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

$$CD_3 + RCH_3 \longrightarrow CD_3H + RCH_2 \qquad (20)$$
$$CD_3 + RCH_3 \longrightarrow CD_3R + CH_3 \qquad (21)$$

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

$$CD_3 + CH_3CH_3 \longrightarrow CD_3CH_3 + CH_3 \qquad (7)$$
$$CD_3 + CH_3OCH_3 \longrightarrow CD_3OCH_3 + CH_3 \qquad (9)$$
$$CD_3 + CH_3COCH_3 \longrightarrow CD_3COCH_3 + CH_3 \qquad (10)$$

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

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

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]

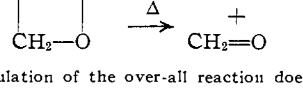
BY D. A. BITTKER AND W. D. WALTERS

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]



$$\begin{array}{l}CH_2{-}CH_2\\ |\qquad\ \ |\\ CH_2{-}O\end{array} \xrightarrow{\Delta} \begin{array}{c}CH_2{=}CH_2\\ +\\ CH_2{=}O\end{array} \qquad (1)$$

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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).

This type of reaction is quite analogous to that already observed for another four-membered ring compound, namely, cyclobutane, which appears to decompose homogeneously at 430–480° to yield two molecules of ethylene by a first-order reaction with no evidence of free radical chain processes.[3]

On the other hand, two cyclic ethers closely related to trimethylene oxide, *viz.*, tetrahydrofuran[4] and ethylene oxide,[5] have been found to decompose by different mechanisms, neither of which is simple. It was of interest, therefore, to study the thermal decomposition of trimethylene oxide.

Experimental

Materials.—Trimethylene oxide, prepared by the reaction of γ-chloropropyl acetate with hot potassium hydroxide, was purchased from the Farchan Research Laboratories and treated under vacuum with potassium hydroxide solution, potassium hydroxide pellets, anhydrous calcium sulfate and freshly cut sodium metal in that order. In certain cases the material was treated with vacuum-distilled sodium. After fractionation in an 85 cm. Lecky–Ewell column all samples which had been given a thorough sodium treatment gave similar experimental results. During the fractionation a slow stream of dry 99.99% nitrogen was passed through the column to keep the trimethylene oxide out of contact with air. A middle fraction, free from aldehydes and peroxides, was taken and stored under vacuum at −78° until used. The refractive indices of the middle fractions from two such purifications were $n^{22.9}\text{D}$ 1.3907 and $n^{23.0}\text{D}$ 1.3905. These values are in good agreement with those reported in the literature[6] (Noller's value $n^{23}\text{D}$ 1.3905).

A sample of trimethylene oxide, prepared in this Laboratory from γ-chloropropyl acetate kindly supplied to us by Dr. C. F. H. Allen of the Eastman Kodak Company, gave after purification results in good agreement with those obtained using the Farchan material. All samples of trimethylene oxide gave essentially identical infrared absorption curves.

Nitric oxide from the Matheson Company was purified by three distillations from −158 to −196°. In several experiments nitric oxide prepared earlier in this Laboratory and recently purified was used. Results were the same for both samples. C.P. propylene (99.5%) was purchased from the Ohio Chemical and Manufacturing Company. Merck reagent grade toluene was dried over anhydrous calcium sulfate and then stored under vacuum. Ethylene oxide was supplied to us by Dr. D. R. Stull of the Dow Chemical Company. Ordinarily the materials were thoroughly degassed at −196° before use.

Apparatus and Method.—The furnace and temperature control used in this static investigation were similar to those employed previously.[7] The temperature was measured with a platinum, platinum–13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. A heated stopcock, lubricated with "Myvacene-S" stopcock grease, was used next to the reaction vessel. With added nitric oxide, propylene or toluene the gas to be added was introduced into the reaction vessel before the trimethylene oxide. The effect of surface was studied by installing a vessel packed with thin-walled Pyrex tubes which increased the surface to volume ratio by a factor of about 30 over the ordinary reaction vessel.

