THERMAL STABILITY OF ORGANIC COMPOUNDS
BY THE ISOTENISCOPE METHOD

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division.

This report covers work conducted from December 1961 to January 1965. The manuscript was released by the authors in June 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved,

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory
ABSTRACT

The thermal stability of some 45 different organic compounds was determined by the isoteniscope method. A mechanistic interpretation of the data was used to discuss structure-stability relationships.

Compounds which appear to possess a high degree of thermal stability are the fluorooxetanes, arylsilylamines, fluoroalkyltriazines and fluoroaromatic compounds.
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SECTION I
INTRODUCTION

Few materials requirements have presented as great a challenge to the synthetic chemist as the demand for nonmetallic materials of high thermal stability.

The development of superior elastomers, fluids, fibers, resins and plastics require a prior knowledge to the heat stability of the more elementary chemical units from which these complex materials are constructed. For several years, the Polymer Branch has conducted a program involving the preparation of unusual chemical structures and the determination of their thermal stability. In this way, we desired to uncover new classes of thermally stable materials and to examine the effects of structural alteration on the stability of the model compounds.

The thermal stability of the selected model compounds was determined by the isoteniscope method. The isoteniscope is basically an instrument to measure the vapor pressure of a compound (Reference 1). Nearly ten years ago Mr. O. M. Ballentine of this laboratory adopted the method for the determination of the thermal stability of lubricating fluids (Reference 2). Since that time, the method has been widely used and the procedure as well as the instrumentation has undergone considerable refinement (References 3 through 5). The definitive report by Blake, Hammann, Edwards et al. (Reference 3) has greatly influenced subsequent work in this area.

Thermal decomposition reactions are time-temperature dependent processes. The temperature at which the rate of decomposition becomes perceptible or important depends on such factors as the sensitivity of the instrumentation, the effect of the thermal decomposition reactions on some important physical property and the time-temperature history of the sample. The decomposition temperature of the sample is therefore not a fundamental thermodynamic property but rather an arbitrarily defined term.

For the purposes of this program, we have followed the data analysis presented by Johns, McElhill and Smith (Reference 4). The decomposition reaction is assumed to be a unimolecular and first-order process giving an increase of one mole of a volatile product for each mole of sample.

For a first-order process:

$$\frac{dn_A}{dt} = k n_A$$

The thermal decomposition temperature \(T_d\) is defined as the temperature where a decomposition rate of 1 mole-percent per hour occurs.

$$k = - \frac{dn_A}{dt} \left( \frac{1}{n_A} \right) = \frac{0.01}{60}$$

$$= + 1.67 \times 10^{-4} \text{ min}^{-1}$$
Assuming that the ideal gas law holds for the volatile product:

\[ \frac{PV}{V} = n_B \frac{RT}{T} \]

\[ \frac{dP}{dt} = \frac{dn_B RT}{dt} \]

from

\[ \frac{dn_B}{dt} = \frac{dn_A}{dt} \]

and

\[ \frac{dn_A}{dt} = - kn_A \]

where:

- \( P \) = Pressure
- \( V \) = Volume
- \( R \) = Gas constant
- \( T \) = Temperature
- \( t \) = Time
- \( n_A \) = Moles of reactant
- \( n_B \) = Moles of gaseous product

The rate of pressure rise is determined at several temperatures, \( k \) is calculated and \( T_d \) is determined graphically by the use of the Arrhenius rate equation:

\[ \ln k = - \frac{\Delta E}{RT} + \ln A \]

In the absence of detailed mechanistic information concerning the thermal processes occurring for each compound, the above treatment may be resorted to for screening purposes. Each sample is appraised in terms of the rate at which volatile products are formed. The procedure is reasonably sound when members of the same chemical class are compared. The same general mechanism may be operative and relative rates may be calculated. When combined with other techniques, the method does provide a reasonable basis for the determination of the relative stability of diverse materials and an estimate of the use temperature. The method is not suited for compounds which degrade to non-volatile products.

An example of the raw data obtained and the calculations involved is given in Appendix I.
SECTION II
THERMAL DECOMPOSITION PROCESSES

Some of the concepts which will be used in the discussion of the effects of temperature on
the stability of organic compounds will be qualitatively reviewed.

