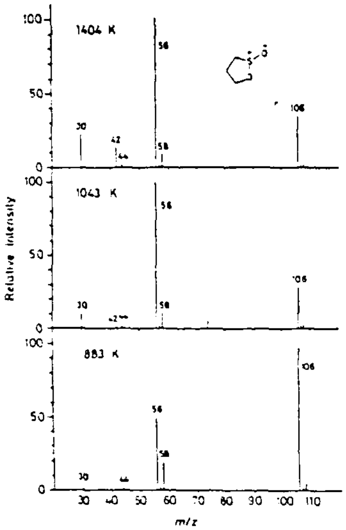


FIGURE 4 Field ionization mass spectra of 1,2-oxathiolan 2-oxide following unimolecular gas phase thermolysis at 883, 1 043, and 1 404 K, respectively

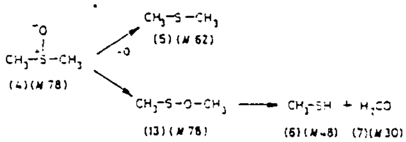
lyses of 1,2-oxathiolan 2-oxide (3) (*M* 106) at 883, 1 043, and 1 404 K, respectively, is very similar to the thermolysis of (2). Additionally formaldehyde (7) (*M* 30) is found in low abundance. An f.i.–c.a. spectrum of acrolein identical to that *mentioned above was obtained.*

It is not possible to calculate the yields of the single species directly from the f.i.–m.s. spectra, as the single compounds may exhibit rather different f.i. sensitivities.[17] However, the relative f.i.-sensitivities of (12), (11), (10), and (8) were determined using the gas inlet system of the mass spectrometer. Tentatively the sensitivities for propene and oxetan, as representatives for (12) and (10), respectively were used. From Figures 2 and 4, supplemented by the relative f.i.-sensitivities, the relative yields of these compounds were estimated (Table).

DISCUSSION

The product formation reported above can be discussed in terms of the two possible reactions mentioned in the Introduction, *i.e.* atomic oxygen extrusion * and rearrangement of sulphoxides to the corresponding sulphenate coupled with consecutive sulphenate decomposition reactions.

The existence of these types of reactions is easily rationalized in the case of dimethyl sulphoxide (4) (Figure 1). It has previously been reported that sulphoxides that do not possess β-hydrogens thermally can be rearranged to the corresponding sulphenates, the



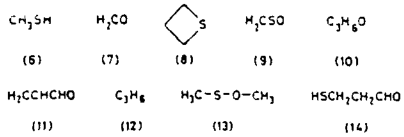
latter consecutively fragmenting into a thiol and a carbonyl compound.[9] In the present case this reaction would result in the formation of methanethiol (6) and formaldehyde (7) likely *via* methyl methanesulphenate (13).

However, a c.a.–m.s. analysis of the peak with *m/z* 78, following thermolysis of (4) at temperatures between 883 and 1 404 K only showed unchanged (4). No signals *corresponding to a contribution of (13) to the* peak of *m/z* 78 were observed, indicating the instability of the latter under the conditions used.

Relative yields of (7), (12), (11), (10), and (8) following unimolecular gas phase thermolyses of (2) and (3) at 783, *883, 1 043, and 1 404 K, respectively. The figures are averages for three experiments*

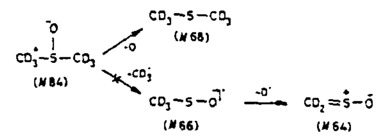
Compound	*M*	*S* [a]	783 K (2)	783 K (3)	883 K (2)	883 K (3)	1 043 K (2)	1 043 K (3)	1 404 K (2)	1 404 K (3)
(7)	30	1.00 [b]				0.02		*0.10*	0.05	0.08
(12)	42	0.17	0.39		0.89		0.61	0.04	0.37	0.37
(11)	66	1.00	0.04	0.34	0.04	0.58	0.11	0.70	0.47	0.46
(10)	58	0.52	0.04	0.66	0.02	0.40	0.02	0.16	0.11	0.09
(8)	74	0.63	0.53		0.04		0.24			
Approx. overall yield			0.10	0.05	0.50	0.40	1.00	0.80	1.00	0.80

[a] Relative f.i. sensitivities. [b] Assumed value equal to that of acrolein.



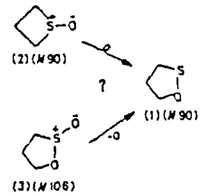
* Since rupture of the semipolar S→O bond in (4) appears to require 86.6 kcal mol⁻¹ (S. W. Benson, *Chem. Rev.*, 1978, 78, 23) the *apparent presence of this mechanism* suggests that the atomic oxygen extrusion reaction may involve surface catalysis. However, since the hot filaments in the reactor are wires of different alloys (the actual composition being determining for the Curie temperature of a given wire) different surface catalytic effects may operate (*cf.* Y. Nishiyama and Y. Tamai, *Chemtech*, 1980, 10, 680), not of necessity giving rise to a smooth variation in yield *with temperature.*

A possible unimolecular formation of sulphine (9) *via* a pathway involving primary loss of a methyl radical from (4) followed by a loss of a hydrogen radical from the resulting MeSO radical is effectively ruled out due to the above mentioned deuterium labelling experiment.



In the case of (2) (Figure 2) atomic oxygen extrusion evidently results in the formation of thietan (8) (*M* 74),* whereas the sulphoxide–sulphenate rearrangement would afford formation of the unknown 1,2-oxathiolan (1); the latter, on the other hand, would also be a result of atomic oxygen extrusion from the S-oxide (3).

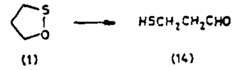
However, when (3) was thermolysed (Figure 4) no product with molecular weight 90 is observed. This could be explained by a consecutive quantitative degradation of (1). It furthermore suggests that, if formed, (1) exhibits a half-life $<10^{-8}$ s under the reaction conditions.[10] Furthermore, formation of (10) and (11) by rearrangements and/or fragmentations directly from both (2) and (3) can be explained only in terms of highly speculative reaction mechanisms, whereas a



straightforward rationalization is possible assuming the existence of the common intermediate (1).

To elucidate the possible degradation pathway of (1), we shall turn to a discussion of the formation of (10) and acrolein (11), the common products for the thermolyses of both (2) and (3). There is a remarkable constancy in the (10) : (11) ratios, when comparing the product distributions following thermolyses of (2) and (3) at the single temperatures (Table). This supports an assumption that these products are formed *via* the same species.

Acrolein formation can be explained in terms of a fragmentation of sulphenate (1), analogous to that observed for (13), resulting in the formation of methanethiol and formaldehyde. However, as the sulphenate moiety in the case of (1) is fixed in a five-membered ring system the fragmentation would lead to generation of 3-mercaptopropanal (14), the latter only being known as its oligomer.[18] We find, however, that the oligomer of (14) at *ca.* 400 K (*in vacuo*) is smoothly cracked into the monomeric species.[19] Cracking the oligomeric species



under conditions where thermolysis of the initially formed (14) would closely mimic those for the thermolyses of (2) and (3), we found that (14) very easily eliminates hydrogen sulphide affording acrolein (Figure 5). The c.a.–m.s. spectrum of the latter is identical with

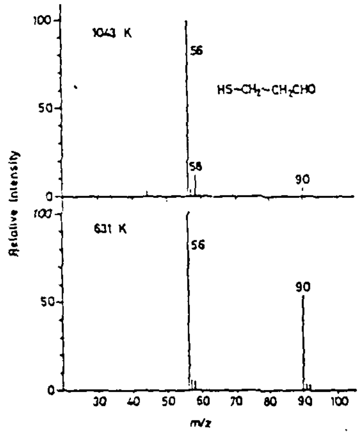


FIGURE 5 Field ionization mass spectra of 3-mercaptopropanal following unimolecular gas phase thermolyses at 631 and 1 043 K, respectively

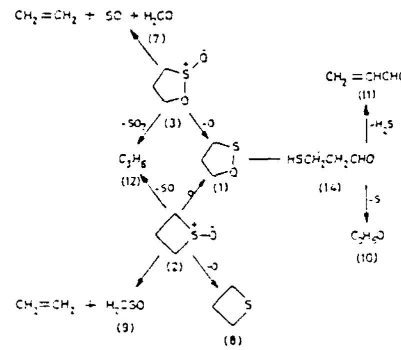
that obtained from authentic acrolein. We find that even at 631 K [200 K below the temperature where (2) and (3) thermolyse to an observable extent] a high degree of H_2S elimination from (14) is observed, and at 1 043 K only very minor amounts of (14) are recovered. In addition, it is seen (Figure 5) that (10) (*M* 58) is formed in low yield; the above mentioned (10) : (11) ratio is also found here to be 0.23 (1 043 K). For comparison, the (10) : (11) ratios following thermolysis of (2) and (3) at 1 043 K are calculated to be 0.18 and 0.23, respectively.

It should finally be mentioned that the electron impact ionization mass spectrum of monomeric (14) suggests some content of the isomeric thietan-2-ol,[18,20] which similarly may contribute to the peak with *m/z* 90 (Figure 5), as well as be responsible for the thermal formation of (10) by sulphur extrusion. From the above,

* Same footnote as on p. 1168.

it is not surprising that we are unable to detect sulphenate (1) and/or the rearranged product (14), but only the corresponding decomposition products, acrolein and (10).

Remaining to be discussed, concerning the thermolysis of (2), is the formation of C_3H_6 (12) (*M* 42), apparently generated by simple sulphur monoxide extrusion, and sulphine (9) (*M* 62), which is likely due to a 2 + 2-retrocycloaddition of ethylene and sulphine, as previously reported by Block.[16] Since sulphine is formed only in



SCHEME

very minor amounts (Figure 2) the apparent lack of a peak corresponding to ethylene (*M* 28) is not unreasonable owing to a very low f.i.-sensitivity of the latter.[13]

In connection with the thermolysis of (3), the two undiscussed products, (12) and (7), are apparently generated by sulphur dioxide extrusion and a simple rearrangement analogous to the recently reported sulphinate thermolyses by Durst *et al.*[21]

In summary we rationalize the unimolecular gas phase thermolyses of (2) and (3) as depicted in the Scheme, taking the results reported into account for the intermediacy of (1). Although cumulative evidence for the intermediacy of 1,2-oxathiolan in the gas phase thermolyses of thietan 1-oxide and 1,2-oxathiolan 2-oxide is high, direct experimental verification under such conditions does not seem likely.

[0/1637 *Received*, 27th *October*, 1980]

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APPENDIX 11.

THERMALLY-INDUCED REARRANGEMENT OF METHYL ACETATE IN THE GAS PHASE

LARS CARLSEN, HELGE EGSGAARD AND PALLE PAGSBERG

J.CHEM.SOC. PERKIN TRANS. 2 (1981) 1256-1259

Gas-phase Thermolyses. Part 5.[1] Thermally-induced Rearrangement of Methyl Acetate in the Gas Phase

By Lars Carlsen,* Helge Egsgaard, and Palle Pagsberg, Chemistry Department, Risø National Laboratory, DK 4000 Roskilde, Denmark

The pure uni-molecular gas-phase thermolysis of ^{18}O-labelled methyl acetate has been investigated by the flash vacuum thermolysis–field ionization mass spectrometry method, in combination with collision-activation mass spectrometry in the temperature range 1 043—1 404 K. *Minor amounts of keten, as a result of 1,2-elimination of methanol, were detected.* The predominant reaction is shown to be the intramolecular oxygen to oxygen methyl group migration. The isomerization is discussed in terms of vibrational excitation of specific in-plane bending modes observed for the methyl acetate molecule. The low-pressure rate constants for the isomerization at 1 253 and 1 404 K were calculated from the collision activation mass spectra.

THE gas-phase thermolyses of carboxylic acid esters, as well as the corresponding monothio-derivatives, have been investigated intensively during the past decade.[2-4] It has been demonstrated that thion carboxylates, in the gas phase, can rearrange thermally into the thermodynamically more stable thiolo-esters. The energy of activation for the thiono→thiolo rearrangement has been estimated to be ca. 45 kcal mol^{-1}, slightly dependent of the nature of the ester alkyl group.[3,4] The reverse reaction has, however, to our knowledge not been observed, apparently owing to the thermodynamic stabilization of the thiolo-esters by ca. 20 kcal mol^{-1} relative to the thiono-compounds.[4] On a possible thermally induced oxygen to oxygen alkyl group migration in carboxylic acid esters little information has appeared.[5] In 1971 Smith and his co-workers reported on the partial (40%) gas-phase thermolysis of ^{18}O-labelled ethyl acetate. The reaction was carried out at 619 K in a stainless steel reactor at a pressure of ca. 500 Torr.[5,6] The mass spectrometric analysis of the reaction products revealed that only minor amounts of oxygen scrambling in the unreacted ester had occurred; the authors therefore excluded the intermediacy of an ion pair, in rapid equilibrium with the ester, as being responsible for the decomposition products, acetic acid and ethylene, formed upon thermolysis of ethyl acetate. No discussion of the observed oxygen scrambling was given. However, it should be noted that the thermolysis was carried out under relatively high pressure conditions, suggesting the possibility of important bimolecular reactions. Potential ester formation from acetic acid and ethylene[7] should be mentioned particularly.

In the present paper we report on the pure unimolecular gas-phase thermolysis of ^{18}O-labelled methyl acetate (95% labelling in the carbonyl group) in the temperature range 1 043—1 404 K, focusing on possible ^{16}O–^{18}O methyl group migration.

EXPERIMENTAL

Methyl [^{18}O]Acetate.—The ^{18}O-labelled methyl acetate was prepared by hydrolysing 1-methoxyethylideneamine hydrochloride (1.09 g)[8] in pyridine (2 ml) by $H_2{}^{18}O$ (0.2 ml; Prochem; 99.5% enriched). After 16 h the precipitate (NH_4Cl and unchanged imino ether hydrochloride) was removed by centrifugation. The supernatant liquid was poured into dilute hydrochloric acid and methyl acetate (ca. 0.5 ml) was stripped off by passing helium through the solution and collecting the ester in a liquid nitrogen trap. The purity was >99% by g.l.c. Minor amounts of water were detected in the sample.

