result that vibrational energy may be lost. One would expect the yield to be pressure dependent and results found in this study show this to be the case. Blacet and Bell worked at only one pressure. The lack of dependence of primary yield on temperature is difficult to explain and further work at this wave length might prove to be of interest.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE CATHOLIC UNIVERSITY OF AMERICA]

The Metathetical Reactions of Methyl Radicals with Ethane, Dimethyl Ether, Acetone and Propylene[1]

BY ROBERT E. VARNERIN[2]

RECEIVED OCTOBER 27, 1954

The reactions of methyl radicals with shielded carbon atoms, oxygen atoms, carbonyl carbon atoms, and with carbon-carbon doubly bonded carbon atoms in organic molecules have been investigated experimentally. CD_3 radicals, produced in the thermal decomposition of CD_3CDO, were allowed to react with CH_3CH_3, CH_3OCH_3, CH_3COCH_3 and $CH_3CH{=}CH_2$. The CD_3–CH_3 exchange reactions with the first three compounds occur to the extent of less than one part in 1500, 2500 and 90, respectively, as compared with H-atom abstraction reactions. The CD_3–CH_3 exchange reaction with propylene could not be detected with high precision and seems to occur to the extent of about one part in ten as compared with H-atom abstraction.

Introduction

Some years ago Rice and Teller[3] considered the question of elementary reactions between radicals and molecules and concluded that the most probable reaction would be the removal of a hydrogen atom from an organic molecule by a free radical. They concluded that the attack on exposed negative atoms, such as chlorine, oxygen or nitrogen, having at least one pair of unshared electrons is unlikely as compared with removal of hydrogen atoms; they also concluded that the attack on a doubly or triply bonded carbon atom is entirely possible. The reaction least likely to occur would be the reaction between a free radical and carbon atom having all four valences joined to four univalent atoms or groups.

Experimentally, Rice, Walters and Ruoff[4] have concluded that the reactions

$$CH_3 + CH_3OCH_2CH_3 \longrightarrow CH_3OCH_3 + CH_3CH_2 \quad (1)$$

$$CH_3 + CH_3CH_2CH_2NH_2 \longrightarrow CH_3NH_2 + CH_3CH_2CH_2 \quad (2)$$

could be neglected in the thermal decomposition of methyl ethyl ether and *n*-propylamine since CH_3OCH_3 or CH_3NH_2 were not detected in the products. Franklin and Shepherd[5] have concluded that when methyl radicals attack isopropyl iodide 0.05–1.5% of the methyl radicals enter the reaction

$$CH_3 + i\text{-}C_3H_7I \longrightarrow C_4H_{10} + I \quad (3)$$

and that

$$CH_3 + i\text{-}C_3H_7I \longrightarrow CH_3I + i\text{-}C_3H_7 \quad (4)$$

might be possible since trace quantities of CH_3I were detected in the products.

Two reactions in which a methyl radical extracts a radical from a molecule have been postulated[6] in the photochemical decomposition of dimethylmercury[7] and biacetyl.[8]

$$CH_3 + CH_3HgCH_3 \longrightarrow CH_3CH_3 + Hg + CH_3 \quad (5)$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO \quad (6)$$

Recently, however, Rebbert and Steacie, and Holroyd and Noyes[9] have suggested that (5) probably does not take place.

Since this matter is extremely important in the study of elementary reactions,[10] an attempt has been made to obtain direct experimental evidence of the following types of reactions.

Attack on a shielded carbon atom

$$CD_3 + CH_3CH_3 \longrightarrow CD_3CH_3 + CH_3 \quad (7)$$

$$CH_3 + CD_3CD_3 \longrightarrow CH_3CD_3 + CD_3 \quad (8)$$

Attack on an exposed oxygen atom

$$CD_3 + CH_3OCH_3 \longrightarrow CD_3OCH_3 + CH_3 \quad (9)$$

Attack on a carbonyl carbon atom

$$CD_3 + CH_3COCH_3 \longrightarrow CD_3COCH_3 + CH_3 \quad (10)$$

Attack on a carbon–carbon doubly bonded carbon atom

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3CH{=}CH_2 + CH_3 \quad (11)$$

These reactions have been studied in the thermal decomposition of the mixtures CD_3CDO–CH_3CH_3, CH_3COCH_3–CD_3CD_3, CD_3CDO–CH_3OCH_3, CD_3CDO–CH_3COCH_3, or CD_3CDO–$CH_3CH{=}CH_2$. Highly precise determination of most of the products of 7 to 11 is made possible by mass spectrometry.