The thermal decomposition process is best described in terms of the kinetic theory of gases. The temperature of a gas is a measure of the average energy of the individual molecules. The equilibrium energy distribution is given by the Maxwell-Boltzmann relationship. The ratio of molecules having an energy between E and E+dE may be approximated by

\[ \frac{N_E}{N} = e^{-\frac{E}{RT}} \]

The relationship follows the curve:

Only those molecules having an energy greater than a critical value \( E_a \) are capable of undergoing decomposition. Raising the temperature has the effect of increasing the ratio of molecules possessing sufficient energy for decomposition.

The mechanisms by which initial decomposition reactions proceed may be grouped into three broad classifications.

The first to be considered are those reactions which proceed by simultaneous bond-breaking and bond-forming steps. The process is best described as involving a concerted electron reorganization. The topic has been reviewed under the heading of "Rearrangements Through No Mechanism Pathways" (Reference 6). These reactions are thermally induced and are relatively insensitive to structural features and external agents. The process constitutes a low energy decomposition path. The activation energies for these reactions are considerably less than the bond strength of the bonds being broken. Examples of these processes are the decomposition of cyclobutane (Reference 7), the decomposition of esters, and possibly the decomposition of alkyl phosphine oxides (Reference 9).

\[ H_2C \equiv CH_2 \quad H_2C \quad CH_2 \quad H_2C \equiv CH_2 \]

\[ H_2C \quad CH_2 \quad H_2C \quad CH_2 \quad H_2C \quad CH_2 \]

\[ E_a = 62.5 \text{ kcal (Ref. 8)} \]
The second classification of thermal degradation reactions involves those reactions which proceed by homolytic bond cleavage to give radicals and a neutral species or two radicals. Examples of these reactions are the decomposition of tetraethyllead IV and the decomposition of toluene V.

IV  \[ \text{Pb}(\text{C}_2\text{H}_3) \rightarrow \text{Pb} + 4 \text{C}_2\text{H}_4 \]  \( E_a = 40 \text{ kcal} \) (Ref. 10)

V  \[ \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2^+ + \text{H}^+ \]  \( E_a = 77.5 \text{ kcal} \) (Ref. 10)

The activation energy for a given elementary reaction

\[ \text{R} - \text{X} \rightleftharpoons \text{R}^+ + \text{X}^- \]

can, under favorable circumstances, be obtained from the kinetics of a thermal reaction. The activation energy of the reverse reaction (recombination) may safely be assumed to be negligible. The activation energy for the reaction is therefore a measure of the strength of the bond which is broken and serves as the definition of the Bond Dissociation Energy \( D(\text{R}-\text{X}) \).

The bond dissociation energy is an experimental quantity. Dissociation will occur when the translational energy, transmitted by collision, is redistributed within the molecule to the extent that the vibrational energy of a particular bond exceeds a certain critical value. Present computation methods do not permit a calculation of the vibrational energy distribution of each bond in a complex molecule. As a result the values of \( D(\text{R}-\text{X}) \) are sensitive to structural changes in the molecule. The values of \( D(\text{R}-\text{X}) \) do fall within a characteristic range as shown below:

\[ D(\text{R-H}) = 85 - 100 \text{ kcal} \]
\[ D(\text{R-CH}_3) = 75 - 85 \text{ kcal} \]
\[ D(\text{R-CH}_2\text{C}_6\text{H}_5) = 50 - 65 \text{ kcal} \]

The third classification of thermal degradation reactions concerns those reactions which proceed by heterolytic bond cleavage. Evidence is accumulating in the literature for such processes in the vapor phase (Reference 11). The transition state for the decomposition
reaction involves a degree of charge separation in the bonds which are to be broken. The reaction is therefore more sensitive to substituent effects than the homolytic or concerted bond cleavage reactions.

The assignment of these classifications to a particular reaction is rarely a simple matter. It is reasonable to expect a gradation of mechanisms with homolytic and heterolytic cleavage reactions as the extreme cases.

\[ E_a = 34.5 \text{ kcal. (Ref. 8) } \]
SECTION III
EXPERIMENTAL RESULTS

All measurements were conducted in a metal high-pressure isoteniscope. The sample chamber is separated from a source of pressurized nitrogen by a thin metal diaphragm. Deformation of the diaphragm is detected by an electrical contact point placed directly above the nitrogen side of the diaphragm. Nitrogen pressure is used to return the diaphragm to its original position. A diagram of the equipment is shown in Appendix I.