Flash Vacuum Thermolysis.—The thermolyses were carried out using the flash vacuum thermolysis–field-ionization mass spectrometry (f.v.t.–f.i.m.s.) technique which has been described in detail previously.[9] The method is based on a direct combination of a thermolysis unit, fulfilling the requirements for a Knudsen reactor, with a Varian MAT CH5D double-focusing mass spectrometer equipped with a combined electron impact ionization–field ionization–field desorption (e.i.–f.i.–f.d.) ion source. Collision activation (c.a.) mass spectra[10] were obtained by introducing helium as the collision gas via a needle valve into the first field free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The c.a. mass spectra of the single ions were obtained by scanning the electrostatic field.

C.a. analyses of thermolysate mixtures are generally carried out on the single field ionized molecules.[9] However, the compound exhibiting the highest molecular weight in the reaction mixture, i.e. in the present case of undecomposed methyl [^{18}O]acetate (M 76), may advantageously be analysed by c.a. mass spectrometry of the molecular ion (present in the e.i.-induced mass spectrum), as this ion evidently is not a result of e.i.-induced fragmentation. The sensitivity of the c.a. analysis is thus considerably enhanced.

The f.i.–f.i. mass spectra following thermolyses were recorded with a scan rate of 50—100 a.u. s^{-1}. The e.i.–c.a. mass spectra of the single ions are recorded within 5 s (signal to noise ratio >1 000).

RESULTS

We find that even at very high temperatures methyl acetate is rather stable and only decomposes to a minor extend. The products were keten and methanol, in agreement with the findings of Hurd and Blunck.[11] The field-ionization mass spectra of unthermolysed methyl [^{18}O]-acetate together with that obtained following thermolysis at 1 404 K are depicted in Figure 1.

In Figure 2a the e.i.–c.a. mass spectrum of the molecular ion of unthermolysed $CH_3C(^{18}O)OCH_3$ (1a) is shown.[18] No electron impact induced ^{16}O–^{18}O scrambling was observed (Scheme 1). In Figures 2b—d the c.a. mass spectra of the

$$CH_3C(^{18}O)OCH_3^{+\cdot} \xrightarrow{\text{He collision}} CH_3C^{18}O^{+} \; / \; CH_3O^{+}$$

(1a) (*m/z* 76) (2a) (*m/z* 45) (3a) (*m/z* 31)

SCHEME 1

$$CH_3C(O)^{18}OCH_3^{+\cdot} \xrightarrow{\text{He collision}} CH_3CO^{+} \; / \; CH_3{}^{18}O^{+}$$

(1b) (*m/z* 76) (2b) (*m/z* 43) (3b) (*m/z* 33)

SCHEME 2

molecular ions of undecomposed ester following thermolysis at 1 043, 1 253, and 1 404 K, respectively, are shown. The presence of the rearranged methyl acetate (1b) is unambiguously demonstrated by the appearance of the corresponding characteristic fragments (2b) and (3b) upon helium-collision (Scheme 2).

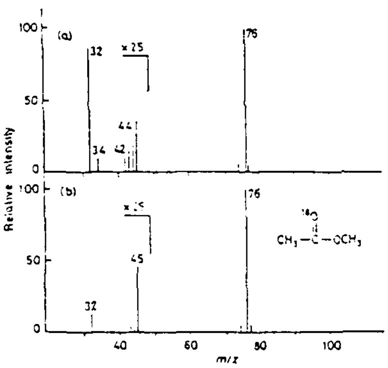


FIGURE 1 Field-ionization mass spectra of methyl [^{18}O]acetate (1a) following thermolysis at 1 404 K (a) and without thermolysis (b)

Based on Figure 2c and d the ratio (1b) : (1a) was calculated to be 0·09 and 0·31 following thermolysis at 1 253 and 1 404 K, respectively

DISCUSSION

The responsibility for the appearance of the rearranged ester (1b) can *a priori* be ascribed to two fundamentally different mechanisms, (a) a purely intramolecular methyl group migration *via* an electron-delocalized four-membered cyclic transition state or (b) a primary cleavage of the methyl–oxygen bond, followed by recombination to ester. The latter reaction can involve either a homolytic cleavage into the acetoxyl and methyl radicals or heterolytic formation of an ion pair. However, ion pair formation is much more energy demanding than homolytic radical generation and can accordingly be left out of consideration. On the other hand, it is necessary to discuss briefly the possible involvement of the acetoxyl–methyl radical pair.

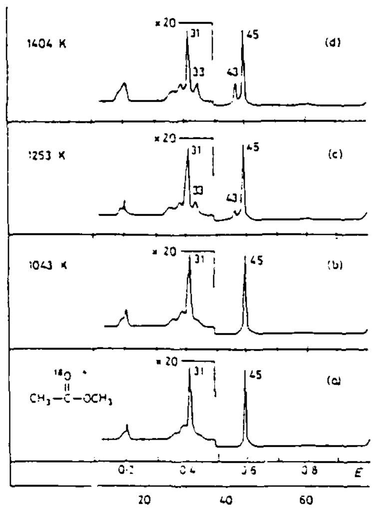


FIGURE 2 Collision activation mass spectra of the electron impact induced molecular ion of methyl [^{18}O]acetate (1a) without thermolysis (a) and following thermolysis at 1 043 K (b), 1 253 K (c), and 1 404 K (d), respectively

It has been reported that acetoxyl radicals decompose unimolecularly into methyl radicals and carbon dioxide. The rate constant (k_1) has been estimated to be of the order of 10^9—10^{10} s^{-1}.[13] The concurrent bimolecular radical reactions (*i.e.* acetoxyl–methyl or acetoxyl–acetoxyl, both leading to the formation of methyl acetate) proceed with rate constants k_2 *ca.* 10^{10} l mol^{-1} s^{-1},* which give rise to the kinetic expressions (1) and (2) for the disappearance of the acetoxyl radicals.

$$(d[CH_3COO^{\cdot}]/dt)_1 = k_1[CH_3COO^{\cdot}] \qquad (1)$$

$$(d[CH_3COO^{\cdot}]/dt)_2 = k_2[CH_3COO^{\cdot}][R^{\cdot}] \qquad (2)$$

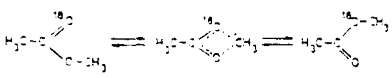
$$R^{\cdot} = CH_3^{\cdot} \text{ or } CH_3COO^{\cdot}$$

Based on our previous study[9] the maximum radical concentrations in the reactor are estimated to be *ca.* 10^{-7} mol l^{-1}. On this background we conclude that under

* Radical recombination reactions generally proceed with rate constants of *ca.* 10^9—10^{10} l mol^{-1} s^{-1}, *i.e.* the choice of $k_2 = 10^{10}$ l mol^{-1} s^{-1} reflects the more conservative case.

the present conditions the unimolecular disappearance of possibly generated acetoxyl radicals will proceed at least 10^6—10^7 times faster than the recombination reactions.

An experimental verification of our exclusion of the possible involvement of acetoxyl radicals in the apparent rearrangement (1a) ⟶ (1b) was obtained by co-thermolysis of the ester (1a) and [$^2H_3$]methyl acetate (M 77) (1c). In Figure 3 the e.i. mass spectrum of the



(1a) (1b)

SCHEME 3

mixture (1a)–(1c) is depicted together with the e.i. mass spectrum obtained following thermolysis of the mixture at 1 404 K. It is thus demonstrated that no methyl group crossover, which would give rise to simultaneous appearance of signals at m/z 74 and 79, takes place. The change in the mutual 43 : 45 ratio, due to thermolysis, is a reflection of methyl group migration only (cf. Figure 2). Consequently we conclude that the *methyl acetate isomerization proceeds purely intramolecularly via an electron-delocalized transition state* (Scheme 3).

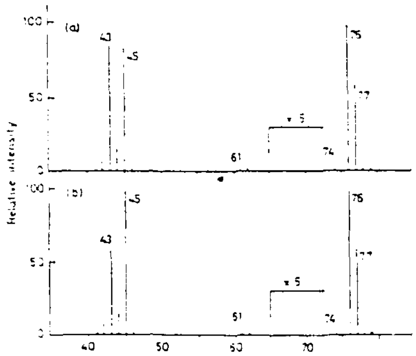


FIGURE 3 Electron impact mass spectra of a mixture of [^{18}O]-methyl acetate (1a) and [$^2H_3$]methyl acetate (1c) following thermolysis at 1 404 K (a) and without thermolysis (b)

On the basis of a vibrational assignment for methyl acetate, which demonstrates that the i.r. band contours are consistent with the ester possessing the *E* configuration,[14,15] we suggest that the thermally induced isomerization of methyl acetate most probably proceeds through a vibrational excitation of two specific normal modes, which bring about the methyl group transfer.

It seems obvious that the vibrational modes, which are active in the methyl group transfer are the two in-plane bending modes ν_{15} 639 (OCO bend) and ν_{17} 303 cm^{-1} (COC bend). Fairly strong coupling between these modes is demonstrated by the appearance of the corresponding combination mode 942 (4) = 303 + 639 cm^{-1} in the i.r. spectrum.[15] Since the reaction, as concluded above, proceeds through a four-centre transition state which, neglecting the isotopic effect on the oxygen–methyl bond length, of necessity is symmetric, the reaction co-ordinate may be expressed in terms of the combination of higher lying vibrational levels ($n\nu_{15}$ + $m\nu_{17}$).

The threshold energy for the methyl group transfer can accordingly be expressed in terms of a critical set of quantum numbers (n_c, m_c) above which the two individual in-plane bending modes degenerate into one single 'hand-to-hand' vibration (Figure 4).

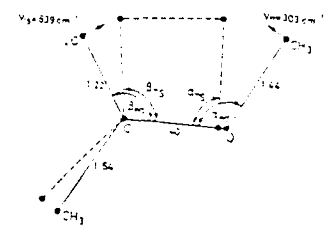


FIGURE 4 Structure of methyl acetate (——) and the transition state for the thermally induced isomerization (— — —)

A direct estimation of the energy of activation on this basis is, unfortunately, not possible, due to the lack of knowledge of the actual shapes of the two bending potentials involved. However, the rate constants for the (1a) ⟶ (1b) conversion can be calculated from the e.i. mass spectra depicted in Figures 2c and d.

The reaction can obviously be regarded as an equilibrium system (1a) ⇌ (1b) with concentrations [1a] = [1a]$_0$ and [1b] = 0 when the ester (1a) enters the reactor (0). Bearing in mind that the reactor fulfils the requirements for a Knudsen reactor,[3] we introduce the specific fluxes R_a and R_b of the esters (1a) and (1b) into the reactor.[16] At low temperatures, *i.e.* no thermolysis taking place, $R_a = k_{ea}[1a]_0$ and $R_b = 0$, k_{ea} being the unimolecular reactor escape rate constant[16] for the ester (1a). At elevated temperatures, where ester isomerization proceeds, the concentration of (1a) is smaller than [1a]$_0$, owing to the reaction taking place, and (1b) is generated, which affords expressions (3) and (4) for the stationary concentrations [1a] and [1b] in the reactor. k_{eb} is the unimolecular escape rate constant of the ester (1b) and k_1 and k_2 refer to the (1a) ⟶ (1b) and (1b) ⟶ (1a) reactions, respectively. Elimination

$$R_a = k_{ea}[1a]_0 = k_{ea}[1a] + k_1[1a] - k_2[1b] \quad (3)$$

$$R_b = 0 = k_{eb}[1b] + k_2[1b] - k_1[1a] \quad (4)$$

of [(1b)] by equation (4) and substitution into (3) gives the rewritten expression (5). In the present case,

$$[(1a)]/([(1a)]_0 - [(1a)]) = k_{ea}/k_1 + k_{ea}k_2/k_{eb}k_1 \quad (5)$$

again neglecting the very small ^{18}O isotopic effect, $k_1 = k_2 \equiv k$. Furthermore, the unimolecular escape rate constants for the two esters must of necessity be identical, *i.e.* $k_{ea} = k_{eb} \equiv k_e$, which by introduction in equation (5) gives (6).

$$k = k_e([(1a)]_0 - [(1a)])/(2[(1a)] - [(1a)]_0) = k_e[(1b)]/([(1a)] - [(1b)]) \quad (6)$$

The unimolecular escape rate constant is equal to the reciprocal value of the mean residence time, τ, of the molecule in the reactor,[16] the latter being calculated according to the Knudsen formula [equation (7)], where V is the reactor volume (0.13 cm^3) and A is the area of the orifice (0.03 cm^2). $\bar{c}$, the mean molecular rate, can be estimated according to the kinetic gas theory [equation (8)], T being the temperature and M the molecular weight of the molecule under investigation, *i.e.* in the present case 76.

$$\tau = 4V/\bar{c}A \text{ s} \quad (7)$$

$$\bar{c} = 1.46 \times 10^4 (T/M)^{\frac{1}{2}} \text{ cm s}^{-1} \quad (8)$$

Since the peaks 43 and 45 (Figure 2), arising from (1b) and (1a), respectively, have equal c.a. probabilities * the intensities of the peaks, I_{43} and I_{45}, can be taken as a direct measure of the mutual amounts of (1b) and (1a). On the above basis we are able to rewrite equation (6) as (9), which is directly applicable to the experimental data obtained. Relevant data and the calculated rate

$$k = k_e I_{43}/(I_{45} - I_{43}) = I_{43}/\tau(I_{45} - I_{43}) \quad (9)$$

constants at the temperatures 1 253 and 1 404 K are given in the Table.