Experimental

The pyrolytic apparatus and mass spectrometer have been described previously.[11] The heavy ethane was a mixture of 97.7% C_2D_6 and 2.3% C_2D_5H and the C_2H_6 was Phillips Research Grade gas 99.3% pure. The CD_3CDO was sup-

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[1] This work was supported by the United States Air Force under Contract No. AF-18(600)-64 monitored by the Office of Scientific Research.

[2] Weston College, Weston 93, Massachusetts.

[3] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

[4] F. O. Rice, W. D. Walters and P. M. Ruoff, *ibid.*, **8**, 259 (1940).

[5] J. L. Franklin and G. R. L. Shepherd, THIS JOURNAL, **76**, 609 (1954).

[6] A. F. Trotman-Dickenson, *Quart. Revs.*, **VII**, 217 (1953); also private communication from the same author.

[7] R. Gomer and W. A. Noyes, Jr, THIS JOURNAL, **71**, 3390 (1949).

[8] F. E. Blacet and W. E. Bell, *Discs. Faraday. Soc.*, **14**, **70** (1953).

[9] R. E. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **31**, 631 (1953); R. A. Holroyd and W. A. Noyes, Jr., THIS JOURNAL, **76**, 1583 (1954).

[10] F. O. Rice and R. E. Varnerin, *ibid.*, **76**, 2629 (1954); **77**, 221 (1955).

[11] F. O. Rice and R. E. Varnerin, *ibid.*, **76**, 324 (1954).

plied by Tracerlab[12] as heavy paraldehyde. This material was pyrolyzed at 300° to generate acetaldehyde-d_4. Only the fraction of heavy acetaldehyde distilling from −78 to −95° was used in the experiments and by mass spectrometric analysis consisted of 93.2% CD_3CDO, and 6.8% acetaldehyde-d_3. The acetone was a Mallinckrodt Analytical Reagent distilled from −60 to −195°. The dimethyl ether was supplied by Ohio Chemicals and the propylene by Matheson.

Since the relative rates for the abstraction of hydrogen and deuterium by methyl radicals are known[10] for the compounds used in this investigation, the concentrations of the components of each mixture were made such that the speeds of hydrogen and deuterium abstraction were about the same. The following mixtures were prepared

A: CD_3CDO 20% and CH_3CH_3 80%
B: CH_3COCH_3 20% and CD_3CD_3 80%
C: CD_3CDO 33% and CH_3OCH_3 67%
D: CD_3CDO 33% and CH_3COCH_3 67%
E: CD_3CDO 31% and $CH_3CH{=}CH_2$ 69%

Three samples of each mixture were pyrolyzed.

It is not clear in the case of all the mixtures how to determine the extent of decomposition of the methyl radical source, CD_3CDO or CH_3COCH_3, on the basis of pressure readings. However, accurate knowledge of this is not essential.

Mass spectrometric analyses are reported only for the compounds given in 7 to 11. In order to obtain as accurate analysis as possible it was desirable to remove non-essential compounds from the decomposed mixture.

In mixtures A and B, the isotopic ethanes were the significant products and these could be removed by distillation at −160°. This removed all but traces, much less than 1%, of the CD_3CDO or CH_3COCH_3 and these small traces did not interfere with the analysis. The spectrum of the ethanes was run from mass 26 to 36. Separation of the ethane patterns by the use of the C_2H_6 and C_2D_6 patterns obtained from standard samples, the C_2D_5H pattern from the C_2D_5H impurity in C_2D_6, the C_2H_5D and $C_2H_4D_2$ patterns calculated according to the method of Schissler, Thompson and Turkevich and the $C_2D_3H_3$ pattern approximated from their data.[13] Data for the $C_2D_4H_2$ pattern were not available.

The isotopic dimethyl ethers were the only significant products of the pyrolysis of mixture C and these could be separated by distillation at −130°. This removed all but 1 to 2% of the CD_3CDO. The spectrum of the isotopic dimethyl ethers was run from mass 44 to 49. Since the molecular weight of CD_3OCH_3 is 49, the detection of this compound was not hindered, as in the case of dimethyl ether-d_1 and dimethyl ether-d_2, by the small concentration of CD_3CDO, molecular weight 48, remaining in the sample. It was impossible to separate the ion currents due to CD_3CDO^+ and dimethyl ether-$d_2{}^+$ on mass 48 so analyses for dimethyl ether-d_2 and dimethyl ether-d_1 are not given. The ratio of the ion currents on masses 49 and 46 corrected for C^{13}, O^{17} and O^{18} content gave a rather accurate ratio of the concentrations of dimethyl ether-d_3 and dimethyl ether.