Analyses.—By the use of the following procedures formaldehyde was identified as an important intermediate product in the decomposition of trimethylene oxide: (a) With an aqueous solution of the decomposition products the Lebbin resorcinol test for formaldehyde[8] gave a positive color change; the Lewin test[9] for acetaldehyde and higher aldehydes gave a negative reaction. (b) Polarograms obtained with aqueous solutions of the products showed one wave only with a half-wave potential corresponding to that obtained with a known solution of formaldehyde and to the literature value for formaldehyde.[10] The absence of a second wave at a more negative potential indicated that neither acetaldehyde nor propionaldehyde was present.

The polarographic technique was adapted also for quantitative analysis according to the method of Whitnack and Moshier.[10] The difference in the values of the diffusion current at −1.4 and −1.9 volts *vs.* pool was found to be proportional to the formaldehyde concentration. A standard formaldehyde solution of approximately the same concentration as the unknown was always analyzed along with the latter. To check this method a colorimetric technique involving the reaction of formaldehyde with chromotropic acid[11] was employed also in six of the decomposition experiments. Results from the two methods were generally in good agreement, and it is believed that the formaldehyde analyses usually have an over-all error no greater than ±5%.

The gaseous products of the reaction were analyzed by the following methods: (a) infrared absorption, (b) mass spectrometric analysis, and (c) conventional gas absorption techniques. In the earlier experiments hydrogen and carbon monoxide were determined by oxidation over heated copper oxide, and the hydrogen and carbon monoxide were found to constitute 100 ± 1% of the non-condensable gases (∼98–99% in a mass spectrometric analysis). The carbon monoxide from most of the later experiments was absorbed in Cosorbent reagent from the Burrell Corporation and the remainder of the gas designated as hydrogen. Before the gas analysis any nitric oxide present was usually removed by reaction with a 16% (by weight) aqueous solution of sodium sulfite.

In four experiments[12] the amount of trimethylene oxide undecomposed at a given time was determined (with an error of approximately 5%) by treating the remaining starting material with a saturated solution of magnesium chloride containing an excess of standard sulfuric acid, in a modification of the Lubatti[13] method for determining ethylene oxide.

To obtain an indication of the presence of ketenes or other acidic products the reaction mixtures from three experiments at 450° were dissolved in water, but no detectable amount of acid constituents was found by titration of the solutions with standard alkali.

Results and Discussion

Pressure–Time Data.—Curve 1 in Fig. 1, which represents a typical pressure–time curve, indicates that the decomposition of pure trimethylene oxide proceeds without an induction period. The ratio of final to initial pressure at 460° is 2.32, showing that more than two molecules of final product are formed from each trimethylene oxide molecule. Likewise, the analyses for trimethylene oxide made during the decomposition showed that, for trimethylene oxide alone, the pressure increase is somewhat greater than the pressure of trimethylene oxide decomposed.

Trimethylene oxide was decomposed also in the presence of various free radical chain reaction inhibitors, namely, nitric oxide, propylene and toluene, to determine the importance of free radicals in the decomposition process. Curve 2 in Fig. 1 shows the effect of an inhibitor on the pressure–time

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[3] C. T. Genaux and W. D. Walters, This Journal, **73**, 4497 (1951); C. T. Genaux, F. Kern and W. D. Walters, *ibid.*, **75**, 6196 (1953); F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S.*, **38**, 937 (1952).

[4] C. H. Klute and W. D. Walters, This Journal, **68**, 506 (1946).

[5] K. H. Mueller and W. D. Walters, *ibid.*, **73**, 1458 (1951); **76**, 330 (1954).

[6] C. R. Noller, *Org. Syntheses*, **29**, 92 (1949); S. Searles, This Journal, **73**, 124 (1951); C. G. Derick and D. W. Bissell, *ibid.*, **38**, 2478 (1916).

[7] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[8] J. F. Walker, "Formaldehyde," Reinhold Publ. Corp., New York, N. Y., 1944, p. 246.

[9] L. Lewin, *Ber.*, **32**, 3388 (1899).

[10] G. C. Whitnack and R. W. Moshier, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 496 (1944).