Intensities of the peaks 43 and 45 in the c.a. mass spectra (*cf.* Figure 2), mean residence times, and unimolecular escape rate constants for ^{18}O-labelled methyl acetate, and calculated low-pressure rate constants for the (1a) ⟶ (1b) reaction at 1 253 and 1 404 K. The *unit for the peak intensities are arbitrary*

T/K	I_{43}	I_{45}	$10^4\tau$/s	$10^{-3}k_e$/s^{-1}	$10^{-3}k$/s^{-1}
1 253	9	100	2.66	3.76	3.72
1 404	31	100	2.52	3.97	17 8

As the thermolyses are carried out in a reactor operating at very low pressure,[9] it is emphasized that the calculated rate constants are low-pressure values. Unfortunately the construction of the reactor used,[9] even fulfilling the requirements for a Knudsen reactor, does not allow us to determine the effective collision frequency. A further disadvantage, from a thermodynamic point of view, is that the Curie Point principle only allows us to operate at a rather limited number of temperatures. Hence, with the present experimental results it is not possible to derive the high-pressure limit Arrhenius parameters for methyl acetate isomerization.

Finally, it should be noted that the above discussion has been carried through on the assumption that isomerization proceeds as a pure unimolecular gas-phase reaction. The possible involvement of a surface catalytic effect, which compared with previous experiments [17] seems rather unlikely, is similarly left for further investigation.

Conclusions.—We have by the present study demonstrated thermally induced methyl acetate isomerization in the gas phase at elevated temperatures. The reaction proceeds unimolecularly *via* an electron-delocalized four-membered cyclic transition state through vibrational excitation of the OCO and COC in-plane bending modes of the ester group.

* The c.a. probability of a given ion X in the c.a. mass spectrum of a single ion with mass M is expressed by $I_X/\sum_{1}^{M-1} I_i$ (see L. Carlsen and H. Egsgaard, submitted for publication).

[1/105 *Received, 26th January, 1981*]

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APPENDIX 12.

1,2-OXATHIOLANE

LARS CARLSEN, HELGE EGSGAARD, GORDON H. WHITHAM AND DAVID N. HARPP

J.CHEM.SOC. CHEM.COMMUN. (1981) 742-743

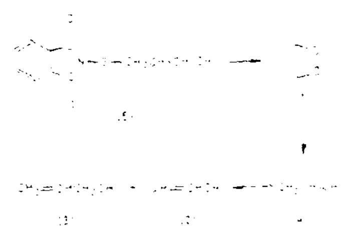
1,2-Oxathiolan

[illegible] and [illegible]
Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark
[illegible]
[illegible]
and [illegible] Harpp
Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

Summary: 1,2-Oxathiolan has been isolated in the gas phase and characterized by its electron-impact and thermally induced decompositions.

In a recent paper we suggested the intermediacy of 1,2-oxathiolan (1), the first unsubstituted [illegible] sulphenate,* in the gas-phase thermolyses of thietan [illegible] and 1,2-oxathiolan 2-oxide,[1] the identity of 1 being established by characterizing the consecutive [illegible] decomposition products acrolein (2) and [illegible] (3) generated via [illegible] (4) by H_2 [illegible] [illegible].

[illegible] and [illegible] investigated the possible formation of 1 by thermal decomposition of [illegible] (5) [illegible] on the basis of [illegible] and 70 eV electron-impact mass spectrometry they suggested that 1 was in fact formed. We report here the isolation of the cyclic sulphenate 1 in the gas phase and the decomposition of 1 under electron-impact and gas-phase thermolytic conditions.



Following [illegible] heating of compound (5) [illegible] at [illegible] K we collected the [illegible] the gas [illegible] of a Varian MAT CH5 [illegible] mass spectrometer equipped with a [illegible] field ionization-field desorption [illegible]

* A heavily substituted sultene has previously been reported [illegible] W. [illegible] and J. C. Martin, J. Am. Chem. Soc., [illegible]

The resulting f.i. mass spectrum revealed only a single peak at *m/z* 90, strongly indicative of the formation of a compound (hereafter called '90') with molecular weight 90 a.m.u. as the only volatile product. Phthalimide was detected as the remaining substance in the reaction chamber. Electron impact (70 eV) induced decomposition of the product '90' gave rise to the following fragments: *m/z* 90 ($M^{+\cdot}$, 74), 73 (17), 63 (7), 62 (11), 59 (17), 45 (25), 43 (10), 42 (24), 41 (100), and 39 (15%). The actual composition of the molecular ion (*m/z* 90) was, by high resolution, established to be C_3H_6OS (found 90·0139, calc.: 90·0139).

The similarities between the 70 eV e.i. mass spectrum and that previously reported for thietan 1-oxide[4] are striking; however, minor but significant differences are observed, especially in the cluster of peaks around *m/z* 60. Thus, thietan 1-oxide must be considered as a likely candidate for the reaction product '90,' in spite of the ^{1}H n.m.r. spectrum recorded by Whitham and Davis,[3] which does not unambiguously define (1).

In addition to 1,2-oxathiolan (1) and thietan 1-oxide a variety of cyclic and non-cyclic compounds have *a priori* to be considered as possible candidates for '90.' However, a common feature of these compounds is the presence of an XH group (X = O, S) as a structural unit. The possible candidature of these compounds was ruled out by isolating the reaction product following cracking of the OD-analogue of (5).‡ No deuterium incorporation in the reaction product was observed, *i.e.* the mass spectra remained unchanged, establishing the absence of a possible XH group in the compound '90.'§

To distinguish between the cyclic sulphenate (1) and thietan 1-oxide the gas-phase thermolytic decomposition of compound '90' appeared to be advantageous, since thietan 1-oxide in addition to the common products (2) and (3) gives rise to the formation of considerable amounts of thietan and C_3H_6 by O and SO extrusions, respectively.[1] Application of flash-vacuum pyrolysis–field-ionization mass spectrometry[6] (f.v.p.–f.i.m.s.) revealed a f.i.m.s. spectrum exhibiting molecular ions corresponding to thermally generated product. Scrutiny of the f.i.m.s. spectrum following thermolysis at 1043 K revealed intense peaks at *m/z* 56 and 58, whereas a total absence of peaks at *m/z* 74 and 42, corresponding to thietan and C_3H_6, respectively, was also noted, on which basis we unambiguously assigned 1,2-oxathiolan as compound '90.'

Field-ionization–collision-activation (f.i.–c.a.) mass spectra of the consecutively formed products, exhibiting molecular ions *m/z* 56 and 58, were found to be identical to those of authentic acrolein and allyl alcohol,¶ respectively.

(*Received, 8th April* 1981; *Com.* 416.)

‡ In order to avoid D–H exchange the gas inlet was first saturated with D_2O vapour.

§ The applicability of this technique has unequivocally been demonstrated by studying 3-mercaptopropanal (4) as a representative of the XH-bearing C_3H_6OS isomers (ref. 5).

¶ Since only quantitative differences in the f.i.–c.a. spectra of allyl alcohol, propanal, and oxetan are observed, we are not able to elucidate whether minor amounts of one of the latter two compounds are present in addition to allyl alcohol.

[1] For part 5 of the series 'Gas-Phase Thermolyses' see L. Carlsen, H. Egsgaard, and P. Pagsberg, *J. Chem. Soc., Perkin Trans. 2*, in the press; for part 4 see ref. 2; for part 3 see L. Carlsen, H. Egsgaard, E. Schaumann, H. Mrotzek, and W.-R. Klein, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1557.
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[4] S. R. Heller and G. W. A. Milne, 'EPA/NIH Mass Spectra Data Base,' NSRDS-NBS 63, vol. 1, 1978.
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APPENDIX 13.

GAS-PHASE THERMOLYSIS OF 1,2,3-OXADITHIOLANE 2-OXIDE AND THIIRAN 1-OXIDE. ON THE INTERMEDIACY OF 1,2-OXATHIETANE

LARS CARLSEN AND HELGE EGSGAARD

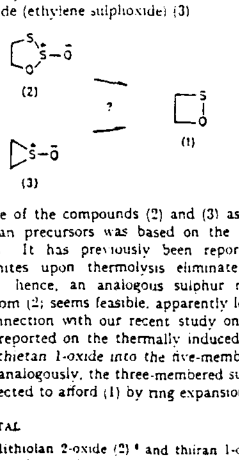
J.CHEM.SOC. PERKIN TRANS. 2 (1982) 279-282

Gas-phase Thermolyses. Part 7.[1] Gas-phase Thermolysis of 1,2,3-Oxadithiolan 2-Oxide and Thiiran 1-Oxide. On the Intermediacy of 1,2-Oxathietan [1]

By Lars Carlsen * and Helge Egsgaard, Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

The unimolecular gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide have been studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) technique in the temperature range from 1 043 to 1 404 K. The reactions are rationalized in terms of sulphoxide–sulphenate rearrangement and atomic oxygen, sulphur monoxide, and sulphur dioxide extrusions. Evidence is presented for the common intermediacy of 1,2-oxathietan from the thermolyses of both 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide

VERY recently we reported on the intermediacy of 1,2-oxathiolan[2] in the gas-phase thermolyses of 1,2-oxathiolan 2-oxide and thietan 1-oxide,[3] the five-membered cyclic sulphenate being characterized partly based on its thermal decomposition into acrolein and allyl alcohol. We have likewise in a series of papers reported on features of the three-membered cyclic sulphenates, *i.e.* the oxathiirans.[4] However, to our knowledge, no reports on the corresponding four-membered sulphenates, the 1,2-oxathietans, have appeared.† In the present study we report investigations on the possible intermediacy of the parent 1,2-oxathietan (1) in the gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide (2), and thiiran 1-oxide (ethylene sulphoxide) (3)



(2) (3) (1)

The choice of the compounds (2) and (3) as possible 1,2-oxathietan precursors was based on the following assumptions It has previously been reported that cyclic sulphites upon thermolysis eliminate sulphur monoxide;[5] hence, an analogous sulphur monoxide extrusion from (2) seems feasible, apparently leading to (1). In connection with our recent study on 1,2-oxathiolan we reported on the thermally induced ring expansion of thietan 1-oxide into the five-membered sulphenate;[3] analogously, the three-membered sulphoxide (3) was expected to afford (1) by ring expansion.

EXPERIMENTAL

1,2,3-Oxadithiolan 2-oxide (2)[6] and thiiran 1-oxide (3)[7] were synthesized according to previously reported procedures.

Flash Vacuum Thermolysis Technique.—The f.v.t. technique used has been described in detail elsewhere[8] and is based on the direct combination of a thermolysis unit with a double focusing Varian MAT CH 5D mass spectrometer, equipped with a combined electron impact ionization–field ionization–field desorption (e.i.–f.i.–f.d.) ion source. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heatable line-of-sight inlet system Samples (*ca.* 50 μg) of the pure compounds were introduced (microsyringe) into the hot zone (reactor) *via* a heated injection block. The contact time in the reactor has been estimated to be *ca.* 10^{-3}—10^{-4} s. The internal geometry of the reactor (*l* 40 mm, i.d. 2 mm) combined with a low actual pressure (*P ca.* 10^{-4} Torr) assures a very low frequency of intermolecular collisions relative to the molecule–hot surface collision frequency, *i.e.* only unimolecular reactions take place However, it should be remembered that surface catalytic effects may operate.

The thermolysis products are detected by recording the field ionization mass spectra immediately after the thermolyses. F.i. gives rise to molecular ions (even of very unstable substances) accompanied only by few, if any, fragment ions.[9]

Further identification of the single compound formed by the gas-phase thermolyses is obtained by recording the collision activation (c.a.) mass spectra[10] of the corresponding molecular ions.[9] The oxiran and acetaldehyde ions are distinguishable by c.a.m.s.[11] However, the conclusive discrimination between the possible C_2H_4O isomers is strongly facilitated by a study of the unimolecular metastable ion spectra.[12] In the present case DADI (Direct Analysis of Daughter Ions) spectra of the molecular ion (*m/z* 44) of oxiran and acetaldehyde, obtained by 70 eV electron impact ionization, have been applied.

RESULTS

The thermolyses of compounds (2) and (3) have been studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) technique[8] in the temperature range from 1 043 to 1 404 K.

In Figure 1 the f.i.m.s. spectra recorded after thermolysis of the monothiosulphite (2) (*M* 124) at 1 043, 1 253, and 1 404 K, respectively, are shown. Based on these spectra and by comparison (c.a.m.s. or DADI, *cf.* Experimental section) with authentic samples, the following products have been identified: ethylene (4) (*M* 28), formaldehyde (5) (*M* 30), keten (6) (*M* 42), acetaldehyde (7) (*M* 44), and thiiran (ethylene sulphide) (8) (*M* 60).

† The parent 1,2-oxathietan has been studied theoretically by semi-empirical CNDO methods (J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, 1977, 99, 2931).

In recent years several authors have reported on the gas-phase thermolysis of thiiran 1-oxide.[13,14] It was concluded that the main reaction was the extrusion of sulphur monoxide, affording ethylene in high yield. Additionally, Saito[14] reported the formation of minor amounts of C_2H_4S,

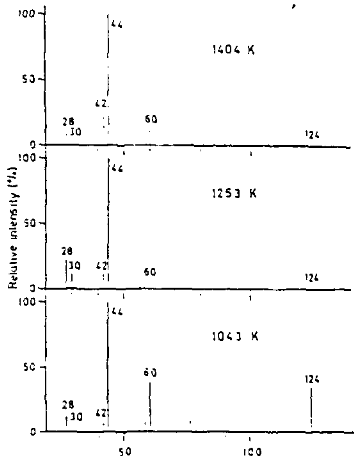


FIGURE 1 Field ionization mass spectra after gas-phase thermolysis of 1,2,3-oxadithiolan 2-oxide at 1 043, 1 253, and 1 404 K

C_2H_4O, and formaldehyde. It should, however, be emphasized that the thermolyses were carried out under conditions where bimolecular reactions certainly could not be excluded. The thermolysis of (3) under pure unimolecular conditions results, nevertheless, in a product composition qualitatively quite *similar* to that reported by Saito.[14]

Scrutiny of the spectra depicted in Figures 1 and 2 reveals the presence of a peak at *m/z* 76. In the case of (3) the peak was *a priori* assigned to undecomposed sulphoxide. However, careful c.a.m.s. analyses disclosed that in both the case of (2) and (3) the correct assignment of *m/z* 76 was carbon disulphide. The appearance of CS_2 among the reaction products seems rather obscure, but the authors are convinced that catalytic effects on the hot surface in the reactor play an important role.*

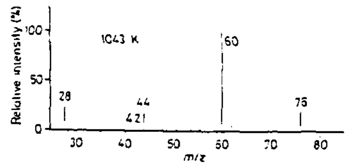


FIGURE 2 Field ionization mass spectrum after gas-phase thermolysis of thiiran 1-oxide at 1 043 K

In addition, it should be emphasized that c.a.m.s. analyses of the *m/z* 76 peak following thermolyses of (3) at temperatures between 631 and 1 043 K showed, besides an increasing amount of carbon disulphide, only unchanged (3). No signals corresponding to a contribution of other possible C_2H_4OS *isomers, e.g.* the sulphenate (1), to the peak *m/z* 76 were observed.