1. ARYLMETALLOIDS

The thermal stability of tetraphenyl compounds of group IVa elements have been reported by Blake and coworkers (Reference 3). These investigators used a low pressure glass isoteniscope and a slightly different definition of the decomposition temperature. It was of interest to determine if significant differences exist between the decomposition temperature obtained by the two methods and to obtain a better comparison of the relative stabilities of the tetraphenyl derivatives of this group. Table I shows that the relative order of stability is maintained. The differences between the decomposition temperatures calculated by the two methods are considered to be within the reproducibility of the methods.

| THERMAL STABILITY OF TERTAARYL DERIVATIVES OF GROUP IVA ELEMENTS* |
|--------------------------|---------|---------|--------------------------|
|                          | $T_D$   | $E_a$   | $T_D$ (Ref.3)            |
| $\phi_4 C$               | -       | -       | 777                      |
| $a\phi_4 Si$             | 873     | 69      | 810**                    |
| $a\phi_4 Ge$             | 788     | 57      | 733                      |
| $a\phi_4 Sn$             | 666     | 33      | 659                      |
| $a\phi_4 Pb$             | ca 448  | -       | -                        |

*All temperatures are in °F, sources of samples are indicated by a lower case letter preceding the structural formula

**Data reported was for tetra (p-biphenyl) silane

The stability decreases on descending the periodic subgroup. The bond length and the bond strength also decreases in the same order (Reference 12).

The thermal stability of several group IVA metal compounds containing the M-M bond was examined. Although hexaphenylethane is known to dissociate readily to the triphenylmethyl radical in solution, it has been shown that hexaaryldigermane, hexaaryldistannane, and hexaaryldiplumbane do not exhibit comparable dissociation. Studies by Gilman have demonstrated the resistance of hexaaryldisilanes to undergo homolytic Si-Si cleavage (Reference 13). The failure of the dimetallo compounds to undergo dissociation in solution is attributed in part (Reference 14) to the absence or lessening of the steric repulsion of the ortho hydrogens. The C-C bond length in hexaarylethane is 1.58Å while in the dimetallo compounds the bond lengths are on the order of 2.3Å for Si-Si, 2.4Å for Ge-Ge, 2.8-3.0Å for Sn-Sn and 3.5Å for
Pb-Pb (Reference 15). From electron impact measurements, Stone has concluded that the bond dissociation energy of the Si-Si bond (Reference 16) and the Si-C bond (Reference 17) are comparable to the B.D.E. of the C-C bond.

The order and magnitude of the thermal decomposition temperatures and $E_a$ of the $\Phi_3^\alpha M$-MO$_3^\alpha$ type compounds shown in Table II are comparable to the $\Phi_4^\alpha M$ compounds of Table I. This would suggest that the decomposition occurs by the rupture of the M-C bond rather than the M-M bond.

### TABLE II

<table>
<thead>
<tr>
<th>Thermal Stability of the $\Phi_3^\alpha M$-MO$_3^\alpha$ Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$\Phi Si-Si\Phi$</td>
</tr>
<tr>
<td>$\Phi Ge-Ge\Phi$</td>
</tr>
<tr>
<td>$\Phi Sn-Sn\Phi$</td>
</tr>
<tr>
<td>$\Phi Pb-Pb\Phi$</td>
</tr>
</tbody>
</table>

2. AMINOMETALLOIDS

Several diphenylamino compounds were prepared (Reference 18) in which nitrogen was bound to elements of varying orbital configuration. In the compound $\Phi_3^\alpha P$-NO$_2^\alpha$, nitrogen is adjacent to an unshared p electron pair. In $\Phi_3^\alpha Si$-NO$_2^\alpha$, nitrogen is adjacent to a vacant d orbital. In $\Phi_3^\alpha C$-NO$_2^\alpha$, nitrogen is adjacent to a filled SP orbital configuration.