[11] C. E. Bricker and H. K. Johnson, *ibid.*, **17**, 400 (1945).

[12] The analyses were performed by Mrs. Virginia Ogden Fenn in this Laboratory.

[13] O. F. Lubatti, *J. Soc. Chem. Ind.*, **54**, 424T (1935).

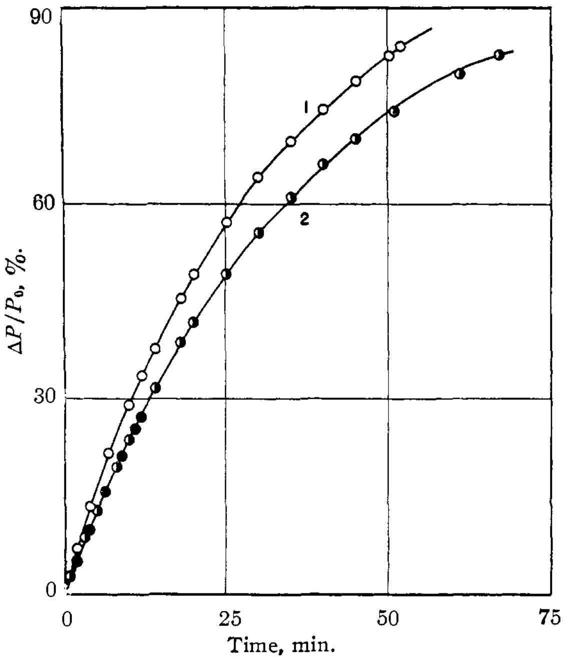

Fig. 1.—Pressure–time curves for the decomposition of trimethylene oxide at 450°: ○, 218 mm. trimethylene oxide; ◑, 2.2 mm. nitric oxide and 216 mm. trimethylene oxide; ●, 152 mm. propylene and 217 mm. trimethylene oxide. P_0 denotes the initial pressure of trimethylene oxide.

curve and the results in Table I indicate that each of these inhibitors, when present in sufficient quantity, decreases the rate of pressure rise of trimethylene oxide to the same extent (*i.e.*, a decrease of about 20%). From the data in Table I and similar results at 460° it was concluded that the addition of 1% nitric oxide is sufficient to give maximum inhibition under the conditions used.

When 2% by volume of ethylene oxide is added to the trimethylene oxide at 430°, the rate of pressure rise is increased about fourfold, as can be seen from the data at the bottom of Table I. Part of this increase can be accounted for by the acceleration of the decomposition of the formaldehyde present as an intermediate, but the magnitude of the acceleration shows that trimethylene oxide itself can undergo a radical sensitized decomposition.

The results from experiments in the packed vessel with thirty times the surface to volume ratio are also shown in Table I. The small decrease in the rate of pressure rise for trimethylene oxide alone is presumably due to the fact that the added surface increases the rate of destruction of free radicals and atoms. In the presence of nitric oxide the rates in the packed and the unpacked vessel are almost the same. In view of the fact that in no case is a large effect observed, compared to the thirty-fold increase in surface, it can be concluded that the reaction in the unpacked vessel is a gas-phase reaction. Another indication of the homogeneity of the decomposition was obtained in several preliminary experiments carried out in the presence of nitric oxide in a vessel coated with potassium chloride and with added propylene in a bulb coated with boric acid. The coating on the inner walls produced no significant change in the rate.

TABLE I

THERMAL DECOMPOSITION OF TRIMETHYLENE OXIDE IN THE PRESENCE OF ADDED SUBSTANCES

Temp., °C.	$P_{0\,C_3H_6O}$, mm.	Added subst.	$P_{A.S.}$, mm.	t'_{25},[a] min.
450	102[b]	..	0	8.8[b]
450	119	NO	1.0	11.0
450	110	NO	1.8	10.8
450	114	NO	9.5	10.8
450	112	C_7H_8	71	10.5
450	114	C_3H_6	76	10.5
450	217	C_3H_6	152	11.0
450	216	NO	2.6	10.7
430	215[c]	..	0	27.9[c]
430p	207	..	0	31.9[d]
430	211	NO	2.5	35.6
430p	210	NO	3.0	33.5[d]
430	104	..	0	29.3
430	111	$(CH_2)_2O$	2.0	7.5

[a] Experimentally observed time for 25% pressure increase uncorrected for dead space. [b] In this case average of three experiments. [c] Data at 430° represent the average of two experiments in each case. [d] Packed bulb with a thirty-fold increase in the surface to volume ratio.