Only the isotopic ethylenes were significant in the pyrolysis of mixture E and these could be separated by distillation at −130° as in the case of mixture C. The spectrum of the isotopic propylenes was run from mass 39 to 48. Separation of the contribution of the small concentration of CD_3CDO in the sample was possible if it was assumed that the ion current on mass 48 was due entirely to CD_3CDO^+. Accurate separation of the spectra of the isotopic propylenes was not possible since data or standard samples were not available for calibration. Although a statistical calculation of the spectra seems highly unsatisfactory, it was the only possible method to approximate the concentration of the isotopic propylenes.

It was not necessary to remove CD_3CDO from mixture D and the spectrum of the isotopic acetones was run from mass 56 to 64. Since the ion current on mass 57 in the spectrum of CH_3COCH_3 is less than 2% of the ion current on mass 58, the relative ion currents on masses 58, 59, ... 64 gave sufficiently accurate relative concentrations of the isotopic acetones present.

Results and Discussion

1. The Reaction of Methyl Radicals with Shielded Carbon Atoms. The Thermal Decomposition of Mixtures of CD_3CDO (20%) and CH_3CH_3 (80%).—The pyrolysis of this mixture was investigated for the occurrence of

$$CD_3 + CH_3CH_3 \longrightarrow CD_3CH_3 + CH_3 \quad (7)$$

as compared with

$$CD_3 + CH_3CH_3 \longrightarrow CD_3H + CH_3CH_2 \quad (12)$$

The mass spectrometer analyses of the isotopic ethanes produced in the pyrolysis of this mixture at 550° are given in Table I. There were no ethanes containing more than three deuterium atoms produced in any experiment. Hence the detection of ethane-d_3 was exceedingly sensitive; the ion current on mass 33 corrected for C^{13} was due to $C_2H_3D_3{}^+$ only and the detection of quantities less than 0.01% was possible. Only in one experiment, #3, was any ethane-d_3 detected. Since the concentrations of ethane-d_1 and ethane-d_2 increase with the CD_3CDO decomposed, it appears quite possible that the formation of the isotopic ethanes might be due to the successive mixing reactions

TABLE I

THE THERMAL DECOMPOSITION OF MIXTURES OF CD_3CDO (20%) AND CH_3CH_3 (80%) AT 550° AND AN INITIAL TOTAL PRESSURE OF 250 MM.

Manometric and mass spectrometric measurements.

		1	2	3
% pressure increase during pyrolysis		5.1	8.6	11.1
Mole %	C_2H_6	98.1	96.1	95.0
	C_2H_5D	1.9	3.6	4.8
	$C_2H_4D_2$	0.1	0.2	0.2
	$C_2H_3D_3$	0	0	0.01

$$C_2H_5 + CD_3CDO \longrightarrow C_2H_5D + CD_3CO \quad (13)$$
$$C_2H_4D + CD_3CDO \longrightarrow C_2H_4D_2 + CD_3CO \quad (14)$$
$$C_2H_3D_2 + CD_3CDO \longrightarrow C_2D_3H_3 + CD_3CO \quad (15)$$

However, if the minute quantity of $C_2D_3H_3$ detected in one experiment was produced only in 7, the CD_3H/CD_3CH_3 ratio indicates that less than one methyl radical in 1500 can enter into 7 as compared with 12.

2. The Reaction of Methyl Radicals with Shielded Carbon Atoms. The Thermal Decomposition of Mixtures of CH_3COCH_3 (20%) and CD_3CD_3 (80%).—The reaction considered is

$$CH_3 + CD_3CD_3 \longrightarrow CH_3CD_3 + CD_3 \quad (8)$$

as compared with

$$CH_3 + CD_3CD_3 \longrightarrow CD_3H + CD_3CD_2 \quad (16)$$

In the case of the isotopic ethanes produced during the pyrolysis of this mixture at 575°, it was not possible to report the percentage of all the ethanes present. Accordingly, the relative ion currents for $C_2D_6{}^+$, $C_2D_5H^+$, $C_2D_4H_2{}^+$ and $C_2D_3H_3{}^+$ plus $C_2D_4H^+$ are given in Table II. Since it was not possible to separate $C_2D_3H_3{}^+$ and $C_2D_4H^+$ and since any error in the successive subtraction of the spectra for C_2D_6, C_2D_5H, . . . is accumulative, no precise quantitative argument can be made on the basis of these experiments. These data, however,

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[12] Under authority granted by the Atomic Energy Commission, Stable Isotope Allocation #B-3878.