DISCUSSION

The above reported product formation is discussed in terms of sulphoxide–sulphenate rearrangement, atomic oxygen extrusion, and sulphur mono- or di-oxide elimination. The latter reaction, however, cannot be distinguished from an atomic oxygen extrusion consecutively accompanied by a rapid sulphur monoxide elimination, as the f.i.m.s. technique does not enable us to verify the possible existence of small in organic fragments such as O, S, and SO † among the reaction products.[8]

The presence of an atomic oxygen extrusion reaction is obvious in the case of thiiran 1-oxide (3), resulting in the

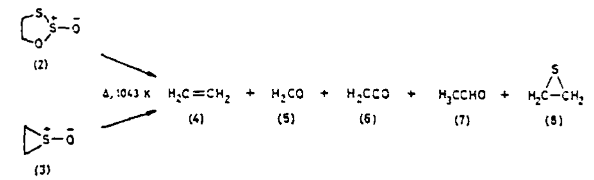


Figure 2 shows the product composition obtained after thermolysis of (3) at 1 043 K. The products are shown to be identical to those generated by thermolysis of (2).*

formation of a considerable amount of thiiran (8) (*M* 60) (*cf.* Figure 2). We have previously reported extrusions of atomic oxygen from organic *S*-oxides;[2,4,15] however,

* It should be noted that the C_2H_4O isomer (*M* 44), unequivocally established by the DADI technique to be acetaldehyde, was reported by Saito[14] as ethylene oxide. However, the present study revealed no evidence for the presence of ethylene oxide among the products.

† Tentatively it is suggested that sulphur monoxide is involved, since we have not been able to detect SO obviously eliminated at least from (3), by normal 70 eV electron impact mass spectrometry.

rupture of the semipolar S–O bond apparently requires *ca.* 90 kcal mol^{-1},[16] which may suggest that surface catalytic effects are operating by this reaction. Evidence for an analogous reaction in the case of (2), which apparently would result in formation of 1,2,3-oxadithiolan, is not obtained, since no signal corresponding to the latter (*M* 108) was detected. Thus, we conclude that, if formed, the 1,2,3-oxadithiolan exhibits a half-life < *ca.* 1 ms under the actual conditions used.[8] However, a rapid series of consecutive reactions, the primary one being a sulphur extrusion from 1,2,3-oxadithiolan, cannot be excluded.

Apart from the ethylene formation from (3), by SO extrusion, (4) may additionally originate from ethylene sulphide (8). Thermolysis of (8) at 1 043 K revealed nearly quantitative ethylene formation which led us to suggest that formation of the latter by thermolysis of (2) most probably appears as a secondary product originating from primarily generated thiiran (8), the latter being a result of sulphur dioxide elimination from (2).

We shall now turn to a discussion of the formation of keten and acetaldehyde. It has previously been reported that sulphoxides that do not possess β-hydrogens can be rearranged thermally into the corresponding sulphenate, the latter consecutively fragmenting into a thiol and a carbonyl compound.[3,17] In the case of (3) a sulphoxide–sulphenate rearrangement evidently would result in the formation of the unknown 1,2-oxathietan (1). On the other hand, a cheletropic elimination of sulphur monoxide from the monothiosulphite (2) analogously would lead to (1).

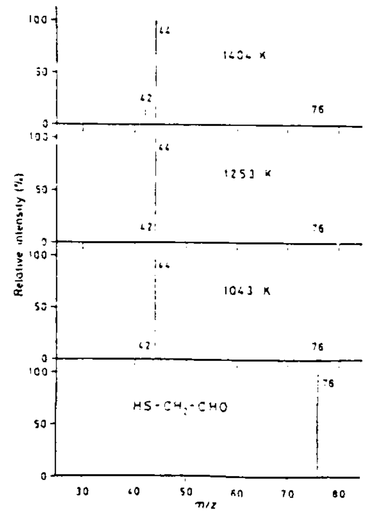


FIGURE 3 Field ionization mass spectra of mercaptoacetaldehyde before thermolysis and after gas-phase thermolysis at 1 043, 1 253, and 1 404 K

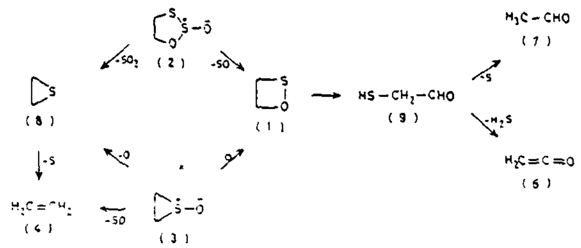
As mentioned above, we have not been able to detect any product with molecular weight *M* 76 corresponding to C_2H_4OS, other than thiiran 1-oxide (1). It is, however, obvious that (1) formed under the present reaction conditions will be generated in a vibrational excited state. Analogous to 1,2-oxathiolan[2,3] it is highly likely that the vibrational relaxation of (1) will lead to a quantitative degradation of the latter. This indicates that, if formed, (1) exhibits a half-life < *ca.* 10^{-3} s under the actual reaction conditions.[8]

Formation of keten (6) and acetaldehyde (7) by rearrangements and/or fragmentations directly from both (2) and (3) can be explained only in terms of highly speculative mechanisms, whereas a straightforward rationalization is possible assuming the common intermediacy of 1,2-oxathietan (1).

Drawing a parallel to the previously reported thermal decomposition of 1,2-oxathiolan[2,3] the first step on the decomposition path for (1) is suggested to be a ring opening to mercaptoacetaldehyde (9), consequently followed by loss of sulphur and hydrogen sulphide to give acetaldehyde and keten, respectively. It has been reported that mercaptoacetaldehyde (9) is generated by cracking the corresponding dimer 2,5-dihydroxy-1,4-dithian.[18] Smooth cracking of the latter *in vacuo* followed by flash vacuum thermolysis of the generated (9) indeed affords a mixture of (6) and (7) (Figure 3), the (6) : (7) intensity ratio being qualitatively in accord with those observed following thermolysis of (2) and (3), respectively.

With this background we rationalize the unimolecular gas-phase thermolyses of (2) and (3) as visualized in the Scheme, taking the above results into account for the intermediacy of (1). Although cumulative evidence for the intermediacy of (1) in the gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide is high a direct experimental verification under such conditions does not seem feasible.

Finally the appearance of formaldehyde (5) shall be discussed. The unimolecular decomposition of 1,2-dioxetans affords the formation of two carbonyl compounds,[19] in general as the only products. By analogy to this it might have been expected that 1,2-oxathietan would lead to formaldehyde and thioformaldehyde, at least to a reasonable extent. However, only very minor amounts of formaldehyde are detected, and it is believed that thioformaldehyde formed in equimolar amounts may well have escaped detection owing to a lower sensitivity of the latter relative to formaldehyde. It is generally assumed that the first step in the case of decomposition of 1,2-dioxetans is a homolytic cleavage of the O–O bond. The driving force in the consecutive cleavage of the carbon–carbon bond to form the two carbonyl compounds may well be the high energy gain by generation of the carbon–oxygen double bonds. In



SCHEME

the case of (1) a similar decomposition pathway would be accompanied by a smaller energy gain. In addition, the rearrangement may be strongly facilitated in the monosulphur case, leading to (9), due to steric effects, the size of the sulphur atom apparently minimizing the strain in the transition state.

[1/865 *Received, 29th May* 1981]

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APPENDIX 14.

GAS-PHASE THERMOLYSIS OF METHYL AND ETHYL MONOTHIOACETATES

LARS CARLSEN AND HELGE EGSGAARD

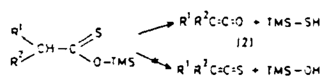
J.CHEM.SOC. PERKIN TRANS. 2 (1982) 1081-1085

Gas-phase Thermolyses. Part 8.[1] Gas-phase Thermolysis of Methyl and Ethyl Monothioacetates [2]

By Lars Carlsen * and Helge Egsgaard, Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

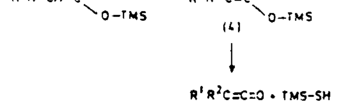
The unimolecular gas-phase thermolyses of the four methyl and ethyl monothioacetates (5)—(8) have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range 883—1 404 K. The types of reactions verified were keten formation, thiono–thiolo rearrangement, and, in the case of the *ethyl esters, ethylene elimination*. *The possible mechanisms for keten formation are discussed*, and it is concluded that the thiono-carboxylates eliminates the mercaptan *via* an enethiolized structure, whereas the decomposition of the thiolo-esters apparently proceeds *via* direct 1,2-elimination of the thiols.

RECENTLY, we investigated the unimolecular gas phase thermolytic decomposition of a series of trimethylsilyl thionocarboxylates (1) in an attempt to study the possible application to thioketen synthesis.[3] However, the conclusion was rather surprising, as we found the major products to be the corresponding ketens (2), whereas only very minor amounts of the thioketens (3) were generated. A possible explanation of this reaction,



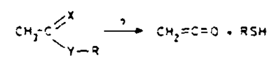
(1) (2) (3)

involving a primary rearrangement to the corresponding thiolo-ester, followed by an immediate and quantitative rethermolysis, was ruled out, partly based on an estimate of the thermodynamics of the former reaction. Assuming $\Delta H_r \approx \Delta G_r \approx -62$ kJ mol^{-1} (*i.e.* $\Delta S_r \approx 0$)[4] for the thiolo-thiono rearrangement, the equilibrium constant for the thiono–thiolo system can, according to the van't Hoff equation, be calculated to be $\log_e K(293\ K) \approx 25$ and $\log_e K(1\ 043\ K) \approx 7$, respectively, *i.e.* even at very elevated temperatures the thiono-esters *will be the thermodynamically more favourable isomers*. On this background we concluded that the ketens most probably were generated directly from the thionocarboxylates. The mechanism was tentatively formulated to involve an enethiolized intermediary structure (4).



(4)

Although the gas-phase thermolyses of some thiono- and thiolo-esters have been reported previously,[5,6] we here report, initiated by the above study, on the pure unimolecular gas-phase thermolyses of the simple methyl and ethyl monothioacetates (5)—(8) focusing on possible keten formation



	R	X	Y
(5)	CH_3	S	O
(6)	CH_3	O	S
(7)	C_2H_5	S	O
(8)	C_2H_5	O	S

EXPERIMENTAL

The esters (6) and (8) were synthesized by alkylation of thioacetic acid by methyl and ethyl iodide, respectively. Compound (6) had b.p. 97—98 °C (lit.,[7] 98 °C) and (8) b.p. 115—116 °C (lit.,[7] 116.4 °C). Compounds (5)[8] and (7)[9] were synthesized according to previously described methods.

Flash Vacuum Thermolysis.—The thermolyses were carried out using the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) technique, which has been described in detail previously.[10] The method is based on a direct combination of a thermolysis unit fulfilling the requirements for a Knudsen reactor, with a Varian MAT CH 5D double focusing mass spectrometer equipped with a combined electron impact ionization-field ionization–field desorption (e.i.–f.i.–f.d.) ion source. The f.i. spectra after thermolysis were recorded with a scan rate of 30—100 a.u. s^{-1} (signal-to-noise >1 000).

Collision activation mass spectra[11] were obtained by introducing helium as the collision gas *via* a needle valve into the second field-free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focused on the ion beam just behind the intermediate focus slit. The c.a. spectra of the single ions were obtained by scanning the electrostatic field.

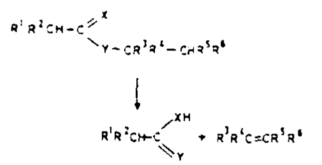
The c.a.m.s. analyses of the thermolysate mixtures are generally carried out on the single field ionized molecules.[10] However, the compound exhibiting the highest molecular weight in the reaction mixture, *i.e.* in the present case the *undecomposed esters, may advantageously be analysed by* c.a.m.s. of the molecular ion in the electron impact induced mass spectrum, as this ion evidently is not a result of e.i. induced fragmentation. The sensitivity of the c.a.m.s. analysis is hereby enhanced strongly. The c.a.m.s. spectra of the single ions are recorded within 5 s [signal-to-noise *ca.* 50 (f.i.-c.a.m.s.), >1 000 (e.i.-c.a.m.s.)]

The relative e.i.-c.a.m.s. and f.i. sensitivities of the single compounds available were determined using the gas inlet system of the mass spectrometer. The relative ester f.i. sensitivities were found to be thiono/thiolo 1.7; the sensitivity of ethylene was calculated to be 0.07 relative to ethyl thionoacetate. Additionally, it should be mentioned that the thiono- and thiolo-esters exhibit equal e.i.-c.a.m.s. sensitivities.

In the present work the thermolysis unit was slightly modified compared to the original version[10] as the injection block was substituted by a 100 ml glass bulb connected to the reactor *via* a glass capillary leak, the leak rate being equal to *ca.* 5×10^{-3} Torr l s^{-1}. Samples of *ca.* 10 µl of the single esters were introduced into the evacuated bulb. This set-up is advantageous for recording c.a. spectra, as it allows a continuous flow of thermolysis products into the ion source; it is, however, only suitable for compounds with rather high vapour pressures.

