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ANNUAL SUMMARY REPORT NO. 3

PERIOD OF REPORT

MARCH 1 1960 THROUGH FEBRUARY 28 1961

TITLE OF REPORT

RESEARCH ON REACTIONS BETWEEN EXCITED MOLECULES AND
MOLECULAR FRAGMENTS .

CONTRACT # AF 61(052)-10 SUPPLEMENTAL AGREEMENT NO. 2

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SIGNATURE OF THE PRINCIPAL INVESTIGATOR

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a. Investigations being undertaken:

This Annual Summary Report No. 3 covers the period March 1, 1960 through February 28, 1961. Work under the contract which has been performed after Annual Summary Report No. 2 has been reported in three QTSR (Nos 7, 8 and 9). In the present annual report a summary will therefore be given of the work reported in these three QTSR plus a report of the work performed from December 1, 1960 to February 28, 1961.

1) High intensity flash photolysis of acetone and some aliphatic aldehydes.

This part of the work is now ready for publication. Thus all the flash photolysis studies on acetone, acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde have been completed. A manuscript has been prepared (G. Wettermark, High intensity photolysis studies of acetone and some aliphatic aldehydes), and includes 80 pages type-written text together with 26 figures and 20 tables. The work will be published in Arkiv för Kemi and provided with your code number AFOSR TN 59-632. Printed preprints will be available about May 15th and will then be immediately forwarded to your office in Brussels. A summary of the work is given below.

The vapour phase photolysis of acetone, acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde has been investigated at very high light intensities.

High intensity flash light sources provided the basis for the experimental investigation. Two of the flash photolysis apparatus, which have been constructed at the Institute of

Physical Chemistry, Uppsala, were employed for this purpose.

Analyses for all major products were made on samples which were exposed to unfiltered light in a cylindrical reaction vessel (Apparatus II). In the present case 1800 joules were discharged in this apparatus, giving absorbed intensities of the order of 10^{25} quanta sec^{-1} litre^{-1} with a flash period of 10 μsec . The stoichiometry of the products showed that all important constituents were measured.

By using a very intense point-discharge (Apparatus III), quantum yields for the formation of the main products have been determined in parallel light. The samples absorbed light in the absorption band around 280 m μ . Flashes of 100,000 joules, which gave absorbed intensities of the order of 10^{23} quanta sec^{-1} litre^{-1} were used throughout. The absorbed light dose was calculated from a knowledge of the various quantities involved. Thus the spectral distribution of the light emitted from the discharge was determined. The duration of the light pulse from Apparatus III was shown to be strongly dependent of the wavelength of the light isolated, and increases from 30 to 500 μsec when the wavelength is varied from 220 to 500 m μ .

In all cases the samples have been subjected to one single flash.

The product yields have been determined by means of gas chromatography using a flame ionisation detector or a high sensitivity thermal conductivity detector.

Helium was added in some experiments in order to determine the influence of the reaction temperatures on the product yields.

It was found that reactions which are first order with

respect to radical concentration could be satisfactorily eliminated. This resulted in a striking simplification of the reaction schemes and has led to new information concerning the primary photochemical mechanisms and the reactions of the formed radicals.

Acetone

Apparatus II. Carbon monoxide and ethane were found to be the major products. Minor products were methane, diacetyl, methyl ethyl ketone, acetaldehyde and hydrogen.

The product yields have been measured as a function of acetone pressure both in the presence and absence of helium.

The addition of helium was found to cause specific changes in the product yields, thus the yield of methane increases whereas the yields of diacetyl and acetaldehyde decreases.

The occurrence of three primary processes has been demonstrated, giving rise to methyl, acetyl, acetylonyl radicals and hydrogen atoms. A complete reaction scheme for the reactions of these radicals is presented and discussed.

Apparatus III. The quantum yield for the formation of ethane has been determined as a function of acetone pressure and was found to decrease from 0.017 to 0.009 in the pressure interval 40 - 170 mm Hg.

The quantum yield determinations show that at high light intensities

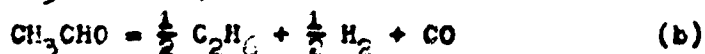
either the recombination of radicals to form acetone increases relative to the other reactions

or triplet molecules are effectively deactivated to the ground state in triplet-triplet collisions. These two possibilities are discussed and treated mathematically.

AldehydesAcetaldehyde

Apparatus II. The product yields have been determined as a function of acetaldehyde pressure.

The analytical results can be described by



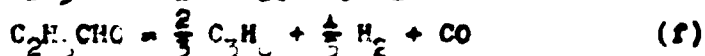
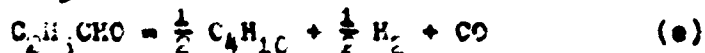
with the relative importance of (a) 45 %, (b) 41 % and (c) 14 %.