Products of the Reaction.—The products have been analyzed for experiments in which trimethylene oxide was decomposed with and without an added inhibitor. Figure 2 shows the results of formaldehyde analyses made at increasing percentages of decomposition. Table II summarizes other formaldehyde analyses made after an essentially constant amount of pressure increase (~28%) but under different experimental conditions. The data from most of the analyses of the gaseous products after removal of formaldehyde are given in Table III.

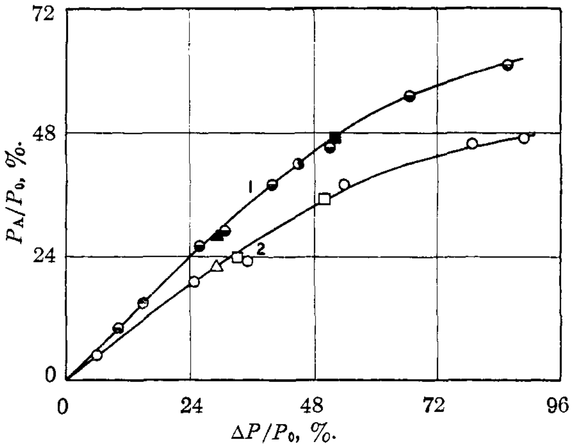

Fig. 2.—Formaldehyde present during the decomposition of trimethylene oxide: P_0 = ~215 mm.; P_A, pressure of formaldehyde present. 440°: △, pure; ▲, 1.2% nitric oxide added. 450°: ○, pure; ◒, 1–1.5% nitric oxide added; ◓, 153 mm. propylene added. 460°: □, pure; ■, 1.5% nitric oxide added. ◑, 107 mm. trimethylene oxide and 2.5 mm. nitric oxide at 450°.

On the basis of the various types of evidence which will be cited below it appears that in the presence of nitric oxide the decomposition during the initial stages yields ethylene and formaldehyde without significant amounts of secondary products. For curve 1, Fig. 2 the value of P_A/P_0 is equal to

TABLE II

AMOUNTS OF FORMALDEHYDE AT VARIOUS INITIAL PRESSURES AND TEMPERATURES

Temp., °C.	P_0, mm.	Added subst.	$P_{\text{A.S.}}$, mm.	$\Delta P/P_0$ [c,d] %	$P_{\text{H}_2\text{CO}}/P_0$, %
450	282	NO	6.4	29	27
450	210	NO	2.2	26	26[a]
450	125	NO	2.1	26	26
450	59	NO	2.5	28	27
460	226	NO	3.3	29	27
430	216	NO	2.5	28	27
430p	207	NO	2.3	26[b]	26[b]
420	163	NO	2.1	28	26
450	217	C_3H_6	152	28	27
450	114	C_3H_6	76	29	28
450	112	C_7H_8	71	27	25
450	62	C_7H_8	40	27	27
450	147	..	...	29	21[a]
450	107	..	...	29	22[a]
450	56	..	...	28	22[a]
460	214	..	...	27	20
440	220	..	...	28	21
430	213	..	...	28	20
430p	205	..	...	27[b]	24[b]
420	216	..	...	28	20

[a] Average of polarographic and colorimetric methods; other values from polarographic method. [b] Packed vessel. [c] ΔP is the pressure increase at the time of removal for analysis. [d] P_0 denotes the initial pressure of trimethylene oxide.