The order of stability was $\Phi_3^\alpha Si$-NO$_2^\alpha > \Phi_2^\alpha P$-NO$_2^\alpha > \Phi_3^\alpha C$-NO$_2^\alpha$. The enhanced stability of N-triphenylsilyldiphenylamine is a consequence of $d_\pi-p_\pi$ overlap of the unshared electron pair of nitrogen with the vacant d orbitals of silicon (Reference 19). The large difference between the electro-negativities of silicon and nitrogen, 1.8 and 3.0 respectively (Reference 20), promotes the formation of a bond with a large bond dissociation energy.

Several other compounds containing the silicon-nitrogen bond were also found to possess a relatively high degree of thermal stability as shown in Table III.

3. TRIAZINES

A variety of triazine derivatives were examined. This class of compounds is particularly inviting for synthetic work since the several reactive intermediates are available and the resonance energy of triazine is greater than that of benzene. The stability data is given in Table IV. The data for several compounds reported by Sheehan et al. (Reference 21) are included.
### TABLE III

**STABILITY OF SOME METALLO-NITROGEN COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^a \phi_3 \text{C-N}\phi_2$</td>
<td>ca 400</td>
</tr>
<tr>
<td>$^a \phi_2 \text{P-N}\phi_2$</td>
<td>570</td>
</tr>
<tr>
<td>$^a \phi_3 \text{Si-N}\phi_2$</td>
<td>845</td>
</tr>
<tr>
<td>$^b \phi_3 \text{Si-N} \bigcirc \text{N-Si}\phi_3$</td>
<td>600</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2 \text{Si-N} \bigcirc \text{N-Si}(\text{CH}_3)_2$</td>
<td>ca 800-900</td>
</tr>
<tr>
<td>$^c \left[\text{CH}_3 \text{Si}\right]_3 \text{N}$</td>
<td>ca 750</td>
</tr>
</tbody>
</table>

The thermal rearrangements of alkoxy triazines to cyanurates was observed by Hofmann in 1870 (Reference 22).

The process, though still not elucidated, appears to involve cleavage of the $-\text{O-CH}_3$ bond. Piskala (Reference 23) isolated several unexpected compounds from the thermal isomerization of 2,4-dimethoxy-1,3,5-triazine.
The formation of these products requires the intramolecular transfer of the methyl group.

The order of stability of the alkoxy and aryloxy triazines reflects the stability of the \(-O-R\) bond towards cleavage. Electron-withdrawing substituents (\(R = C_6F_5^-, RfCH_2^-\)) increase the stability of the triazine with respect to the derivatives possessing electron donating substituents (\(R = C_6H_5^-, CH_3^-\)).

The tris-(phenyl)triazine is a very stable compound. The tris-(heptafluoropropyl)triazine is an extremely stable low melting fluid. Johns et al. (Reference 24) reported a decomposition temperature of 900°F for tris-(trifluoromethyl)-triazine. Trifluoroacetonitrile was identified as a decomposition product. These authors also observed the remarkable stability of the structurally similar tetra-(trifluoromethyl)-pyrazane (\(T_d > 1000°F\)).

**TABLE IV**

<table>
<thead>
<tr>
<th>R</th>
<th>(T_d \ degree \ F)</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^6H (C_7F_{14}) CH_2O^-)</td>
<td>680</td>
<td>79</td>
</tr>
<tr>
<td>(^6C_6F_5O^-)</td>
<td>ca 620</td>
<td>--</td>
</tr>
<tr>
<td>(^dC_6H_5O^-)</td>
<td>497</td>
<td>--</td>
</tr>
<tr>
<td>(^dC_6H_5^-)</td>
<td>870</td>
<td>--</td>
</tr>
<tr>
<td>(^eC_3F^-)</td>
<td>958</td>
<td>88</td>
</tr>
<tr>
<td>(C_6H_{11}O^-)</td>
<td>ca 450</td>
<td>--</td>
</tr>
</tbody>
</table>

4. PHOSPHONITRILES

Derivatives of phosphonitrilic chloride have been the subject of numerous efforts in inorganic polymer chemistry. The \(-P=N-\) repeating unit can be used to prepare small to macrocyclic ring systems and linear polymers (Reference 25).