RESULTS AND DISCUSSION

During the past decades the gas-phase thermolyses of alkyl carboxylates, as well as the corresponding monothio derivatives, have been studied intensively.[5,6,12] However, the investigations have almost exclusively been limited to compounds possessing a β-hydrogen atom in the ester alkyl group in order to elucidate the elimination of alkenes from these esters to yield the corresponding acids (Scheme 1). In contrast to this, methyl esters



SCHEME 1

have only been studied rarely,[5,13,14] apparently due to their lack of ability to undergo a similar reaction. In no cases thermolyses under pure molecular conditions have been reported. From a very recent study on the unimolecular gas-phase thermolysis of methyl acetate in the temperature range 1 043—1 404 K we concluded that the predominant reaction is an oxygen-oxygen methyl group migration accompanied by very minor amounts of keten formation only.[15]

Thermolysing (5) and (6) at 1 043 K resulted in the development of nearly identical spectra (Figure 1). In both cases the major products are keten (9) (*M* 42) and methanethiol (10) (*M* 48). The low intensity peak at *m/z* 58, which *a priori* could be explained as a minor amount of thioketen, was, upon high resolution, surprisingly found to be a C_3H_6O isomer, the unimolecular formation of this compound, however, at the present being unclear.*

It is observed (Figure 1) that considerable amounts of the esters (*M* 90) are recovered. In this connection it should be noted that Figure 1 is only a representation of the relative product distributions following thermolyses

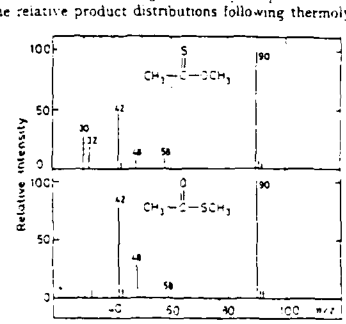
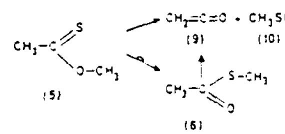


FIGURE 1 Field ionization mass spectra of methyl thionoacetate and methyl thioloacetate following thermolysis at 1 043 K

of the respective esters, whereas a mutual comparison of the individual yields is not possible.[10]

It has been reported previously that thiono-esters may be rearranged thermally into the corresponding thermodynamically more favourable thiolo-compounds.[5,6,16] On this background, in combination with the above-mentioned product distribution, it is conceivable that besides direct keten formation from the single esters, one should, in the case of (5), take a reaction involving primary thiono-thiolo rearrangement followed by methanethiol elimination from (6) into account (*cf.* Scheme 2). Hence, it is obvious that a detailed examination of the peak with *m/z* 90 (*cf.* Figure 1) corresponding to the so-called unreacted ester is appropriate. For this purpose we studied the c.a. spectra of the peak with *m/z* 90 after thermolysis of the two esters.



SCHEME 2

In Figures 2a and e the c.a. spectra of the molecular ion (*m/z* 90) of unthermolysed (5) and (6) are shown, respectively. Additionally, the c.a. spectra of the peak with *m/z* 90 after thermolysis of (5) at 883, 1 043, and 1 404 K are depicted in Figures 2b, c, and d, respectively. By elevating the thermolysis temperature a progressive relative increase in the intensity of the peak of *m/z*

* A possible candidate is acetone; however, owing to the very minor amounts of C_3H_6O formed, we were unable to obtain satisfactory c.a. spectra to elucidate the actual structure (*cf.* ref. 11*b*).

43.* corresponding to a thermally induced intramolecular thiono–thiolo [(5) ⟶ (6)] rearrangement, is seen. The (5) : (6) ratios are, based on the spectra depicted in Figure 2, calculated to be 0, 1.0, and <0.05 following thermolysis at 1 043, 1 253 (not shown), and 1 404 K, respectively. The reverse reaction, *i.e.* a possible (6) ⟶ (5) rearrangement, is not observed, in agreement with the much higher energy of activation for the latter reaction, due to the thermodynamic stabilization of (6) by *ca.* 80 kJ mol^{-1} relative to (5).[3]

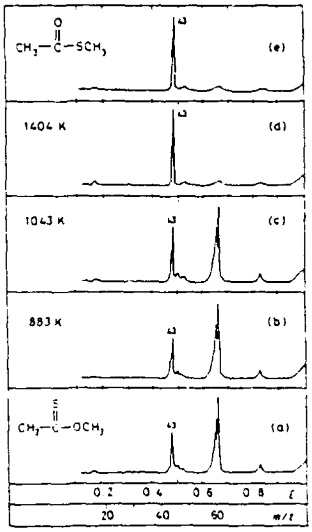


FIGURE 2 Collision activation mass spectra of the electron impact-induced molecular ions of methyl thionoacetate without thermolysis (a), following thermolysis at 883 K (b), 1 043 K (c), and 1 404 K (d), respectively, and unthermolysed methyl thioloacetate (e)

To elucidate the relative importance of the possible mechanistic pathways for keten formation outlined above, the keten : methyl thioloacetate ratio [(9) : (6)] seems to be crucial. Taking the above calculated (5) : (6) ratio as well as the relative thiono–thiolo f.i. sensitivities (1.7, see Experimental section) into account, the (9) : (6) ratios after thermolysis of (5) and (6) at 1 043 K were calculated to be 8.8 and 0.8, respectively (*cf.* Figure 1). Thus, by thermolysis of (5) no more than *ca.* 10% of the keten formed can be generated *via* a pathway involving primary rearrangement into (6) followed by quantitative rethermolysis of the latter. However, in general the f.v.t. method used only causes very low degrees of rethermolyses, owing to the very short contact times applied (*ca.* 300 μs).[10] On this background we conclude that the major fraction of the keten formed originates directly from the single esters (5) and (6), respectively. Finally, it should be mentioned that the absolute yield of keten is *ca.* 1.5 times higher after thermolysis of (6) than of (5) at 1043 K.

In Figure 3 the f.i. spectra recorded after thermolysis of the ethyl monothioacetates (7) and (8) at 1 404 K are shown. It is immediately seen that the ethyl case, not unexpectedly, is much more complicated than the above methyl case.

Four thermally generated fragments dominate the picture. These are ethylene (11) (*M* 28), keten (9) (*M* 42), acetaldehyde (12) (*M* 44), and ethanethiol (13) (*M* 62). In addition considerable amounts of so-called unreacted ester (*M* 104) are observed. As in the methyl case the low intensity peaks at *m/z* 58 were identified as 'C_3H_6O'. In the following we shall first turn to a discussion of the actual composition of the ester peak at *m/z* 104 based on a c.a.m.s. analysis.

The c.a.m.s. spectra of unthermolysed (7) and (8) are depicted in Figures 4a and e, respectively. In Figures 4b—d the c.a. spectra of (7) after thermolysis at 883, 1 043, and 1 404 K, respectively, are shown. Similar to the methyl ester case a smooth progressive conversion from the pure unthermolysed thiono-ester (Figure 4a) to the corresponding thiolo-ester (Figure 4e) as a function of temperature is observed. Based on these spectra we calculate that following the thermolysis at 1 404 K > 95% of the so-called unreacted ethyl thionoacetate (7) has rearranged into the thermodynamically more stable thiolo-ester (8), *i.e.* the peak at *m/z* 104 in Figure 3a reflects the rearranged ester (8) and not unreacted (7). On the other hand the *m/z* 104 peak in Figure 3b truly

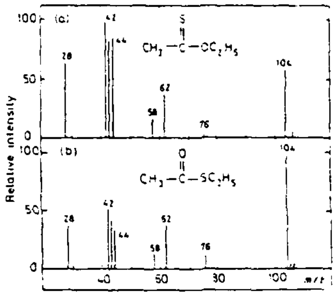


FIGURE 3 Field-ionization mass spectra of ethyl thionoacetate and ethyl thioloacetate following thermolysis at 1 404 K

* The presence of an *m/z* 43 ion ($CH_3C≡O^+$) in the c.a. spectra of thionoacetates reflects the thiono–thiolo isomerization in the ionized state (A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Org. Mass Spectrom.*, 1970, 3, 261)

reflects unreacted (8), as no thiolo–thiono rearrangement has been observed in the temperature range studied.

As mentioned above the thermolysis products obtained from the ethyl monothioacetates include ethylene (11) (*m/z* 28) and acetaldehyde (12) (*m/z* 44) (*cf.* Figure

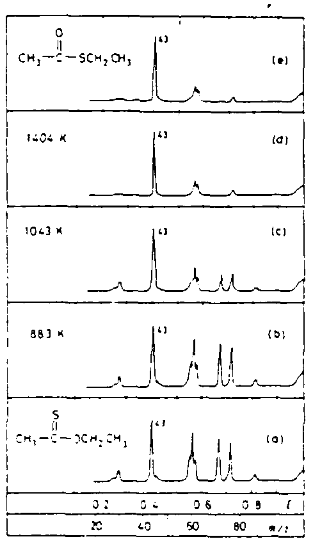


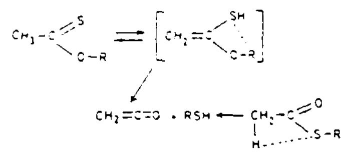
FIGURE 4 Collision activation mass spectra of the electron impact induced molecular ions of ethyl thionoacetate without thermolysis (a), following thermolysis at 883 K (b), 1 043 K (c), and 1 404 K (d), respectively, and unthermolysed ethyl thioloacetate (e)

3). Both products are likewise found after thermolysis of ethyl acetate. The ethylene formation is explained by the previously mentioned arrangement (*cf.* Scheme 1). The acetaldehyde is tentatively suggested to originate exclusively from the ester alkoxy moiety, partly based on analogy to ethyl acetate [17] and partly due to the fact that no acetaldehyde is observed after thermolysis of the corresponding methyl esters (see above).

Finally the keten–ethanethiol formation is discussed. In contrast to keten–methanethiol formation following thermolysis of (5) and (6), the possible elucidation of the formation of (9) and (13) following thermolysis of (7) and (8) is somewhat complicated, owing to the concurrent formation of monothioacetic acid (14) (*cf.* Scheme 1), since a possible rethermolysis of the latter will lead to an additional keten formation.* However studying the ratios between the absolute yields of keten (9), ethylene (11), and ethanethiol (13) following thermolysis of (7) and (8), respectively, at 1 404 K, gives valuable information. These ratios were calculated, based on the mass spectra, to be keten *ca.* 5, ethylene *ca.* 4—5, and ethanethiol *ca.* 2·5, respectively. The value for ethylene formation is in close agreement with previously reported data by Bigley [5] and Louw [6] showing the higher decomposition rate for the thiono-ester. The crucial figure, however, is the value for ethanethiol formation, of necessity following keten formation, which unambiguously demonstrates that 2·5 times more keten–ethanethiol are generated from (7) than from (8), excluding a rethermolysis of primarily generated (8) as responsible for the major part of keten–ethanethiol detected following thermolysis of (7).

On the above background we are forced to consider a mechanism for keten formation by unimolecular gas-phase thermolysis of thionoacetates which does not involve a primary rearrangement to the thermodynamically more stable thioloacetates although the existence of the latter reaction has been demonstrated unequivocally. The only reasonable alternative appears to be the assumption of a primary 1,3 carbon to sulphur hydrogen migration, followed by elimination of the mercaptan. However, it is emphasized that we are unable to conclude whether the enethiolized structure can be regarded as an intermediate in the reaction or simply as a transition state.

The keten–mercaptan formation from the thiolo-esters, on the other hand, most probably takes place by



direct 1,2 elimination since no evidence has been obtained for a primary enolization, which similarly has been ruled out in the cases of methyl and ethyl acetate by ^{18}O labelling experiments.[15,17]

[1 1895 *Received, 7th December*, 1981]

* Flash vacuum thermolysis of (14) has been shown to lead to considerable amounts of keten [18] apart from the previously described COS and methane.[9]

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APPENDIX 15.

UNIMOLECULAR GAS-PHASE THERMOLYSIS OF ETHYL ACETATE

HELGE EGSGAARD AND LARS CARLSEN

INT.J.MASS SPECTROM. ION PHYS. 47 (1983) 55-58

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UNIMOLECULAR GAS-PHASE THERMOLYSIS OF ETHYL ACETATE*

HELGE EGSGAARD and LARS CARLSEN

Chemistry Department, Riso National Laboratory, DK-4000 Roskilde (Denmark)

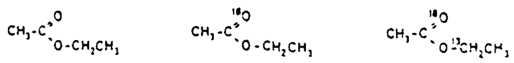
ABSTRACT

The unimolecular gas-phase thermolysis of ethyl acetate has been investigated by the Flash-Vacuum-Thermolysis/Field-Ionization Mass Spectrometry (FVT/FI-MS) method in combination with Collision Activation (CA) mass spectrometry at 1253K. Two predominant reactions are observed: elimination of ethylene affording acetic acid, the latter to some extent consecutively yielding ketene, and intramolecular oxygen to oxygen ethyl group migration. Additionally minor amounts of acetaldehyde is formed. The mechanistic aspects are discussed based on ^{18}O and ^{18}O/^{13}C labelling.

INTRODUCTION

In the past decades several groups have studied the fate of carboxylic acid esters under gas-phase thermolytic conditions (ref.1). Especially esters possessing a β-hydrogen in the ester alkyl moiety have been studied extensively, owing to the ability to eliminate alkene yielding the corresponding carboxylic acid. A variety of reports on the gas-phase thermolysis of ethyl acetate, focusing on the formation of ethylene and acetic acid, have appeared (ref.2). However, no detailed study on the mechanisms, possibly involved, based on extensive isotopic labelling, has been reported.

The present paper reports on the mechanistic aspects of the thermal decomposition of ethyl acetate (1a) in the gas-phase, based on ^{18}O and ^{18}O/^{13}C labelling.



1a 1b 1c

The thermolyses were carried out using the Flash-Vacuum-Thermolysis/Field-Ionization Mass Spectrometry (FVT/FI-MS) technique, which has been described in detail previously (ref.3-5). To eliminate possible surface catalytic effects all thermolyses were carried out using gold-plated filaments (ref.6).