TABLE III

GASEOUS PRODUCTS FROM THE DECOMPOSITION OF TRIMETHYLENE OXIDE

$P_0\text{C}_3\text{H}_6\text{O}$, mm.	$P_0\text{NO}$, mm.	ΔP, mm.	P_{H_2}, mm.	P_{CO}, mm.	$P_{\text{C}_2\text{H}_4}$, mm.	$P_{\text{res.}}$,[a] mm.
			Temp., 430°			
205	2.6	55.0	0.4	1.1	52.6	0.6
213[f]	3.0	54.4p	0.2	1.0	53.7	0.6
218	0	56.9	6.0	8.7	47.0	3.4
209[f]	0	54.8p	1.1	2.1	52.1	1.0
			Temp., 450°			
204	2.4	53.9	0.3	0.7	51.4	0.5
202	2.3	53.9	...1.0[d]...		53.1[b]	0.0
219	2.6	114	0.9	3.8	97.6	3.2[c]
56	2.3	14.5	...0.1[d]...		13.8	0.2
56	0	14.6	1.0	1.1	12.6	0.6
216	0	56.7	6.1	7.5	48.5	2.9
219	0	59.1	7.1[b]	8.0[b]	51.3[b]	2.4[b,e]
167	0	89.8	8.2	14.7	74.5	6.7
205	0	156	16.2	37.6	119	18.4
205	0	177	20.5	52.5	131	25.5
			Temp., 460°			
217	2.5	61.0	0.2	0.7	53.6	2.7[c]

[a] Gases non-volatile at −196° and volatile at −137°, not absorbed in activated sulfuric acid, mainly C_2H_6 plus traces of unremoved C_2H_4, CO and H_2. [b] Gases analyzed mass spectrometrically by the Consolidated Engineering Corporation. [c] Value includes unreacted nitric oxide. [d] Total non-condensable fraction. [e] Represents C_2H_6 determined by the mass spectrometer. Gases other than C_2H_4, C_2H_6 and H_2 in the −137° fraction amounted to less than 0.2%. [f] Packed vessel.

$\Delta P/P_0$ until approximately 30% decomposition as would be expected according to equation 1 when there is no appreciable disappearance of formaldehyde. The data in Table II give evidence that with an inhibitor present the near equality of the pressure of formaldehyde and the pressure increase (for $\Delta P/P_0 = 28\%$) exists over the temperature range 420–460° and at pressures from 60 to 280 mm. In this same region the results in Table III show that with added nitric oxide the only other important gaseous product is ethylene. In the inhibited decomposition carried to 27% reaction at 450° examination of the reaction products volatile at −137° and below (other than formaldehyde) gave the following results. The amount of non-condensable gases (H_2 + CO) was only 2% of the total quantity of condensable products and of the latter ethylene constituted at least 99% (~99.9% by a mass spectrometric analysis). In the later portions of the decomposition subsequent reactions result in the loss of formaldehyde and cause the final pressure at 460° to reach a value of about $2.28P_0$.

In the absence of an inhibitor the major portion of the decomposition can be represented by equation 1, but it is apparent that other reactions are occurring since the pressure of formaldehyde is smaller than the pressure increase even during the initial stages of the reaction (curve 2, Fig. 2). The results in Table II indicate that although the formaldehyde pressure is smaller than the pressure increase, the ratio of the quantities remains constant over the temperature and pressure regions studied. An exception was observed in the case of the packed bulb where the increased surface partially suppresses the processes leading to the disappearance of formaldehyde. The gas analyses (Table III) show that without an inhibitor appreciable quantities of ethane, hydrogen and carbon monoxide are formed as a result of secondary reactions of ethylene and formaldehyde or by side reactions.

In order to obtain information concerning the consistency of the data and the possibility of the formation of unidentified products, the analytical results have been employed for several comparisons, as shown in Table IV. It is seen that the pressure of ethylene plus ethane ($P_{\text{cond.}}$) is approximately equal to the sum of the pressures of carbon monoxide and formaldehyde, the latter having been obtained from the data in Fig. 2 and Table II. The agreement between these values shows that in the initial stages of the decomposition where the formaldehyde concentration is not high, no significant quantities of formaldehyde react to form methanol and carbon monoxide. If one assumes that the average of the values shown in columns 3 and 4 in Table IV represents the amount of trimethylene oxide decomposed, the pressure increase can be calculated by the use of the analyzed amounts of products formed. A comparison between the calculated pressure increases ($\Delta P_{\text{t}}^{\text{calc.}}$) and the observed pressure increases ($\Delta P_{\text{t}}^{\text{obs.}}$) at the time of re-