Apparatus III. The quantum yields for the formation of methane and ethane have been determined as a function of acetaldehyde pressure. In the pressure interval 40 - 270 mm Hg the quantum yield of methane was found to decrease from 0.020 to 0.005 and that of ethane from 0.017 to 0.007.

Propionaldehyde

Apparatus II. The product yields have been determined as a function of propionaldehyde pressure.

The analytical results can be described by



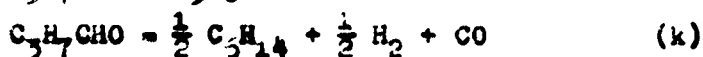
with the relative importance of (d) 51 %, (e) 37 %, (f) 0.6 %, (g) 4.6 % and (h) 1.2 %.

Apparatus III. The quantum yield for the formation of ethane has been determined to be about 0.02 and was found to decrease with increasing propionaldehyde pressures.

n-butyraldehyde

Apparatus II. The product yields have been determined at a n-butyraldehyde pressure of 30 mm Hg.

The analytical results can be described by



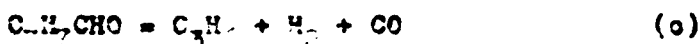
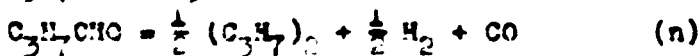
with the relative importance of (i) 50 %, (j) 22 %, (k) 25 % and (l) 2.7 %. Trace quantities of butane and pentane were also found.

Apparatus III. The quantum yields for the formation of propane and ethylene have been determined at 40 mm Hg pressure of n-butyraldehyde and found to be 0.013 and 0.022 respectively.

Isobutyraldehyde

Apparatus II. The product yields have been determined at an isobutyraldehyde pressure of 30 mm Hg.

The analytical results can be described by



with the relative importance of (m) 54 %, (n) 34 % and (o) 12 %.

Apparatus III. The quantum yield for the formation of propane has been determined at 40 mm Hg pressure of isobutyraldehyde and found to be 0.038.

Complete reaction schemes for the reactions between the occurring free radicals are presented and discussed. Some of the

information obtained concerning these reactions are as follows:

The reaction between two formyl radicals has been shown to give mainly hydrogen and carbon monoxide.

The predominant reaction as a result of a collision between a methyl and a formyl radical is the formation of methane and carbon monoxide.

The ratio between the rate constant of disproportionation and the rate constant of combination of n-propyl radicals has been determined to be 0.2 .

The ratio between the rate constant of disproportionation and the rate constant of combination of isopropyl radicals has been determined to be 0.68.

There is indication that long-lived electronically-excited aldehyde molecules are formed which are deactivated to the ground state in collisions between two such molecules. In particular, for acetaldehyde this is supported by the results obtained from a mathematical treatment of the data.

2) Flash heating studies.

A large number of data has been collected from the flash heating studies of benzene and various substituted aromatics. In these experiments a quartz capillary is placed inside the "point-discharge" of Apparatus III (QTSR No. 8). The results from the flash heating studies of benzene, mesitylene, ethylbenzene and phenantrene were submitted in QTSR No. 9 .

3) Mass-spectrometry.

Mass-spectrometry has progressed according to plans and some results have been mentioned in previous QTSR's. Also it has been very useful as a check and complement to the gas chromatographic work which has been indispensable for the work reported under 1).

b. Difficulties, if any, encountered during the reporting period which may hinder progress of the work.

No particular or remarkable difficulties have been encountered during the period of this report.

c. A brief statement of research plans for the next period.

The work mentioned in the previous QTSR No. 9 will be completed and the results included in the Final (Technical) Report which is now under preparation in order to be ready before June 30, 1961.

d. Personnel and administration

(1) As previously mentioned fil.mag. Gösta Palm is temporarily working on the project. Fil.lic. Lars-Olof Sundelöf has measured diffusion by means of light absorption. From January 1 Mr. Öbran Rämme has started to work in this field under the leadership of lic. Holmström and has already proved to be a very able coworker. The following persons have thus been working on the project

- As Project Director Professor Stig Claesson
- As Research assistants Fil.lic. Bertil Holmström
- Fil.lic. Gunnar Wettermark
- Fil.kand.Lave Fischer
- Mr. Öbran Rämme
- Fil.mag. Gösta Palm
- Fil.lic. Lars-Olof Sundelöf
- As Laboratory technicians Mr. Andor Papdi
- Mr. Bo Malmros
- Mr. Gösta Larsson
- Mr. Georg Haglund

(2) Other significant actions, such as important correspondence and conferences.

The preparations for the Fifth International Symposium on Free Radicals on July 6 and 7, 1961, are proceeding according to the plans and the proposals for contributions promise a very interesting meeting.

Dr. Klänning from the Department of Photography at the Technical University in Copenhagen spent three weeks here in December to learn about our experimental technique.