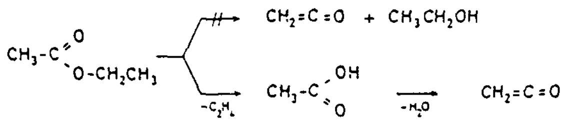
RESULTS AND DISCUSSION

Gas-phase thermolysis of ethyl acetate (1a) at 1253K afforded formation of

*Gas-Phase Thermolyses part 9; for part 8: see L. Carlsen and H. Egsgaard, J. Chem.Soc. Perkin Trans. 2, (1982) 0000 ethylene (M 28), ketene (M 42), acetaldehyde (M 44), ethanol (M 46), and acetic acid (M 60)[§] (Fig.1a). *Significant changes are observed by introduction of* ^{18}O *in the* carbonyl group (1b), as the following products are observed: ethylene (M 28), ketene (M 42), ketene-^{18}O/acetaldehyde (M 44), ethanol (M 46), and acetic acid-^{18}O (M 62) (Fig.1b). Additional isotopic labelling with ^{13}C in the ester group (1c) affords further characteristic changes in the product composition: ethylene-^{13}C (M 29), ketene (M 42), ketene-^{18}O (M 44), acetaldehyde-^{13}C (M 45), ethanol-^{13}C (M 47), and acetic acid-^{18}O (M 62) (Fig.1c).

Based on these results *the following conclusions can be drawn* concerning the formation of acetaldehyde and ketene: The formation of acetaldehyde is exclusively associated with the ethoxy group in ethyl acetate, since only acetaldehyde-^{13}C (M 45) and no acetaldehyde-^{18}O/^{13}C (M 47) was observed *after thermolysis of* 1c (Fig.1c). In addition thermolysis of ethyl-D_5 acetate resulted in the formation of acetaldehyde-D_4 only. A mechanism involving a homolytic cleavage of the C-O bond, leading to acetyl- and ethoxy radicals, the latter consecutively decomposing into $H^{\cdot}$ and acetaldehyde seems not to be operating, as ethoxy radicals are known to decompose unimolecularly to methyl radicals and formaldehyde; only very minor amounts of acetaldehyde could be detected (ref.7). Furthermore, the homolytic C-O bond cleavage *would require ca.* 83-90 kcal/mol (ref.8), which most probably is not achievable by the method here applied. A more reasonable explanation appears to be elimination of acetaldehyde *via* a five-centered transition state, involving an α-hydrogen in the ethoxy group, leaving CH_3COH, which is suggested to decompose consecutively into methane and carbon monoxide.

Ketene may *a priori* be generated by two possible pathways: a) directly from the ester by ethanol elimination, or b) consecutively from primary formed acetic acid. *Taken the* FI-sensitivity of ethanol into account, it can be estimated that the latter is formed in very minor amounts only, *i.e.* a predominant ketene formation directly from ethyl acetate can be excluded, in agreement with the reported thermal stability *of methyl acetate towards ketene/methanol formation* (ref.3). Consequently ketene is generated consecutively from acetic acid by water elimination.



An interesting feature of the ketene formation is the apparent involvment of the carbonyl- as well as the ether oxygen in ethyl acetate, the two ketenes ap-

§Due to differences in FI-sensitivities the relative intensities of the single peaks cannot be taken as a measure of chemical yields.

parently being formed in identical yields, as demonstrated by ^{13}C labelling (*cf.* Fig.'s 1b,1c).[x] However, since the water elimination from acetic acid involves the OH group only, *i.e.* the ketene retains exclusively the carbonyl oxygen, the acetic acid of necessity has to be completly isomerized in order to explain the results visualized in Fig.1.

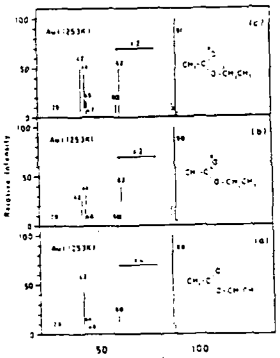


Figure 1. Field-ionization mass spectra of the ethyl acetates 1a, 1b, and 1c following thermolysis at 1253K

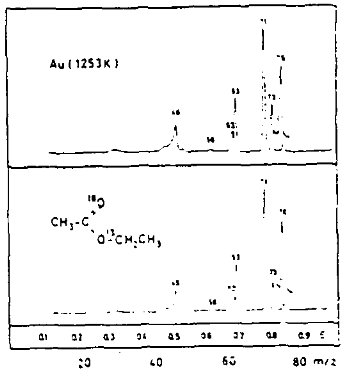


Figure 2. Collision activation mass spectra of the electron impact induced molecular ion of ethyl acetate 1c without thermolysis and following thermolysis at 1253K

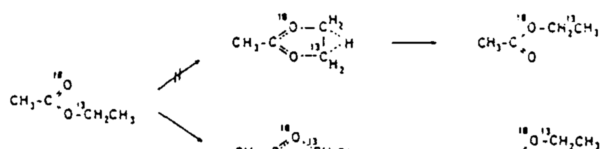
The existence of the isomeric mixture of acetic acid may either be a result of primary isomerization of the ester followed by ethylene elimination, or a consequence of an isomerization of the acetic acid itself. Fig.2 depicts the CA mass spectrum of the EI-induced molecular ion of 1c before and after thermolysis, unambiguously demonstrating the isomerization of the ester (*cf.* ref.5). The degree of isomerization, *Q*, is reflected in the *m/z* 73:71 ion intensity ratio, changing from 0.27 in the authentic sample to 0.42 after thermolysis, in agreement with previous results reported for 1b (ref.5). On this basis *Q* is estimated to be 0.17. Obviously, *Q* should be equal to 1.0 in order to explain formation of fully

[x]The relative intensities of *m/z* 42 and *m/z* 44 have to be corrected due to contributions from acetaldehyde (*m/z* 44) (Fig.1b) and the amounts of ketene (*m/z* 42) generated *via* unlabelled acetic acid (Fig.'s 1b,1c).

isomerized acetic acid by ethylene elimination. Furthermore, an equal *m/z* 42:44 ion intensity ratio is observed following thermolysis at 1043K, at which temperature no isomerization of the ester could be detected. Hence, we conclude that the isomerization takes place in the acetic acid state.

It should in this connection be noted that intramolecular isomerization of acetic acid appears to be rather energy demanding, the activation energy being calculated to be *ca.* 60 kcal/mol (ref.9).⁺ On the other hand, the activation energy for ethylene elimination is 48.0 kcal/mol (ref.2). Thus, an intramolecular isomerization of acetic acid, even taken into account that the latter is generated in a vibrationally excited state, will probably not occur. Analysis of the gas-phase thermolysis of ethyl-D_5 acetate, obviously resulting in the formation of acetic acid(OD), revealed only unlabelled acetic acid. Hence, we conclude that the apparent isomerization is a result of surface promoted hydrogen exchange.

Finally the ester isomerization reaction shall be discussed. In the case of methyl acetate (ref.3) it was demonstrated that isomerization takes place *via* a four-centered transition state. In the present case a five-centered transition state, involving a simultaneous hydrogen shift has *a priori* to be taken into account. However, Fig.2 unambiguously demonstrates that no scrambling of the carbon atoms in the ester group takes place upon thermolysis, since only *m/z* 76, corresponding to loss of $CH_3^{\cdot}$ is observed.



1c

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⁺Data available for methyl acetate (ref.3) suggest an activation energy for methyl group migration at *ca.* 62 kcal/mol.

APPENDIX 16.

THERMAL DECOMPOSITION OF 1,2-OXATHIOLANE IN THE GAS PHASE

LARS CARLSEN AND HELGE EGSGAARD

CHEM.BER. 117 (1984) 1393-1399

Chem. Ber. 117, 1393 – 1399 (1984)

Thermal Decomposition of 1,2-Oxathiolane in the Gas Phase [1]

*Lars Carlsen** and *Helge Egsgaard*

Chemistry Department, Risø National Laboratory,
DK-4000 Roskilde, Denmark

Received June 28, 1983

The cyclic sulfenic ester 1,2-oxathiolane (1) decomposes thermally (400 – 450 K) exclusively to give acrolein (3) via 3-mercaptopropanal (2) by loss of hydrogen sulfide. Isotopic labelling experiments reveal the presence of a 1,2-oxathiolane-thietane 1-oxide equilibrium (1 ⇌ 4).

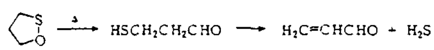
Thermischer Zerfall von 1,2-Oxathiolan in der Gasphase [1]

Der cyclische Sulfensaureester 1,2-Oxathiolan (1) zersetzt sich thermisch (400 – 450 K) über 3-Mercaptopropanal (2) unter Verlust von H_2S ausschließlich zu Acrolein (3). Experimente mit isotopenmarkierten Verbindungen weisen auf ein 1,2-Oxathiolan-Thietan-1-oxid-Gleichgewicht (1 ⇌ 4).

In recent papers we reported the decomposition of the simple five-membered cyclic sulfenate 1,2-oxathiolane (1) in the gas phase under flash vacuum pyrolytic (FVP) conditions [1a–3]. Acrolein (3) was found to be the major product [1a,2]; however, a significant amount of allyl alcohol was supplementary observed [2,3]. Formally, the products are formed by elimination of hydrogen sulfide and elemental sulfur, respectively. The present paper reports a study on the thermal decomposition of gaseous 1,2-oxathiolane [2] in a static system in the temperature range 400 – 450 K (p(1) = 0.1 Torr). The reactions were carried out in the thermostated gas-inlet system of a double focusing mass spectrometer, the progress of reactions being followed by field ionization (FI) and collision activation (CA) mass spectrometry [3,4,5].

Results and Discussion

Thermolysis of the sulfenate 1 (M = 90) in the temperature range 400 – 450 K afforded, in contrast to the FVP studies, formation of acrolein (3) (M = 56) as the exclusive product (Fig. 1a).



1 2 3

We have previously discussed the formation of 3 in terms of a primary rearrangement of 1 into 3-mercaptopropanal (2) (M = 90) [1a–3] as sulfenates have been reported to decompose into a carbonyl compound and a mercaptane [6], and since an identical decomposition pattern for 2 and 1 was observed [1,2]. Also under the present conditions identical thermal behaviour of 1 and 2 was seen, *i. e.* 2 decomposes exclusively to acrolein (3). Thus, following the thermal decomposition of 1 by means of collisional activation (CA) mass spectrometry of the molecular ion m/z = 90, the intermediacy of

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2 in the thermal decomposition of 1 was clearly demonstrated by the appearence of a new set of signals in the CA mass spectrum as a function of time (Fig. 2). In Fig. 2b and c the CA mass spectra of the ion $m/z = 90$, present in the mass spectrum obtained after 35 and 50 min thermolysis, respectively, of 1 at 450 K are shown. Comparison with the CA mass spectra of the molecular ions of authentic 1,2-oxathiolane[2] (Fig. 2a) and 3-mercaptopropanal[7] (Fig. 2d) unambiguously lead to the assignment of the spectra in Fig. 2b and c as superpositions of the spectra in Fig. 2a and 2d, hence, demonstrating the intermediacy of 2, the latter apparently being formed by intramolecular rearrangement of the sulfenate.

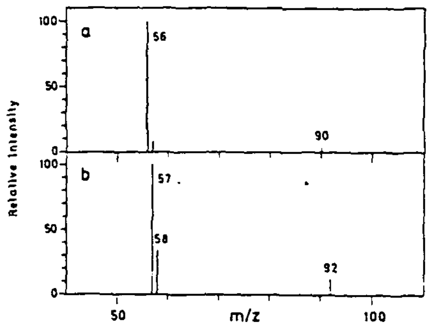
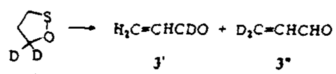


Fig. 1. Field Ionization Mass Spectra Obtained Following 25 min Thermolysis (425 K) of 1,2-Oxathiolane (1) (a) and [5,5-$^2H_2$]-1,2-Oxathiolane (1') (b)

No data on the strength of the S – O single bonds in sulfenic esters have been reported. However, it seems reasonable to assume that the 1 → 2 rearrangement involves a S – O bond cleavage followed by transfer of one of the hydrogen atoms in the 5-position to the sulfur atom, 3 being consecutively generated by a 1,2-elimination of hydrogen sulfide. To obtain experimental verification on the actual mechanism we studied the thermal decomposition of the [5,5-$^2H_2$]-1,2-oxathiolane (1'). Thermolysis of 1' (425 K) surprisingly gave rise to formation of two deuterium-labelled acroleins with molecular weights 57 and 58, corresponding to the presence of one and two deuterium atoms, respectively (Fig. 1b). The actual identity of the acroleins 3' and 3'' was established by CAMS. In Fig. 4 the CA mass spectra of the field ionized molecular ions of the acroleins 3 ($m/z = 56$), 3' ($m/z = 57$), and 3'' ($m/z = 58$), obtained by thermolysis of 1 and 1', respectively, are visualized. A predominant feature in the CA mass spectrum of 3 (Fig. 4c) appears to be the presence of an $[M - 1]^+$ ion, the hydrogen



1' 3' 3''

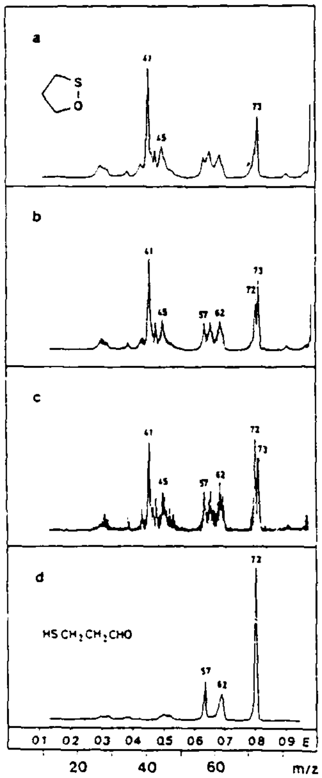


Fig. 2

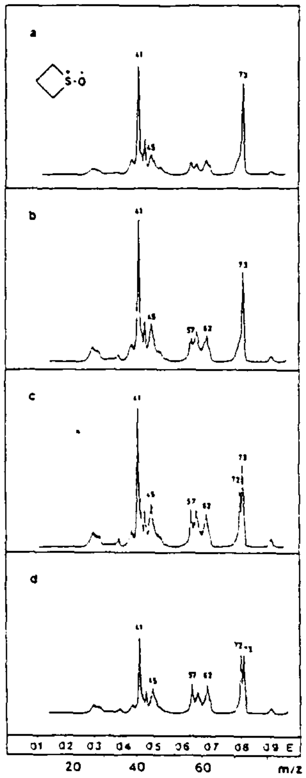


Fig. 3

Fig. 2 (left). Collision Activation Mass Spectra (CAMS) of the Electron Impact-Induced Molecular Ions of Authentic 1,2-Oxathiolane (1) (a) and 3-Mercaptopropanal (2) (d), and of the Ion m/z = 90 Obtained Following 35 (b) and 50 (c) min Thermolysis (450 K) of 1, respectively

