FREE RADICALS BY MASS SPECTROMETRY PART II.—THE THERMAL DECOMPOSITION OF ETHYLENE OXIDE, PROPYLENE OXIDE, DIMETHYL ETHER, AND DIOXANE*

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The thermal decompositions of ethylene oxide, propylene oxide, dimethyl ether and dioxane in a stream of helium have been studied by means of a mass spectrometer designed to permit the measurement of free radical concentrations. With ethylene oxide it was found that each molecule decomposing gave rise to about 0.6 methyl radicals, and in propylene oxide the corresponding number had a lower limit of 0.36. Methyl radicals were also abundant in the decomposition of dimethyl ether. In the decomposition of dioxane only a small number of methyl radicals were found, and they probably come from a secondary reaction. No other radicals were detected, although formaldehyde was found to be a comparatively long-lived intermediate in the decomposition of dimethyl ether. The effect of the addition of nitric oxide on the decomposition of ethylene oxide was examined. Average values for the collision efficiency of the nitric oxide+methyl radical reaction at 950°, and the methyl radical recombination reaction from 925° to 975° were found to be 2×10^{-4} and 2.5×10^{-2} respectively.

A number of studies of reaction intermediates in gaseous reactions have been made using mass spectrometers. A study of relatively long-lived intermediates in the thermal decomposition of dimethyl ether and acetaldehyde was carried out by Leifer and Urey.¹ The detection of free radicals such as methyl from the pyrolysis of methane and lead tetramethyl, methylene from diazomethane, allyl from propylene, and ethyl from ethane, as well as a study of the role of intermediates in low pressure flames, was made by Eltenton.^{2, 3} The measurement of the ionization potential of methyl radicals produced by the thermal decomposition of lead tetramethyl was carried out by Hipple and Stevenson.⁴ Robertson ⁵ detected methyl and ethyl radicals in the pyrolysis of methane and ethane on a platinum filament.

For the detection of radicals, the authors mentioned above made use of the fact that the ionization potential of a free radical is less than its appearance potential from a given compound by an amount of energy equal to the sum of the strength of the bond broken and the kinetic energy of the fragments formed by electron impact. In most cases the ion current due to R^+ formed by electron

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dissociation of RR' will disappear at an electron energy a few volts higher than the ion current due to R^+ produced by ionization of the radical R already present from the thermal dissociation of RR'. By careful selection of an electron energy greater than the ionization potential of R but less than the appearance potential, the presence of the radical was demonstrated. However, because of the more or less exponential shape of the feet of the ionization efficiency curves a clear separation of the two processes results, in most cases, in a very low ionization efficiency (sensitivity) for the process

$$\mathbf{R} + \mathbf{e} \rightarrow \mathbf{R}^+ + 2\mathbf{e}$$
.

Since the ionization efficiency is not only low at these electron energies, but varies with the energy in a manner that is not easily calculated, these conditions are not very suitable for the quantitative determination of the concentration of the radicals. The reproducibility of the ionization efficiency at low electron energy is complicated further by the difficulty of maintaining constant the contact potential and the energy distribution of the electrons.

In the present work the method outlined above has been used for the qualitative detection of free radicals, but the quantitative measurements have been made by measuring the mass spectra using an electron accelerating potential of 50 V. Under these conditions the ionization efficiencies and the mass spectral patterns are almost independent of small changes in the electron energy. If all the reaction products which contribute to the radical peak are identified, these contributions can then be subtracted by reference to calibration spectra in the manner well known in the analysis of hydrocarbons.⁶ In this way a net peak height is obtained which is a measure of the partial pressure of the radical. The use of this method to obtain the sensitivity for methyl radicals formed by the thermal dissociation of mercury dimethyl and di-*tert*.-butyl peroxide has been described.⁷ A brief summary of this method is given below under the heading of *Calibration* for methyl radical sensitivity.

In the present work the thermal decompositions of ethylene oxide, propylene oxide, dimethyl ether, and dioxane have been examined by this method to determine the extent to which free radicals play a part. An analysis of the stable products was also made.