[13] D. O. Schissler, S. O. Thompson and J. Turkevich, *Discs. Faraday Soc.*, **10**, 46 (1951).

seem to substantiate the same conclusions as in the case of the experiments with CD_3CDO and CH_3CH_3.

TABLE II

THE THERMAL DECOMPOSITION OF MIXTURES OF CH_3COCH_3 (20%) AND CD_3CD_3 (80%) AT 575° AND AN INITIAL TOTAL PRESSURE OF 300 MM.

Manometric and mass spectrometric measurements.

	4	5	6
% pressure increase during pyrolysis	4.6	7.8	10.8
% of relative ion currents			
$C_2D_6^+$	89.5	90.7	88.0
$C_2D_5H^+$	4.5	6.0	7.0
$C_2D_4H_2^+$	3.8	2.1	2.8
$C_2D_3H_3^+$ plus $C_2D_4H^+$	2.2	1.2	2.2

3. **The Reaction of Methyl Radicals with Oxygen Atoms Having Two Unshared Pairs of Electrons. The Thermal Decomposition of Mixtures of CD_3CDO (33%) and CH_3OCHO (67%).**—The reaction studied in the pyrolysis of this mixture at 550° was

$$CD_3 + CH_3OCH_3 \longrightarrow CD_3OCH_3 + CH_3 \qquad (9)$$

as compared with

$$CD_3 + CH_3OCH_3 \longrightarrow CD_3H + CH_3OCH_2 \qquad (17)$$

Only in one experiment was dimethyl ether-d_3 detected at all and then only in a concentration of less than 0.01% of the undecomposed dimethyl ether present. It is possible that this very small amount of dimethyl ether-d_3 was formed in other mixing reactions, of the type 13, 14 and 15. If, however, it was formed in 9 only, the CD_3H/CD_3OCH_3 ratio indicates that one methyl radical in 2800 can enter into reaction 9 as compared with 17. However, this is of the degree of precision possible in these experiments and is not necessarily positive evidence for the presence of 9.

4. **The Reaction of Methyl Radicals with Carbonyl Carbon Atoms. The Thermal Decomposition of Mixtures of CD_3CDO (33%) and CH_3COCH_3 (67%).**—The reaction considered in the pyrolysis of this mixture at 550° is

$$CD_3 + CH_3COCH_3 \longrightarrow CD_3COCH_3 + CH_3 \qquad (10)$$

as compared with

$$CD_3 + CH_3COCH_3 \longrightarrow CD_3H + CH_3COCH_2 \qquad (18)$$

The mass spectrometer analyses for the isotopic acetones produced in the pyrolysis of this mixture are given in Table III.

TABLE III

THE THERMAL DECOMPOSITION OF MIXTURES OF CD_3CDO (33%) AND CH_3COCH_3 (67%) AT 550° AND AN INITIAL TOTAL PRESSURE OF 250 MM.

Manometric and mass spectrometric measurements.

		10	11	12
% pressure increase during pyrolysis		10.5	16.0	22.5
Mole %	Acetone	94.1	90.1	88.8
	Acetone-d_1	7.6	8.8	9.9
	Acetone-d_2	0.7	0.8	0.9
	Acetone-d_3	.12	.20	.25
	Acetone-d_4	.10	.10	.15
	Acetone-d_5	.01	.01	.01
	Acetone-d_6	.01	.01	.01
CD_3H/CD_3COCH_3		89	84	94

The presence of all the isotopic acetones at all stages of the pyrolysis seems to indicate that the isotopic acetones are formed in exchange reactions of the type of 13, 14 and 15. If this were entirely true, it would exclude any appreciable attack on carbonyl carbon atoms by methyl radicals. However, even if all the acetone-d_3 is formed in 10, the CD_3H/CD_3COCH_3 ratio indicates that about one methyl radical in 90 reacts according to 10 as compared with 18.