Hexaphenyl triphosphonitrile is stable to 810°F. This value probably sets an upper limit for the ring system. The hexa(heptafluoropropyl)triphenylphosphonitrile, in contrast to the tris-(heptafluoropropyl)triazine, is not particularly stable decomposing below 600°F. The phosphonitrilic triphenylphosphonitrilane prepared from the \(C_4\) telemer alcohol decomposed at 680°F. The pentafluorophenoxyc derivative exhibited comparable stability. The aryloxy substituted phosphonitriles are somewhat more stable, decomposing in the temperature range of 710-740°F. We have not observed a significant difference in the stability between like-substituted trimer and tetramer.
Shaw (Reference 26) has recently reported a study of the phosphazene-phosphazane rearrangement.

\[
\begin{align*}
\text{OR} & \quad \text{OR} \\
\text{N} & \quad \text{OR}
\end{align*}
\]

The 1,1-dihydrofluoroalkoxy- and phenoxyphosphazenes were unchanged at 575°F. The mechanism suggested involves nucleophilic attack by nitrogen at carbon with concerted or subsequent cleavage of the O-C bond. The order of stability of the isoteniscope method was found to be

\[
\text{CF}_3\text{C}_6\text{H}_4\text{O}^- > \text{C}_6\text{H}_5\text{O}^- > \text{RfCH}_2\text{O}^- > \text{COF}_5\text{O}^-
\]

This order does not reflect the strength of the -O-R bond as observed with the triazine derivatives. There may be increased participation by nitrogen. This is indicated by the low stability of hexa(pentafluorophenoxy)triphosphonitrile. Fluoroaromatics are highly susceptible to nucleophilic attack.

**TABLE V**

STABILITY OF PHOSPHONITRILES

<table>
<thead>
<tr>
<th>((R_2P = N-)_3)</th>
<th>Trimer TD</th>
<th>(E_a)</th>
<th>Tetramer TD</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f-C(_6)H(_5)</td>
<td>810</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>g-C(_3)F(_7)</td>
<td>547</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-OCH(_2)C(_3)F(_7)</td>
<td>681</td>
<td>121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f-OC(_6)H(_5)</td>
<td>710</td>
<td>62</td>
<td>714</td>
<td>55</td>
</tr>
<tr>
<td>d-OC(_6)F(_5)</td>
<td>676</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f-OC(_6)H(_4)mCF(_3)</td>
<td>724</td>
<td>24</td>
<td>766</td>
<td>123</td>
</tr>
<tr>
<td>f-OC(_6)H(_4)mOCF(_3)</td>
<td>740</td>
<td>61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. OXADIAZOLES

Fluoroalkyl substituted oxadiazoles are under current consideration as high temperature elastomers. Several representative samples were obtained and the thermal decomposition temperatures were determined. Preliminary stability data was available. A comparison of the stability of the oxadiazoles in static tests with the isoteniscope determined stability afforded an opportunity to examine the reliability of the latter method. As shown in Table VI both methods clearly discriminate between the relatively unstable pentafluoroethyl substituted oxadiazole and the other two compounds.
TABLE VI
STABILITY OF OXADIAZOLES

<table>
<thead>
<tr>
<th>Structure</th>
<th>T_D</th>
<th>E_a</th>
<th>Percent Recovery after 5.5 hrs. at 708°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₃C ₇-₇-₇-C₇-₇-C₇-CF₅</td>
<td>625</td>
<td>65</td>
<td>78</td>
</tr>
<tr>
<td>F₅C₂ ₇-₇-₇-C₇-O-C₇-₇-CF₅</td>
<td>488</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>F₇C₃ ₇-₇-₇-C₇-₇-C₇-C₃F₇</td>
<td>635</td>
<td>44</td>
<td>68</td>
</tr>
<tr>
<td>F₅C₆ ₇-₇-₇-C₇-₇-C₆F₅</td>
<td>500-600</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Although the order of stability can not be rationalized at this time, anomalies in the migrating aptitudes of fluoroalkanes of different carbon lengths have been observed by other workers (Reference 27).