Fig. 3 (right). Collision Activation Mass Spectra (CAMS) of the Electron Impact-Induced Molecular Ions of Authentic Thietane 1-Oxide (4) (a) and of the Ion m/z = 90 Obtained Following 4 (b), 40 (c), and 80 (d) min Thermolysis (450 K) of 4, respectively

being lost from the aldehyde group[9]. On this background the mono deuterium-labelled acrolein (3') (Fig. 4b) immediately can be identified as [1-^{2}H]acrolein, since an $[M - 2]^+$ ion was detected. By analogy, it is obvious that the double labelled species 3'' does not exhibit deuterium labelling in the aldehyde function. A detailed study on the CA fragmentations (Fig. 4, central sections) does not disclose the identity of 3'', as both the [3,3-$^2H_2$]- and the [2,3-$^2H_2$] derivatives would give rise to the spectrum depicted in Fig. 4a. However, formation of [2,3-$^2H_2$]acrolein has to be a result of primary formation of 3-mercapto-[2,3-$^2H_2$]propanal, which by H_2S/HDS loss would lead to a mixture of [2,3-$^2H_2$]- and [3-^{2}H]acrolein, the latter, however, unequivocally being ruled out, as the only mono-labelled acrolein found (cf. Fig. 4b) exhibits the labelling in the aldehyde function (*vide supra*). Hence, we conclude that 3'' has to be assigned to [3,3-$^2H_2$]acrolein.

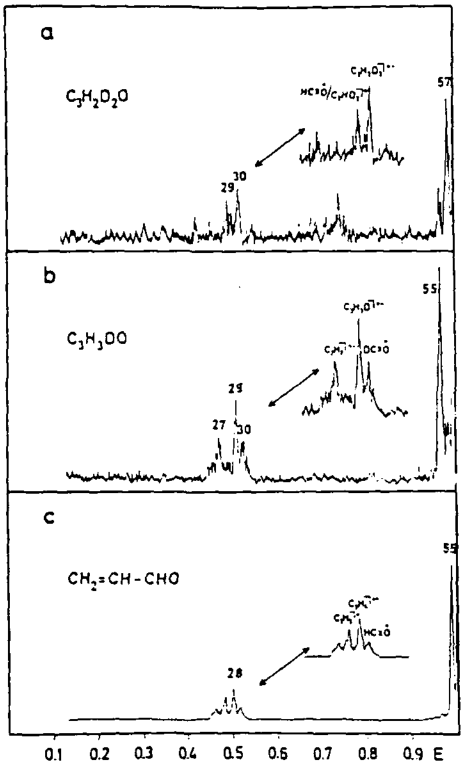


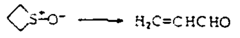
Fig. 4. Collision Activation Mass Spectra of the Field Ionized Molecular Ions of the Acroleins 3 (c), 3' (b), and 3'' (a) Obtained Following Thermolysis of 1 and 1', respectively

Obviously, the apparent formation of the acroleins 3' and 3'' from 1' is a result of primary formation of the labelled 3-mercaptopropanals 2' and 2'', consecutively eliminating HDS and H_2S, respectively.

$$\underset{2'}{DSCH_2CH_2CDO} \longrightarrow \underset{3'}{H_2C{=}CHCDO} + HDS$$

$$\underset{2''}{HSCD_2CH_2CHO} \longrightarrow \underset{3''}{D_2C{=}CHCHO} + H_2S$$

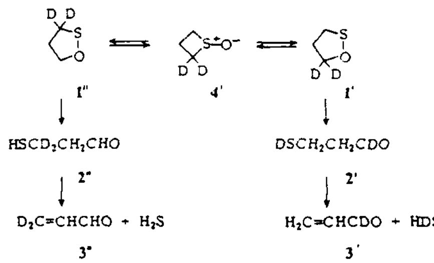
The formation of 3' is in complete accord with the above proposed mechanism. On the other hand, the presence of 3'' among the reaction products is, by analogy, easily explained by decomposition of [3,3-$^2H_2$]-1,2-oxathiolane (1''), *i. e.* apart from the 1' → 2' → 3' reaction, a 1' ⇄ 1'' isomerization has to be taken into account. It has been reported that sulfenates may rearrange into sulfoxides[9], and in previous papers[1a,10] we reported on the thermally induced rearrangements of sulfoxides into sulfenates. Hence, it seems reasonable to formulate the 1' ⇄ 1'' isomerization to proceed *via* the sulfoxide, [2,2-$^2H_2$]thietane 1-oxide (4'). Experimental verification was obtained by a study on the gas phase thermolysis of thietane 1-oxide (4) under conditions as described above. In Fig. 3 the CA mass spectra of m/z = 90 originating from 4 before thermolysis (a) and following thermolysis at 450 K for 4 (b), 40 (c), and 80 min (d), respectively, are depicted. Comparison of Fig. 3b and 2a strongly suggests the presence of considerable amounts of 1 in the reaction mixture responsible for the former spectrum, the significant ion being m/z = 45. Prolonged thermolysis (Fig. 3c and d) resulted in the characteristic change of m/z = 73 (loss of ·OH) to m/z = 72 (loss of H_2O), the latter being accompanied by an increase in the relative intensity of m/z = 57. Both these fragments appear to be characteristic for the mercapto aldehyde 2 (cf. Fig. 2d). The eventual product in the thermal decomposition of 4 was exclusively found to be acrolein.



4 → 3

On the present background we are able to rationalize the thermal decomposition of the sulfenate 1 as illustrated in Scheme 1 by the thermolysis of 1'.

Scheme 1



It should be noted that the here observed sulfenate-sulfoxide equilibrium to our knowledge is the first example of this type of reaction, which involves purely aliphatic species.

On the present knowledge no conclusions can be drawn on the actual pathway for the **1** → **2** rearrangement. However, we suggest that a 1,5-biradical is involved formed by homolytic cleavage of the S – O bond. Detailed studies, including kinetic measurements on this reaction, are left for separate investigations.

Experimental Part

3-(Phthalimidothio)-1-propanol and 3-(Phthalimidothio)-[1,1-²H₂]-1-propanol were synthesized according to *Davis* and *Whitham*[11].

3-Mercapto-[1,1-²H₂]-1-propanol: Under nitrogen 28 g (0.26 mol) of 3-mercaptopropanoic acid dissolved in 100 ml of dry THF was slowly added (ca. 2 h) to a slurry of 8.4 g (0.20 mol) of $LiAlD_4$ in 200 ml of dry THF. The resulting mixture was refluxed for 2 h. After cooling to 0°C D_2O (40 ml) was cautiously added (ca. 1 drop/5 s) to deactivate the complex. After completion of the deactivation the reaction mixture was filtered and the precipitate washed with 3 × 50 ml of THF. The combined THF-phase was dried (Na_2SO_4) and evaporated. The crude product (11.9 g) was purified by distillation: b.p. 86 – 87°C/14 Torr (lit.[12] 87°C at 14 mmHg), yield 5.7 g (23%).

A substantial amount of the corresponding 3-mercaptopropanal oligomer was obtained as by-product, owing to the rapid oligomerization of intermediary 3-mercaptopropanal in the reduction (cf. ref.[13]).

The *1,2-oxathiolanes* **1**, **1'** *were prepared in the gas phase* by smooth cracking (*in vacuo*) at about 80 – 100°C of the corresponding phthalimidothiopropanols. The gaseous sulfenates were collected directly in the thermostated gas-inlet system (2000 ml, $p = 10^{-1}$ Torr, T 400 – 450 K) of the mass spectrometer, which acted as reaction vessel in the thermolysis experiments.

Authentic *3-mercaptopropanal* (**2**) was prepared by smooth cracking *in vacuo* (≈ 100°C) of the corresponding oligomer, which was synthesized as described previously by *Schnobel* et al[13] (cf. also ref.[7]).

Mass Spectrometry: Varian MAT CH 5 D double focusing mass spectrometer with combined EI/FI/FD ion source. FI-spectra: 10 μm tungsten wire, activated in benzonitrile vapour, as emitter. In the MS/MS analyses the primary ions were selected at a resolution of ca. 500 and collisionally activated in the second field free region by means of a molecular He-gas beam. The CA mass spectra are obtained under identical conditions (*i. e.* energy resolution, collision gas pressure) and are uncorrected for contributions of unimolecular fragmentation processes. The application of FI and CA mass spectrometry as analytical procedure for gas phase reactions has been described in detail previously[3,4].

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[218/83]

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APPENDIX 17.

GAS-PHASE PYROLYSIS OF METHYL DITHIOACETATE. THE ABSENCE OF A 1,3-METHYL GROUP MIGRATION

LARS CARLSEN AND HELGE EGSGAARD

J.CHEM.RES. (s) (1984) 340-341

340 J. CHEM RESEARCH (S), 1984

Gas-phase Pyrolysis of Methyl Dithioacetate. The Absence of a 1,3-Methyl Group Migration[1]†

J. Chem. Research, 1984, 340–341

LARS CARLSEN* and HELGE EGSGAARD

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

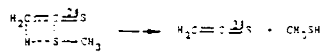
We have studied the flash vacuum pyrolysis of methyl dithioacetate (1) by application of the gas-phase Curie-point pyrolysis technique, with mechanistic information being obtained by use of specific sulphur-34 labelling; application of a D_2O-saturated pyrolysis system revealed evidence for the intermediacy of an enethiolized tautomer of (1).

In recent papers we reported on the unimolecular 1,3-oxygen-to-oxygen methyl group migration in methyl acetate,[2] as well as the thioxo-to-thiolo rearrangement of methyl thioxoacetate[3] under flash-vacuum-pyrolytic conditions. In contrast to carboxylic esters, reports on gas-phase pyrolyses of the corresponding dithio analogues are rather limited, and only esters possessing a β-hydrogen in the ester alkyl function have been considered,[4] owing to their ability to eliminate alkene. In order to study the unimolecular ester pyrolysis we studied the flash vacuum pyrolysis of methyl dithioacetate, possibly to elucidate an expected 1,3-sulphur-to-sulphur methyl group migration.

It has been reported that methyl dithioacetate (1), in the absence of surface-catalytic reactions, upon gas-phase pyrolysis apparently gives rise to the thioketene (2) and methanethiol (3) only.[5] However, owing to the equality of the two hetero-atoms in (1), we were unable to elucidate the possible simultaneous operation of a 1,3-sulphur-to-sulphur methyl group migration. In order to obtain mechanistic insight, sulphur-34 labelling of the thiocarbonyl group of (1) was carried out.

Results and Discussion

The mass-spectrometric analysis of the product composition following pyrolysis of ^{34}S-labelled (1) ($T \leq 1253$ K) revealed that the isotopic pattern in the resulting thioketene mimicked that in the starting material, whereas the corresponding methanethiol exhibited only the natural abundance of ^{34}S (Figure 1). Hence, we conclude that the exclusive formation of (2) is a result of a 1,2-elimination of (3).



In previous papers we have, by application of collision-activation mass spectrometry, unambiguously demonstrated the presence of pyrolytically induced isomerizations of methyl acetate[2] and methyl thioxoacetate.[3] However, in contrast to methyl acetate[2] and methyl thioxoacetate[3] an analysis of the molecular ion of the ^{34}S-labelled (1) (m/z 108) by collision-activation mass spectrometry revealed that no isomerization of (1) apparently takes place ($T \leq 1253$ K), since the spectra appear virtually identical before and after pyrolysis. On this basis we are forced to conclude that no 1,3-sulphur-to-sulphur methyl group migration takes place to any significant degree upon pyrolysis of (1).[6]

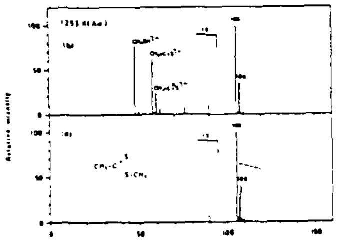


Figure 1 Field-ionization mass spectra of ^{34}S-labelled methyl dithioacetate (a) before pyrolysis and (b) of the product mixture following pyrolysis at 1253 K

The apparent absence of the 1,3-methyl group migration seems surprising for the following reasons: (*a*) geometrically the isomerization would be as favourable as that of methyl acetate,[2] the reaction passing through a symmetric transition state; (*b*) (1) possesses *cis*-geometry in the gas phase;[7] and (*c*) the involved bending modes (< SCS and < CSC) are expected to exhibit force constants of lower values than the corresponding modes in methyl acetate. Although no knowledge of the actual magnitude of these force constants in (1) is available, the latter argument has been supported by semi-empirical MNDO calculations, suggesting the activation barrier for the isomerization of (1) to be *ca.* 30 kJ mol^{-1} lower than that for methyl acetate.[8]

From this background we concluded that the isomerization reaction was hindered, most probably owing to change of the thiocarbonyl function. *A priori* it is suggested that pyrolytic formation of the enethiol tautomer (4) of (1),[9] the latter immediately reversing to (1) by thermal quenching upon collision with the cold reactor walls, is responsible for the thiocarbonyl blockade.

It is well established[10] that labile hydrogens, as *e.g.* HS—, may exchange with hydrogens, present as surface-bound water by molecule–wall collisions, in contrast to, *e.g.*, CH hydrogens, which in general are left unaffected

* To receive any correspondence.