TABLE IV

DECOMPOSITION OF TRIMETHYLENE OXIDE AT 450°

$P_0\text{C}_3\text{H}_6\text{O}$, mm.	$P_0\text{NO}$, mm.	$P_{\text{cond.}}$, mm.	$P_{\text{H}_2\text{CO}+\text{CO}}$, mm.	$\Delta P\text{t}$, mm. Obsd.	Calcd.
204	2.4	51.9	52.7	53.9	52.7
202	2.3	53.1	52.8	53.9	53.2
56	2.3	14.0	14.2	14.5	14.1
215	0	51.4	50.7	56.7	57.1
45	0	13.2	12.5	14.6	13.8

moval (t) for analysis is shown in columns 5 and 6 of Table IV.

From the data shown in Tables III and IV it appears that in the early portion of the inhibited decomposition the pressure increase is very nearly a direct measure of the amount of trimethylene oxide disappearing. Moreover, even without added inhibitor the amount of decomposition at about the quarter-time, as indicated by the product analyses, bears a rather constant relationship (~90%) to the pressure increase for the experimental range studied. Thus the rate of pressure rise in the initial stages seems to be a satisfactory relative measure of the rate of decomposition of trimethylene oxide for the determination of the kinetics.

Order of the Reaction.—Experiments with and without added nitric oxide were performed at 450° in order to observe the change in rate with initial pressure over the range 50–330 mm. Plots of log t_{25} *vs.* log P_0 and log $(\mathrm{d}P/\mathrm{d}t)_0$ *vs.* log P_0 are shown in Fig. 3. The quantity t_{25} is the time (min.) for 25% pressure increase corrected for dead space. Since $t_{25} \propto P_0^{1-n}$ where n is the order of the decomposition, the values of n were determined from curves 1 and 2 and found to be 1.0 for the reaction with added nitric oxide and 1.1 for the decomposition without inhibitor. The slopes of curves 3 and 4 showing the change in the logarithm of the initial rate of pressure rise $[(\mathrm{d}P/\mathrm{d}t)_0]$ with the logarithm of the initial pressure (P_0) also give values of 1.0 and 1.1 for the orders in the presence and absence of nitric oxide, respectively. Dead space corrections[14] were applied to the values of the initial rate.

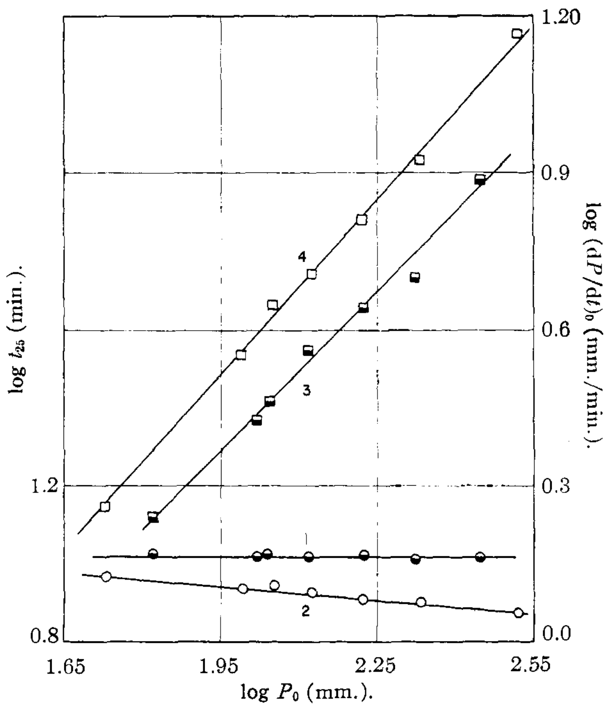

Fig. 3.—Effect of initial pressure upon the rate of decomposition of trimethylene oxide at 450°. log t_{25}: ○, pure; ◒, 1.8–2.1 mm. nitric oxide added. log $(\mathrm{d}P/\mathrm{d}t)_0$: □, pure; ⬓, 1.8–2.1 mm. nitric oxide added.