6. PERFLUOROARYLMETALLOIDS

Several compounds of this class were examined. These perfluoroaryl compounds show interesting differences when compared with their hydrogenic analogs. The perfluorotetraphenylsilane is definitely less stable than tetraphenylsilane. The perfluoroarylmetalloys have relatively low $E_a$ values. This is suggestive of a concerted transition state. It is tempting to speculate on a decomposition path leading to a benzyne intermediate.

\[
\begin{align*}
\text{Si} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F} \\
\text{F} & \quad \text{F}
\end{align*}
\]

7. FLUOROAROMATICS

Hexafluorobenzene is known to possess remarkable stability. Unfortunately many of the derivatives of hexafluorobenzene have not maintained the stability of the parent compound. In many cases the hydrogen analogs are of greater or comparable stability (Reference 28). Too little is known about the thermal reactions of fluoroaromatics to attempt any discussion of the results. In the case of pentafluorobenzene the presence of one residual hydrogen has not resulted in an observable decrease of stability from that of hexafluorobenzene. Hydrogen containing substituents may in some case be tolerated.
### TABLE VII

**STABILITY OF PERFLUOROARYLMETALLOIDS**

<table>
<thead>
<tr>
<th>AR₄M</th>
<th>T_D°F</th>
<th>Eₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR₄Si</td>
<td>704</td>
<td>45</td>
</tr>
<tr>
<td>AR₄Ge</td>
<td>780</td>
<td>38</td>
</tr>
<tr>
<td>AR₄Sn</td>
<td>750</td>
<td>27</td>
</tr>
<tr>
<td>AR₄Pb</td>
<td>500</td>
<td>--</td>
</tr>
<tr>
<td>AR₅P</td>
<td>731</td>
<td>28</td>
</tr>
</tbody>
</table>
### TABLE VIII
STABILITY OF FLUOROAROMATIC COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_D^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{J} C_6 F_6$</td>
<td>above 1000</td>
</tr>
<tr>
<td>$\text{J} C_6 F_5 H$</td>
<td>above 1000</td>
</tr>
<tr>
<td>$\text{J} C_6 F_5 - C_6 F_5$</td>
<td></td>
</tr>
<tr>
<td>$\text{O} - \text{O}$</td>
<td>ca 540</td>
</tr>
<tr>
<td>$\text{J} C_6 F_5 \text{C} - \text{O} - \text{CC}_6 F_5$</td>
<td>ca 320</td>
</tr>
<tr>
<td>$\text{J} C_6 F_5 \text{NCC}_6 F_5$</td>
<td></td>
</tr>
<tr>
<td>$\text{a}(C_6 F_5)_2 \text{NH}$</td>
<td>675</td>
</tr>
<tr>
<td>$\text{a}(C_6 F_5)_2 \text{NC} \text{CH}_3$</td>
<td>below 600</td>
</tr>
<tr>
<td>$\text{a}(C_6 F_5)_2 \text{NC} C_6 F_5$</td>
<td>ca 800</td>
</tr>
<tr>
<td>$\text{a}(C_6 F_5)_2 \text{N} - \text{CH}_3$</td>
<td>ca 540</td>
</tr>
<tr>
<td>$\text{J}$</td>
<td>above 1000</td>
</tr>
<tr>
<td>$\text{a}(C_6 H_5)_2 \text{N} - \text{N}(C_6 H_5)_2$</td>
<td>840</td>
</tr>
</tbody>
</table>
8. MISCELLANEOUS

TABLE IX
MISCELLANEOUS COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>dSilylcarborane</td>
<td>866°C</td>
</tr>
<tr>
<td>N-Phenylsydnone</td>
<td>817°C</td>
</tr>
<tr>
<td>Oxetane</td>
<td>837°C</td>
</tr>
</tbody>
</table>

![Chemical Structure Images](image1.png)

![Chemical Structure Images](image2.png)
SECTION IV
DISCUSSION OF RESULTS

The kinetic treatment of the isothermal rate of pressure rise is a very naive one. The kinetic order, molecularity and the stoichiometry of the decomposition reaction may be quite different from the assumed values. The initial amount of the sample is assumed to be still present at each temperature increment. The number of phases present at each temperature is also an unknown quantity. The metal walls of the cell may catalyze some of the reactions. In view of these limitations, the data can not be considered to be a valid measurement of a particular degradation reaction.