5. **The Reaction of Methyl Radicals with Carbon–Carbon Doubly Bonded Carbon Atoms. The Thermal Decomposition of Mixtures of CD_3CDO (31%) and $CH_3CH{=}CH_2$ (69%).**—The reaction considered in the pyrolysis of this mixture at 550° is

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3CH{=}CH_2 + CH_3 \qquad (11)$$

as compared with

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3H + CH_3CH{=}CH \qquad (19)$$

The mass spectrometer analyses for the relative ion currents for masses 42 to 47 and the relative approximate concentration of the isotopic propylenes formed in the pyrolysis of this mixture was given in Table IV. The relative concentrations of the propylenes were obtained on the basis of a pure statistical calculation of the spectra. This calculation is an unsatisfactory method[14] for rigorous separation of the spectra but it is the only possible method at present and does seem to be a reasonable approximation. The Schissler, Thompson, Turkevich modification[13] could not be introduced into this calculation since there are three different carbon–hydrogen bonds in propylene and it would be impossible to guess the proper "a" and "b" factors for all of these.

TABLE IV

THE THERMAL DECOMPOSITION OF MIXTURES OF CD_3CDO (31%) AND $CH_3CH{=}CH_2$ (69%) AT 550° AND AN INITIAL TOTAL PRESSURE OF 225 MM.

Manometric and mass spectrometric measurements.

		13	14	15
% pressure increase during pyrolysis		8.7	17.1	22.0
% of relative ion currents:				
Mass 42 (ions: $C_3H_6^+$, $C_3H_4D^+$, $C_3H_2D_2^+$, $C_3D_3^+$)		90.6	88.3	78.1
Mass 43 (ions: $C_3H_5D^+$, $C_3H_3D_2^+$, $C_3D_3H^+$)		5.9	13.9	14.7
Mass 44 (ions: $C_3H_4D_2^+$, $C_3D_4^+$, $C_3D_3H_2^+$)		2.1	4.3	4.2
Mass 45 (ions: $C_3D_3H_3^+$, $C_3D_4H^+$)		1.5	2.6	2.7
Mass 46 (ions: $C_3D_4H_2^+$, $C_3D_5^+$)		0.11	0.20	0.28
Mass 47 (ions: $C_3D_5H^+$)		0.07	0.08	0.09
Mole %[a]	Propylene	93.3	84.0	82.4
	Propylene-d_1	4.1	10.6	12.3
	Propylene-d_2	0.9	2.4	2.1
	Propylene-d_3	1.5	2.7	2.9
	Propylene-d_4	0.1	0.2	0.3
	Propylene-d_5	0.1	0.1	0.1
$CD_3H/CD_3CH{=}CH_2$[b]		8.8	10.0	10.8

[a] Calculated on the basis of a pure statistical calculation of the spectra of the isotopic propylenes. [b] Calculated on the assumption that all the propylene-d_3 is $CD_3CH{=}CH_2$ formed in the reaction 11.

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(14) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **45**, 441 (1945); M. W. Evans, N. Bauer and J. Y. Beach, *J. Chem. Phys.*, **14**, 701 (1946).

In all cases the concentration of propylene-d_3 is significantly greater than that of propylene-d_2. This fact is strong evidence that 11 does take place. It is impossible to determine how much propylene-d_3 was formed in 11 or in successive mixing reactions of the type of 13, 14 and 15. However, since the concentrations of propylene-d_1, propylene-d_2 and propylene-d_3 would be successively smaller if they were formed in successive mixing reactions only, it would seem that approximately 80% of the propylene-d_3 is $CD_3CD{=}CH_2$ formed in reaction 11. This approximation introduces a degree of uncertainty into the conclusion. Accordingly, the $CD_3H/CD_3CH{=}CH_2$ ratio indicates that 5 to 10% of the methyl radicals reacting with propylene do so according to 11 as compared with 19.

Conclusion

In this work a general method has been developed to determine the relative speeds with which methyl radicals attack hydrogen atoms or other atoms in an organic molecule. The method consists in principle of pyrolyzing some CD_3 radical source, such as CD_3CDO, so that the CD_3 radicals attack various compounds of the type RCH_3. The concentrations of CD_3H and CD_3R produced in the reactions

$$CD_3 + RCH_3 \longrightarrow CD_3H + RCH_2 \tag{20}$$
$$CD_3 + RCH_3 \longrightarrow CD_3R + CH_3 \tag{21}$$

are interpreted as a measure of the relative frequency of hydrogen abstraction and attack on another atom in the organic molecule.