It has been observed that during an experiment the reaction with nitric oxide present obeys a first-order law up to at least 40% decomposition as evidenced by the linearity of a plot of log $(P_0 - \Delta P)$ *vs.* time.

Temperature Coefficient.—Figure 4 shows plots of log t_{25} *vs.* $1/T$ with trimethylene oxide pressures of 100–110 mm. The activation energies were evaluated by visual determination of the best lines through the data and by the method of least squares. The results indicated that the same activation energy, 60 ± 1 kcal./mole, can be assigned to the decomposition with or without nitric oxide.

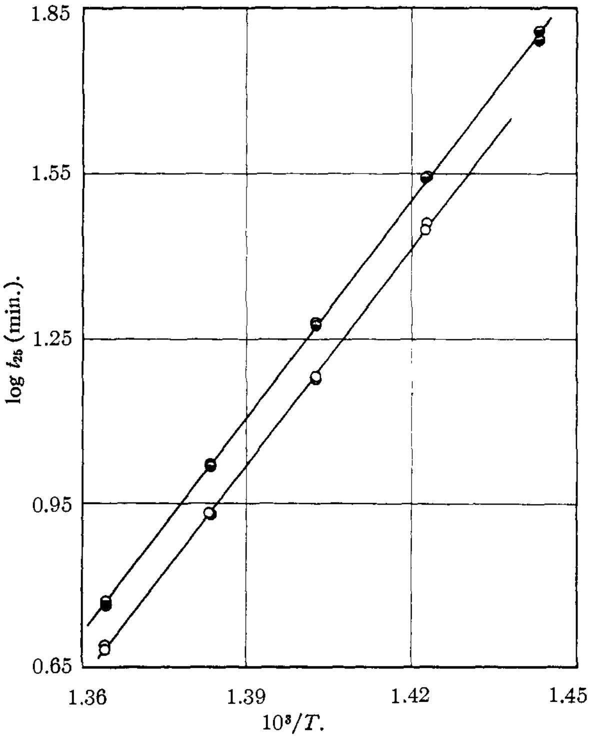

Fig. 4.—Change of the time for 25% pressure increase with temperature: initial pressure of trimethylene oxide, 100–110 mm. ○, pure; ◒, 1–6% nitric oxide added, usually ~1.8% NO.

Since the analytical results showed that on the average a 25% pressure increase corresponds to 24.6% decomposition in the experiments with inhibitor and 22.3% decomposition in the experiments without inhibitor, first order rate constants can be calculated from the values of t_{25} and the observed percentage decomposition. On the basis of the activation energy given above the first-order rate constant for the decomposition with added nitric oxide can be expressed as $k = 6.1 \times 10^{14} e^{-60000/RT}$ sec.$^{-1}$ and for the normal decomposition at a pressure of 100–110 mm. without inhibitor as $k = 6.6 \times 10^{14} e^{-60000/RT}$ sec.$^{-1}$. By equating the experimental frequency factor to $\kappa e(kT/h)\, e^{\Delta S\ddagger/R}$ (with κ assumed to be one) a value of 5.4 cal./deg. mole has been calculated for the entropy of activation of the decomposition at 450° with added nitric oxide.

For the reaction in the presence of nitric oxide the rate constants were also calculated from the

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[14] M. Letort, A. Boyer and M. Niclause, *J. chim. phys.*, **49**, 337 (1952).

initial rates of pressure rise for twelve experiments from 420 to 460°. The values calculated by this second method agreed with those obtained from t_{25} within ±2.2% on an average.