EXPERIMENTAL

THE REACTOR AND MASS SPECTROMETER.—A diagram of the reactor and the ion source of the mass spectrometer used in this work is shown in fig. 1. The reactor consisted of a quartz tube of 7 mm internal diameter which was heated by an element consisting of a sheet of tantalum 0.005 in. in thickness rolled into a cylinder 12.7 mm in diameter and held in this shape by lugs spotwelded at the edge. The upper end of the heating element fitted over, and was spotwelded to a steel tube which was bored out to make a sliding fit over the upper end of the quartz tube. The lower end of the element was spotwelded to the inside of a ring which made electrical contact to the outer steel jacket through four heavy iron legs. The legs were soft-soldered to the inside of the steel jacket after assembly. The lower end of the quartz tube extended to the lower edge of the ring. The expansion of the heating element was taken up by a bellows which was silver-soldered over a sliding joint in the upper steel tube. The furnace was surrounded by a radiation shield of thin quartz coated with aquadag. A thermocouple well of thin quartz tubing was sealed into the side of the quartz tube 2 cm from the lower end, and passed out through holes in the heating element and the radiation shield. A chromel-p alumel thermocouple was used to measure the temperature. The outer steel jacket was provided with a cooling coil of copper tubing through which water was passed. Electrical contact to the lower end of the heating element was made through this coil and to the upper end through the inner steel tube. A ring of glass sealed to two rings of Kovar prevented the short-circuiting of the element by the outer steel jacket.

The current required to heat the reactor to 1200° C was about 250 A at 4 V. This was supplied from a transformer consisting of eight turns of $\frac{1}{4}$ in. copper tubing wound on the core of a 50 A Variac. Electrical connection from this winding to the heating

element was made using $\frac{1}{4}$ in. copper tubing connected by pressure fittings. This enabled the transformer secondary to be cooled by circulating water, to prevent large temperature changes which would cause the temperature of the reactor to drift. The primary current to the 50 A Variac was controlled by a 10 A Variac operated from a 110 V line stabilized

FIG. 1.—Reactor and ion source.

by a Sorenson electronic regulator. This form of reactor was found to be quite satisfactory and did not have a large temperature lag. The temperature could be held within $\pm 1^{\circ}$ C for long periods. The effective length of the furnace, although rather uncertain, was taken to be 7 cm.

The flow of gas from the reactor into the mass spectrometer took place through a hole in a thin quartz thimble which projected into the heated zone of the reactor. The diameter of the hole was 30 microns and the thickness of the wall surrounding the hole was about 16 microns. The hole was formed by means of an electric spark as previously described,7 and was almost perfectly circular with smooth edges. The bottom of the thimble was thickened and ground flat, and was cemented to a silver disc with silver chloride. The disc was soft-soldered to a threaded steel cap which closed the end of the reactor. The major part of the gas entering the reactor passed out through the space around the outside of the heating element, but a small portion issued from the orifice in the quartz thimble into a region of very low pressure as a molecular beam which was directed into a hole 2 mm in diameter in the plate covering the ionization chamber. The distance from the orifice to the electron beam was about 1.5 cm.

The mass spectrometer itself 7 was a 90° sector type instrument using an ion source with drawing-out potentials as described by Nier,⁸ but with a modification to provide

for differential pumping of the filament chamber. The analyzer tube and the chamber into which the reactor and the ion source projected were pumped separately by high speed mercury diffusion pumps. The electronic controls for the mass spectrometer were similar to those described by Thode.⁹ Magnetic scanning and pen recording ¹⁰ were employed. The sensitivity of recording was such that an ion current of 3×10^{-14} A gave a deflection of 1 cm on the Speedomax recorder.

THE FLOW SYSTEM.—All the decomposition experiments were carried out in a stream of helium at pressures in the region of 10 mm. The flow of helium was regulated by a small metal needle valve opening from a 31. flask in which a pressure of about 10 cm of helium was maintained by a rough manostat. The flow of reactant gas was controlled by a metal needle valve opening from a trap in which a fixed pressure in the region of 5-15 cm of reactant was maintained by means of a freezing bath of an appropriate substance. By this means a flow of helium at about 10 mm pressure containing a partial pressure of a few microns of reactant could be held constant for an hour or more with a drift of only a few per cent. This could be allowed for by timing all measurements and using a linear time correction.

METHOD OF OPERATION.—A flow of helium containing a small partial pressure of reactant was passed through the reactor as described above, and mass spectra were obtained at several reactor temperatures below and through the range of temperature in which the reactant decomposed. The method of detection of methyl radicals from mercury dimethyl using an electron energy of about 11 V is shown in fig. 2. The mass 15 peak in the upper spectrum, which was obtained at 200° C where no decomposition occurred, was due to CH_3^+ formed from mercury dimethyl by electron dissociation.