One difficulty inherent in the method is that it is impossible to distinguish between RCD_3 formed in 21 and the trideuterated product, of the same molecular weight as RCD_3, formed in mixing reactions of the type of 13, 14 and 15. The results with regard to attack on a shielded carbon atom, on an oxygen atom, and on a carbonyl carbon atom are measures of the maximum possible relative speeds of

$$CD_3 + CH_3CH_3 \longrightarrow CD_3CH_3 + CH_3 \tag{7}$$
$$CD_3 + CH_3OCH_3 \longrightarrow CD_3OCH_3 + CH_3 \tag{9}$$
$$CD_3 + CH_3COCH_3 \longrightarrow CD_3COCH_3 + CH_3 \tag{10}$$

as compared with the hydrogen abstraction reactions 12, 17 and 18. Accordingly, 7, 9 and 10 occur to less than one part in 1500, 2500 and 90, respectively, as compared with hydrogen abstraction. Since hydrogen abstraction predominates to such an extent in these reactions, the results indicate that in the hydrogen abstraction studies[15] on these classes of compounds any inherent error introduced by reactions of the general type of 21 is not appreciable.

The attack on a carbon–carbon doubly bonded carbon atom represents a different situation. Even if considerable propylene-d_3 is produced in successive mixing reactions, at least 5% of the methyl radicals enter into reaction 11

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3CH{=}CH_2 + CH_3 \tag{11}$$

as compared with hydrogen abstraction. This result indicates that an error has been introduced into the hydrogen abstraction studies on compounds in which there is a carbon–carbon double bond; it is impossible to determine the effect this error has on the calculation of the activation energy of hydrogen abstraction because the activation energy of 11 is not known.

Acknowledgment.—I wish to thank Dr. F. O. Rice for his helpful suggestion in all phases of this work and Ronald B. Ingalls for helpful discussions concerning the experimental details.

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[15] A. F. Trotman-Dickenson, *Quart. Revs.*, **VII**, 198 (1953); F. O. Rice and R. E. Varnerin, THIS JOURNAL, **77**, 221 (1955); J. R. McNesby, T. W. Davis and A. S. Gordon, *ibid.*, **76**, 824 (1954); J. R. McNesby and A. S. Gordon, *ibid.*, **76**, 1416, 4196 (1954).

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Trimethylene Oxide[1]

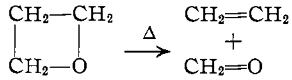
BY D. A. BITTKER AND W. D. WALTERS

RECEIVED OCTOBER 28, 1954

The thermal decomposition of trimethylene oxide has been studied in the temperature range from 420 to 460° at initial pressures of 54–330 mm. with and without the presence of nitric oxide, propylene or toluene. In the presence of an inhibitor the decomposition in the early stages proceeds according to the equation $C_3H_6O \rightarrow C_2H_4 + CH_2O$. In the absence of an inhibitor the trimethylene oxide disappears approximately 10% faster and significant quantities of the ethylene and formaldehyde undergo subsequent reactions. Experiments with a change in the amount or nature of the surface showed that the trimethylene oxide decomposition under the conditions used is predominantly homogeneous. The experimentally determined orders are 1.0 and 1.1 for the decomposition with and without nitric oxide as an inhibitor. The activation energy is 60 ± 1 kcal./mole in either case, and on the basis of the calculated first order constants for 100 mm. experiments frequency factors of 6.1×10^{14} and 6.6×10^{14} sec.$^{-1}$ were obtained for the decomposition in the presence and absence of nitric oxide.

Introduction

There appears to have been no previous report of an investigation of the homogeneous thermal decomposition of trimethylene oxide, but the following type of ring cleavage might have been expected for the over-all reaction[2]



(1)

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[1] Financial support for the initial phases of this study was received from the Office of Naval Research. Abstracted from the Ph.D. thesis submitted by D. A. Bittker who held a Beaunit Mills Fellowship during 1951–1952.

[2] This formulation of the over-all reaction does not mean that a biradical may not be an intermediate. For a consideration of the ring cleavage of cyclic compounds on the basis of the principle of least motion see F. O. Rice and M. T. Murphy, THIS JOURNAL, **64**, 898 (1942).