For some of the compounds examined, the T_d must be approximated by even cruder methods. At 655°F the rate of pressure rise for N,N'-di(triphenylsilyl)-piperazine was only 0.049 lbs/in.²/min corresponding to k = 5.2x10⁻⁴ min⁻¹. Increasing the temperature to 690°F resulted in a vigorous evolution of volatile products. The T_d was estimated, on the basis of one point of questionable accuracy, to be 600°F. The compound tri(Si-dimethyl-N-phenylsilazane) presented a different problem. The pressure rise data shown below was obtained:

<table>
<thead>
<tr>
<th>T°F</th>
<th>ΔP/ΔT lbs/in.²/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.011</td>
</tr>
<tr>
<td>696</td>
<td>0.024</td>
</tr>
<tr>
<td>890</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Examination of the sample after the test revealed that moderate decomposition had taken place. Apparently the decomposition proceeds to give non-volatile products. A T_d of 800°F was estimated for this compound.

To determine the significance and reliability of the calculated T_d and E_a values it is instructive to examine the effect of experimental error. A typical Arrhenius plot is shown in Figure 1. The pressure readings are estimated to ±0.1 lbs. The error in the difference between two measurements will be ±0.2 lbs. At low decomposition rates (2 lbs. in 30 min.) this represents an error of ±10 percent. At higher rates the error is reduced to about ±1 percent. The shaded areas in Figure 2 represent the envelope of ±10 percent error at the low pressure rise rate and ±1 percent error at the high pressure rate data. The extreme values for T_d temperatures are 710°F and 704°F. The values for E_a vary from 57 to 66 Kcal. This order of precision is not believed to be frequently achieved.

Duplicate measurements are not commonly conducted. Several duplicate determinations have been made and the results are compared below:

<table>
<thead>
<tr>
<th></th>
<th>T_D</th>
<th>E_a</th>
<th>T_D</th>
<th>E_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₃N₃(OC₆H₅)₀₆</td>
<td>675</td>
<td>26</td>
<td>35</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₃N₃(OC₆H₄CF₃)₀₆</td>
<td>740</td>
<td>118</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>736</td>
<td>80</td>
<td>4</td>
<td>38</td>
</tr>
<tr>
<td>Si(C₆F₅)₀₄</td>
<td>721</td>
<td>45</td>
<td>23</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>698</td>
<td>228</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Although the variations in the $T_d$ values are not considered serious, the large variations in the $E_a$ values casts considerable doubt as to the merit of such a calculation until the method is further refined.

The decomposition temperature as determined by the isoteniscope method does give an indication of the maximum use temperature. If the useful life of a material is arbitrarily taken as the time to reach 10 percent decomposition, then from Figure 1 it can be estimated that at 707°F the useful life of the sample is 10 hours. At 50°F above the $T_d$ the useful life is 1.28 hours, at 100 above the $T_d$ the useful life of the sample is only 0.32 hours. Mahoney et al. (Reference 29) have made extensive use of isoteniscope data in this manner.
SECTION V
RECOMMENDATIONS

The isoteniscope method was originally developed to provide a rapid, reproducible method by which the thermal stability of a material may be judged. Some of the limitations of this method are discussed in this report. The method is unfortunately neither rapid nor particularly reproducible. A further difficulty concerns the terms - thermal stability and decomposition temperature. These terms when used in conjunction with specific temperatures but without adequate definition leads to serious misconceptions. Satisfactory definitions require knowledge of the decomposition reactions and the rate at which they occur. Major modifications in the isoteniscope method must be made in order to obtain reliable kinetic data.

Future work in this area should be directed towards improvements in instrumentation and a more critical examination of the decomposition processes. A much more sensitive pressure sensing detector is required. This will allow the use of smaller samples, and more accurate data may be obtained. Chemical analysis of the volatile products and of the residue as a function of time and temperature is necessary to characterize decomposition reactions.
REFERENCES

2. O. M. Ballentine, WADC TR 54-417, March 1955.
22. A. W. Hofmann and O. Olshausen, Ber., 3, 269 (1870).
SECTION VII
SOURCE OF SAMPLES

a. Air Force Materials Laboratory
b. Iowa State University
c. Midwest Research Institute
d. Olin-Mathieson Chemical Corporation
e. University of Florida
f. E. I. duPont de Nemours
g. U. S. Naval Ordinance
h. Allied Chemical Corporation
i. Withheld
j. Imperial Smelting Corporation Ltd.
APPENDIX I