This was the remainder of a peak which was over 100 times as large when measured using 50 V electrons. The peaks at 18 and 28 are those of residual water and carbon monoxide which are present in all spectra. The lower spectrum was obtained with the same electron energy but with the reactor at 800° C and with a contact time of $2\cdot1 \times 10^{-3}$ sec. The increase in the mass 15 peak corresponds to CH₃⁺ formed by the ionization of methyl radicals produced in the thermal decomposition of the mercury dimethyl. A trace of the ethane spectrum can be seen at the mass 28-30 region. This method was used for detecting radicals, but the quantitative measurements were made by measuring the spectra obtained with 50 V electrons, and subtracting the superposed spectra of the reaction products as described above.



FIG. 2.—Detection of methyl radicals from mercury dimethyl. The upper spectrum was obtained at 200° C, the lower at 800° C. The electron energy was 11 V.

CALIBRATION FOR STABLE PRODUCTS.—The mass spectral patterns of the reactants and the stable products were determined in separate experiments by passing through the reactor a stream of helium containing a convenient amount of the gas to be examined. By comparing spectra obtained at different reactor temperatures, it was found that in many cases the spectra changed slightly with temperature as previously reported for hydrocarbons.^{11, 12} For the reactants, this effect could not be measured over the whole temperature range since decomposition occurred. The mass spectral patterns of the reactants at the higher temperatures were obtained by extrapolation from lower temperatures.

In addition to the change in the patterns, it was found that the sensitivity for a given substance decreased with increasing temperature. This effect could be ascribed partly to the effect of temperature on the flow of gas through the orifice, and partly to the effect of increased molecular velocity on the ionization probability. Since the flow through the orifice was partly molecular and partly viscous at these pressures, the relation between sensitivity and temperature was not simple, and was obtained by calibration. The "temperature coefficient of sensitivity" measured in this way was applied as a correction to the partial pressures of the products measured at any temperature. This coefficient was in some cases as large as 0.50 for a range of 800° C.

The sensitivities for the reactants and products relative to that for methane were measured in separate experiments. Known proportions of methane and the gas in question were passed in a stream of helium through the reactor at a fixed temperature. These relative sensitivities were then related to the actual pressure in the reactor by measuring the sensitivity for a known partial pressure of methane, and could be expressed as a peak height per micron pressure.

CALIBRATION FOR METHYL RADICAL SENSITIVITY.—The ratio of the sensitivity for methyl radicals to that for methane with 50 V electrons was previously determined 7 by decomposing a known quantity of mercury dimethyl and by making a continuous analysis of the products, of which methyl was the major component. The stable products were ethane and methane. The net peak height at mass 15 due to methyl was obtained by subtracting from the total mass 15 peak the known contributions from methane, ethane, and mercury dimethyl. The sensitivity to methyl was then obtained by assuming a 100 % carbon balance. In order to be more independent of instrumental factors, this sensitivity was reported relative to that for methane. The value of sensitivity for CH₄ was 0.47 \pm 0.07.

MATERIALS.—The helium was of 99.8 % purity or better and was further purified by passing it through a charcoal trap immersed in liquid nitrogen. The oxygen content was reduced to less than 0.005 % by this means. The ethylene oxide was obtained from

the Matheson Co., the propylene oxide from the Eastman Kodak Co., the 1:4-dioxane from Anachemia Chemicals Ltd., and the dimethyl ether from the Ohio Chemical and Manufacturing Co. All these materials were purified by several distillations at reduced pressure.

RESULTS AND DISCUSSION

ETHYLENE OXIDE.—The decomposition of ethylene oxide was investigated in the temperature range 800° to 1000° . The rate constants given (at 850°) in table 1 show the reaction to be first order with respect to the partial pressure of the ethylene oxide, but the order appears to depend slightly on the helium pressure. The activation energy is independent of both ethylene oxide and helium pressures; a mean value of $42\cdot1$ kcal was obtained which is in closer agreement with that of Rice and Johnston ¹³ value for the split into free radicals (44 kcal) than with activation energies measured in static systems for the overall reaction.

TABLE 1.—EFFECT OF HELIUM AND ETHYLENE OXIDE PRESSURES ON k and E

helium pressure (mm)	ethylene oxide pressure (μ)	k at 850° C (sec ⁻¹)	activation energy (kcal)
5.0	5.68	42.4	41.6
10.0	1.64	54.6	41.0
15.0	1.37	55.7	41.2
15.0	1.58	54.1	42.5
15.0	10.98	55-2	43.8

The products of reaction, at three different temperatures and slightly differing times of contact, are given in table 2. The partial pressures of the products are given in microns. The reliability of the data is evaluated in table 3 which shows the amounts of carbon, hydrogen, and oxygen found in the products expressed as a percentage of the amount which should be present as calculated from the amount of ethylene oxide decomposed, e.g.,

% carbon found =
$$\frac{\Sigma(CH_3 + 2C_2H_6 + CH_4 + 2CH_2CO + CO)}{2(CH_2)_2O_{decomp.}} \times 100.$$

The carbon and oxygen balances are fairly good, but the hydrogen balance is particularly susceptible to slight changes in the relative amounts of the different products. The last column in table 3 shows the number of methyl radicals formed per ethylene oxide molecule decomposed. The values are based on the assumption that all the ethane formed comes from the recombination of two methyl radicals.