Discussion.—The reaction in the presence of an inhibitor will be considered first since it appears to be simpler; moreover, the portion of the reaction which is not inhibited by nitric oxide also accounts for most of the decomposition in the absence of an inhibitor. The results indicate that in the temperature range used for this study the decomposition of trimethylene oxide which takes place with sufficient inhibitor present proceeds in the gas phase as a first order reaction without involving a free radical chain mechanism to an appreciable extent. One piece of evidence supporting the idea that essentially all free radical processes have been suppressed is the fact that nitric oxide, propylene or toluene produces the same limiting rate of reaction. Another type of evidence is the observation that up to 30% decomposition the formaldehyde does not decompose significantly. It has been observed that formaldehyde decomposes rapidly at 380–440° in the presence of free radicals, but reacts only slowly in their absence.[15] In the later stages of the reaction the free radical chain processes do not appear to be completely inhibited. Since the products in the early portion of the trimethylene oxide decomposition do not contain propionaldehyde and do not correspond to the products of the thermal decomposition of propionaldehyde,[16] the trimethylene oxide decomposition in the presence of nitric oxide does not appear to proceed by an initial isomerization to propionaldehyde. However, the present study does not permit a decision concerning whether a trimethylene oxide molecule yields ethylene and formaldehyde directly or forms a discrete biradical as an intermediate. With respect to the manner of ring cleavage, the order and the activation energy, the non-chain decomposition of trimethylene oxide bears considerable resemblance to the decomposition of cyclobutane.[3]

The decomposition of trimethylene oxide in the absence of inhibitor is complex. That a portion of the decomposition is due to free radical processes is indicated by the fact that part of the reaction can be suppressed either by the addition of an inhibitor or by an increase in the surface to volume ratio. Since in the neighborhood of 400–450° formaldehyde does not decompose readily without added free radicals, the considerable decomposition of formaldehyde is evidence that in the absence of an inhibitor free radicals are present. The following results indicate that ethane which amounts to 4–5% of the C_2 fraction at 25% decomposition is probably formed by free radical reactions rather than by a molecular reaction between ethylene and formaldehyde. It has been observed that pure ethylene does not react with formaldehyde at an appreciable rate at 415°[15]; moreover, ethane does not occur to any significant extent in the products of the decomposition of trimethylene oxide in the early portion of the reaction with nitric oxide present. It has been found in the present work that the addition of free radicals at 437° from decomposing ethylene oxide causes a chain reaction to take place in a mixture of 95 mm. ethylene and 105 mm. formaldehyde resulting in the formation of carbon monoxide and hydrogen as non-condensable gases. Since the hydrogen amounted to only 32% of the carbon monoxide, most of the remainder of the hydrogen probably disappeared in the hydrogenation of ethylene.

The following reactions, all of which are known to occur in the temperature range used, can be written to explain the formation of carbon monoxide, ethane and hydrogen

$$\begin{gathered} R + H_2CO \longrightarrow RH + HCO \\ HCO \longrightarrow H + CO \\ H + H_2CO \longrightarrow H_2 + HCO \\ H + C_2H_4 \longrightarrow C_2H_5 \\ C_2H_5 + M \longrightarrow C_2H_6 + R' \end{gathered}$$

where M is a molecule with an abstractable hydrogen.

The free radicals not only promote the secondary reactions of formaldehyde and ethylene but also accelerate slightly the decomposition of trimethylene oxide itself. This is shown by the experiments in which free radicals from ethylene oxide were added to trimethylene oxide at 430° and by the fact that the rate of trimethylene oxide disappearance with added inhibitor is smaller than that without inhibitor. If it is assumed that a radical abstracts a hydrogen atom from trimethylene oxide leaving a C_3H_5O radical which subsequently decomposes, satisfactory chain-carrying steps can be written to explain the 10% of the decomposition which proceeds as a free radical chain reaction.

Concerning the chain-initiating reaction no definite experimental evidence has been obtained, but it appears that some of the trimethylene oxide molecules can decompose into free radicals. There is the possibility that a trace of undetected and unremoved impurity produces the free radicals. This does not appear probable since similar rates are observed for different samples of trimethylene oxide after thorough purification.

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[15] Unpublished results of J. E. Longfield obtained in this Laboratory.

[16] A. Boyer and M. Niclause, *J. chim. phys.*, **49**, 354 (1952).