SAMPLE CALCULATION OF $T_D$ and $E_a$

Sample:  

\[
\begin{align*}
N = P = N \\
P = N = P = \phi
\end{align*}
\]

\[M. \ W. \ 598.6\]

wt. sample : 1.2141

moles sample: $2.15 \times 10^{-3}$

at 801°F (1261°R) \(\frac{\Delta P}{\Delta t} = 0.212 \text{ lbs/in}^2/\text{min}\)

\[k = \frac{v}{nRT} \frac{\Delta p}{\Delta t}\]

\[v = v_{cell} - v_{sample}\]

\[= 13.98 - 1.21 \quad \text{assume } p_{sample} = 1\]

\[= 12.77 \text{ ml.}\]

\[k = \frac{(12.77)(0.212)}{(2.15 \times 10^{-3})(670)(1261)}\]

\[k = 1.49 \times 10^{-3} \text{ min}^{-1}\]

at 826°F (1286°R) \(\frac{P}{t} = 0.364 \text{ lbs/ in}^2/\text{min}\)

\[k = \frac{(12.77)(0.364)}{(2.15 \times 10^{-3})(670)(1286)}\]

\[= 2.50 \times 10^{-3}\]

at 843°F (1303°R) \(\Delta P/\Delta t = 0.534 \text{ lbs/ in}^2/\text{min}\)

\[k = \frac{(12.77)(0.534)}{(2.15 \times 10^{-3})(670)(1303)}\]

\[= 3.64 \times 10^{-3}\]

from Figure I \(k = 1.67 \times 10^{-4}\) at \(\frac{1}{T} = 0.859 \times 10^{-3}\)

\[T_D = 1164°R\]

\[T_D = 704°F\]
Calculation of $E_a$
from graph:

\[
\begin{align*}
k_1 & = 2.45 \times 10^{-3} \\
k_2 & = 6.20 \times 10^{-4}
\end{align*}
\]

\[
\begin{align*}
\frac{1}{T_1} & = 0.780 \times 10^{-3} \\
\frac{1}{T_2} & = 0.820 \times 10^{-3}
\end{align*}
\]

\[
\frac{1}{T_2} - \frac{1}{T_1} = 0.040 \times 10^{-3}
\]

\[
\frac{k_1}{k_2} = 3.95
\]

\[
\log \frac{k_1}{k_2} = 0.597
\]

\[
\log \frac{k_2}{k_1} = -\log \frac{k_1}{k_2}
\]

slope is: \[
\log \frac{k_2}{k_1} = \frac{1}{T_2} - \frac{1}{T_1} = -14.93 \times 10^3 \text{ °R}
\]

Slope = \[
-\Delta E
\]

\[
\frac{2.303 R}{2.303} = R \text{ is } 1.987 \text{ cal/°C}
\]

\[
2.303 = 4.57 \text{ cal/°C}
\]

To correct slope from °R to °C

\[
slope \times \frac{5}{9} = \text{slope °C}
\]

\[
E = \text{slope °C} \times 2.303 \times 1.987 \times \frac{5}{9}
\]

= slope $\times 2.54$

= $14.93 \times 10^3 \times 2.54$

= $37.9 \times 10^3$
APPENDIX II

DIAGRAM OF THE ISOTENISCOPE APPARATUS
Figure 1. Typical Graph of Experimental Data in the Form of the Arrhenius Equation

Figure 2. Error Envelope of Experimental Data in the Form of the Arrhenius Equation
THERMAL STABILITY OF ORGANIC COMPOUNDS BY THE ISOTENISCOPE METHOD

Summary Report (December 1961 - January 1965)

Baum, George and Short, Frank

May 1966

33

AFML-TR-65-347

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED.

Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, WPAFB, O.

The thermal stability of some 45 different organic compounds was determined by the isoteniscope method. A mechanistic interpretation of the data was used to discuss structure-stability relationships.

Compounds which appear to possess a high degree of thermal stability are the fluorooxetanes, arylsilylamines, fluoroalkyltriazines and fluoroaromatic compounds.
Plutoarocas

Phosphonitriles

Triazines

Perfluoroorganometalloids

Fluoroaromatics

UNCLASSIFIED

Security Classification

14.

KEY WORDS

Thermal Stability
Isoteniscope
Arylmetalloys
Aminometalloids
Triazines
Phosphonitriles
Oxadiazoles
Perfluoroorganometalloids
Fluoroaromatics

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