† This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)*, 1984, Issue 1, p. iv]; there is therefore no corresponding material in *J. Chem. Research (M)*.

To study a possible exchange reaction, which apparently would demonstrate the presence of the enethiol structure, we studied the molecular ion pattern of (1) before and after pyrolysis applying a reactor continuously being saturated with D_2O (*cf.* Experimental section). Following pyrolysis the relative intensity of the ion of *m/z* 107 unambiguously increased (relative *m/z* 106/107/108; intensity ratio before pyrolysis, 100/5.0/9.1; after pyrolysis (T = 1043 K), 100/11.1/10.5), unequivocally demonstrating incorporation of deuterium in the ester, which escapes the reactor undecomposed ($C_3H_5DS_2^{+\cdot}$: *m/z* 107).

In order to elucidate the actual position of the deuterium atom in this ester we studied the collision-activation mass spectra of the ion *m/z* 107 before and after pyrolysis of (1) in the presence of D_2O. Figure 2

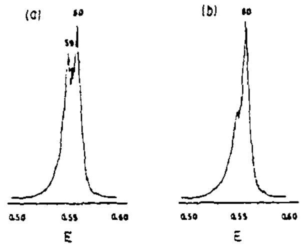
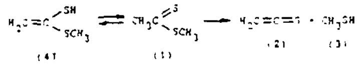


Figure 2 Partial CA mass spectra (0.5–0.6 E) of the electron-impact-induced *m/z* 107 ion of methyl dithioacetate (a) in the presence of D_2O before pyrolysis and (b) after pyrolysis at 1043 K

visualizes partial collision-activation mass spectra (0.5–0.6 E) of the ion *m/z* 107 before and after pyrolysis. Before pyrolysis this ion consists of contributions from (1) carrying one ^{13}C or one ^{33}S. The peaks at *m/z* 59 and 60 in the collision-activation spectrum [Figure 2(a)] reflect the permutation of these isotopes in the $CH_3C{\equiv}S^+$ ion. The *m/z* 59:60 intensity ratio can, based on the natural abundances of ^{13}C and ^{33}S, be calculated to be 0.63, which agrees with the pattern depicted in Figure 2(a). Obviously incorporation of a deuterium atom in the acid methyl group in (1) would, upon collision-activation, result in an increased intensity of the *m/z* 60 peak relative to *m/z* 59, owing to a contribution from $CH_2DC{\equiv}S^+$, corresponding to the contribution of $CH_2DC(S)SCH_3^{+\cdot}$ to *m/z* 107, whereas deuterium incorporation in the ester methyl would increase the *m/z* 59:60 ratio. The spectrum depicted in Figure 2(b) unambiguously demonstrates the former effect. In the case of methyl acetate, whereas no indications of an intermediary enol structure have been obtained,[6] an analogous experiment revealed no deuterium incorporation, *i.e.* no direct H–D exchange of the methyl hydrogens apparently takes place. Hence, the intermediacy of the enethiol tautomer (4) is hereby visualized, *i.e.* the gas-phase pyrolysis of (1) can be rationalized in terms of two concurrent reactions, which are (*a*) methanethiol elimination to generate (2) and (*b*) a (1)–(4) tautomerization.



(4) (1) (2) (3)

From the above we conclude that, although the 1,3-methyl group migration from a theoretical point of view appears reasonable and feasible, the experiments, demonstrating the operation of the (1)–(4) tautomerization, explain the absence of the former reaction.

A comprehensive study on the possible significance of enol/enethiol structures in the thermally induced reactions of simple acetic esters, and the corresponding mono- and dithio-analogues, is presently being conducted. It should, nevertheless, be noted that the thioketene/methanethiol formation apparently takes place directly from the non-enethiolized (1); however, the present technique does not allow determination of the (4):(1) ratio at pyrolysis temperatures.

Experimental

The flash vacuum pyrolysis experiments were carried out by the FVP–FIMS technique as described in previous papers.[11,12] Product compositions were obtained by field-ionization mass spectrometry;[11] possible isomerization reactions were studied by collision-activation mass spectrometry of the electron-impact-induced molecular ions.[12] In general the pyrolysis technique here applied (FVP–FIMS) gives rise only to unimolecular reactions.[11,12] All pyrolyses were carried out by application of *gold-plated filaments in order to avoid surface-catalytic reactions.*[13]

Co-pyrolysis experiments were carried out by simultaneous introduction of the ester (1) and D_2O to the pyrolysis reactor using the continuous-flow-inlet system.[14]

S-Methyl [$^{34}S_1$]*Dithioacetate.* – The ester (1) (1 mmol) was heated to 100 °C for 60 h together with ^{34}S (1 mmol) (90%; Monsanto Research Corporation) in a sealed, evacuated glass ampoule (*cf.* ref. 15). The reaction mixture, containing $CH_3C(^{34}S)SCH_3$ in *ca.* 30% yield, was used without further *purification.*

We are grateful to the Carlsberg Research Foundation for financial support, which enabled us to purchase the sulphur-34 necessary for this study.

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APPENDIX 18.

PYROLYSIS OF $H_4N_4S_4$. FIRST EVIDENCE FOR THE FORMATION OF SULPHUR DIIMIDE

LARS CARLSEN, HELGE EGGSGAARD AND SUSANNE ELBEL

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PYROLYSIS OF $H_4N_4S_4$. FIRST EVIDENCE FOR THE FORMATION OF SULPHUR DIIMIDE

Lars Carlsen and Helge Egsgaard
Chemistry Department, Risø National Laboratory,
DK-4000 Roskilde, Denmark.

Susanne Elbel
Institut für Anorganische und Angewandte Chemie,
der Universät Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, Deutschland

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Summary: Pyrolytic decomposition of the eight-membered $H_4N_4S_4$ ring has been studied by field ionization mass spectrometry and uv-photoelectron spectroscopy. Evidence for the formation of the parent sulphur diimide is presented. A similar behaviour was observed for the methyl derivative $Me_4N_4S_4$

Key-words: Sulphur Diimide, Pyrolysis, Field Ionization Mass Spectrometry, Photoelectron Spectroscopy

Sulphur diimides 1 (R = alkyl, aryl) are well known compounds, their physical properties being well established.[1] However, the parent species, sulphur diimide 1 (R = H), has hitherto remained undetected. The present communication describes the formation of sulphur diimide (1, R = H) by pyrolytic decomposition of the eight-membered ring system $R_4N_4S_4$ 2 (R = H).

As part of a progressing study on the possible formation of thionitroso compounds (R-N=S), we studied the pyrolytic decomposition of 2, since the latter formally can be regarded as a R-N=S tetramer, the pyrolyzates being analyzed by field ionization mass spectrometry (fims)[2] and photoelectron spectroscopy (pes).[3]

To elucidate the decomposition of 2 (R = H), we pyrolyzed the latter under flash vacuum conditions, applying the Curie point pyrolysis principle[2] at 1043 and 1251K, the reaction mixture being analyzed by fims (Figure 1). In order to avoid surface promoted reactions, all hot surfaces were gold-plated.[4]

Pyrolysis at 1043K revealed the formation of a single major product only, exhibiting a molecular weight of 62. Increasing the pyrolysis temperature to 1251K af-

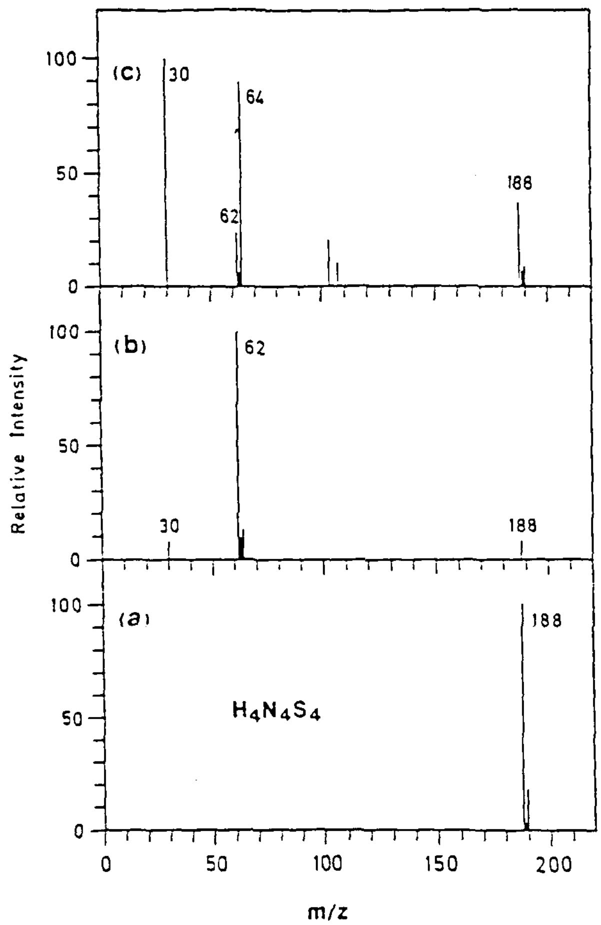

Figure 1. Field ionization mass spectra of undecomposed 2 (R = H) (a), and following pyrolyses at 1043K (b) and 1251K (c), respectively.

forded a pronounced decrease in the yield of "62" with a simultaneous appearance of a product with molecular weight 30. Taking into account that the two products can consist of hydrogen, nitrogen, and sulphur atoms only, we unambiguously could assign the "62" to H_2N_2S and "30" to H_2N_2, respectively.

A priori sulphur diimide 1 (R = H) as well as two further H_2N_2S isomers, the thiaziridine (3) and the thionitroso amine (4), respectively, have to be considered as possible candidates for "62", whereas diimine (5) most probably can be assigned to "30".

1 3 4 5

For comparison we carried out an analogous series of experiments using the tetramethyl derivative of $R_4N_4S_4$ (2, R = CH_3).

Fvp-fims at 1043K revealed formation of compounds with molecular weights of 90 (major) and 58 (minor), respectively. In accordance with the above discussion, the "90" could be assigned to $(CH_3)_2N_2S$, i.e. the sulphur diimide, the thiaziridine, or the thionitroso amine isomer. The pes analysis of the pyrolyzates disclosed, on comparison with known ip.'s, dimethyl sulphur diimide[5] being generated from 2 (R = CH_3: ip.'s 8.10, 9.05, 10.91, 11.60, 12.50, 13.1, and 13.7 eV) besides traces of S_2 at T < 800K, S_2, H_2S, N_2, and methyl radicals being the main products at temperatures above 1000K. In contrast to the parent compound, 2 (R = CH_3) was seen in the pe spectrum, as this species was easily volatizable.

It has previously been reported that 2 (R = H) thermally decomposes uncontrollably, the final products being S_4N_4, S_2, and NH_3.[6] This was confirmed in the pre-present study by analyzing the pyrolyzates using uv-pes: Apparently 2 (R = H) did not sublime from the sample reservoir, but rearranged obviously in the molten state under extrusion of S_4N_4, SN, N_2, S_2, NH_3, and H_2S, all of which were identified by comparison with known pe data. It should be noted that small inorganic fragments in general escape detection by the fims technique.[2] However, it must be considered that some of the decomposition products observed by the pes analysis, which apparently are results of extensive degradations, obviously may be a consequence of surface (Mo as well as Al_2O_3) promotion.

Taking the data obtained for the methyl derivative as supportive, we conclude that flash vacuum pyrolysis of 2 (R = H, CH_3) leads to the formation of the sulphur diimides 1 (R = H, CH_3), the formation of the parent compound 1 (R = H) hereby being established for the first time. At higher temperatures, the sulphur diimides apparently eliminate sulphur, possibly _via_ the three-membered thiaziridines to form the corresponding diimines.

$$\underset{\underline{2}}{R_4N_4S_4} \xrightarrow{\Delta} \underset{\underline{1}}{RN{=}S{=}NR} \xrightarrow{\Delta} \underset{\underline{5}}{RN{=}NR} + S$$

$$R = H,\ CH_3$$

A thorough discussion of the pe spectroscopic data with special emphasis on conformational features of 1 (R = H) will be given elsewhere.[7]

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Title and author(s)

ANALYSIS OF LOW-PRESSURE GAS-PHASE PYROLYTIC REACTIONS BY MASS SPECTROMETRIC TECHNIQUES

Lars Carlsen

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Pages 276 **Tables** 2 **Illustrations** 34 **References** 87

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Abstract (Max. 2000 char.)

The report is divided into seven chapters: Chapter 1 gives a short introduction to applications of pyrolysis techniques in different areas of chemical research. Chapter 2 is devoted to the application of mass spectrometric techniques for the analysis of gas-phase reactions. The applicability of field ionization and collision activation mass spectrometry is illustrated by studies on isomerization reactions of carboxylic acid esters and the thermal decomposition of *1,2-oxathiolane*. The importance of reference structures is discussed. Chapter 3 gives details on the sample/inlet systems applicable to the pyrolysis-mass spectrometry system. Chapter 4 discusses the low-pressure pyrolysis reaction, with special emphasis on reactors based on the inductive heating principle. The temperature control of the reactors is discussed in terms of a 'multitemperature' filament, as the basis for the concept of Pulse Pyrolysis. The influence

to be continued next page

Descriptors – INIS

CHEMICAL REACTION KINETICS; CURIE POINT; GAS ANALYSIS; HIGH TEMPERATURE; HIGH VACUUM; MASS SPECTROSCOPY; MOLECULE COLLISIONS; PYROLYSIS; PYROLYSIS PRODUCTS; REAL TIME SYSTEMS; SURFACE COATING

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of surface composition on the course of reaction is discussed, advocating for the application of gold coated surfaces to minimize surface-promoted reactions. Chapter 5 deals with low-pressure gas-kinetics on the basis of an empirical 'effective temperature' approach. Chapter 6 gives a short summary of the main achievements, which are the basis for the present report and Chapter 7 is the reference list. A Danish summary and 18 appendices, consisting of previously published papers in the period 1980-1986 are included as separate sections.

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