All the products listed have been reported previously.¹⁴⁻¹⁹ In particular methyl radicals were specifically reported by Rice and Johnston.¹³ Methylene radicals, first postulated by Fletcher and Rollefson,¹⁵ have never been detected

Table 2.—The thermal decomposition of $9{\cdot}24\mu$ of ethylene oxide in 15 mm helium

(Partial pressures of products are given in microns)

temp. (°C)	contact time (sec \times 10 ⁻³)	% decomp	со	CH₄	C_2H_6	H ₂	CH3	CH ₂ =CO
875	0.90	16.7	1.49	0.40	0.055	0.73	0.70	0.087
925	0.86	32.0	2.76	0.74	0.11	1.77	1.63	0.17
975	0.83	50.1	4 ·28	1.19	0.20	2.84	2.65	0.30

TABLE 3.—THERMAL DECOMPOSITION OF 9.24 μ of ethylene oxide

temp. (°C)	% carbon found in products	% hydrogen found in products	% oxygen found in products	CH ₃ radicals formed per C ₂ H ₄ O mol. decomp.
875	92	91	101	0.520
925	96	105	99	0.626
975	99	110	100	0.663

experimentally and we too were unable to find them. Nor were any hydrogen atoms detected, though the large amount of hydrogen gas in the products indicates that these may play some part in the reaction. They will, however, recombine very readily and are therefore not very susceptible to detection by the present method. We were not able to discover any propane,¹⁸ formaldehyde (a postulated intermediate ¹⁵) nor any acetaldehyde.¹⁸ In a separate experiment it was shown that acetaldehyde did not decompose under our experimental conditions. At 850° there were no products of greater molecular weight than ethylene oxide in the mass range 50 to 100.

ADDITION OF NITRIC OXIDE.—Although some previous measurements have been made on the inhibiting effect of both nitric oxide ^{15, 16c, 20} and propylene ^{19, 21} on the decomposition of ethylene oxide, no direct measurements have previously been made on the change in methyl radical concentrations caused by the addition of an inhibitor. So in order to obtain additional information as to the extent to which methyl radicals play a part in the decomposition, some experiments were carried out in which nitric oxide was added to the reacting gas stream. The effect of added nitric oxide (table 4) is to decrease slightly the amount of ethylene oxide decomposed, i.e. there is partial inhibition of the reaction. Methyl radicals are still present but are not so abundant and the concentration of methane in the products is also decreased. The decrease in methane and methyl concentrations are given as a percentage of the amounts present in the absence of nitric oxide.

Table 4.—Thermal decomposition at 950° C of 28 μ of ethylene oxide in presence of nitric oxide

(Carrier gas 15 mm helium; contact time 0.83×10^{-3} sec)

pressure of NO (µ)	inhibition of decom- position	decrease of [CH4] caused by addition of NO	decrease of [CH ₃] caused by addition of NO	$\frac{\Delta CH_4}{\Delta CH_3}$
(1) 186	3.8 %	12·8 %	22·9 %	0.56
(2) 402	3.5 %	18·7 %	28·6 %	0.65

The final column in table 4 gives the ratio of the decrease in methane to the decrease in methyl concentration. This ratio, virtually constant for a 2.3 fold change in nitric oxide concentration, has a value of 0.6 or 3/5. There are two fundamentally different reactions by which methane can be formed during the thermal decomposition of ethylene oxide, viz.,

$$(CH_2)_2 O \rightarrow CH_4 (+ CO) \tag{1}$$

$$CH_3 + RH \rightarrow CH_4 (+ R)$$
 (2)

If the concentration of RH is not affected by the addition of nitric oxide, i.e. if it is not a radical itself, then 2/5 of the methane will be formed by reaction (1) and 3/5 by reaction (2). From the analytical data at 975° it is seen that 26 % of the ethylene oxide decomposed gives rise to methane. Assuming RH to be ethylene oxide, this can be divided between reactions (1) and (2), i.e. at 975° reaction (1) occurs to $26 \times 2/5 = 10.4$ % and reaction (2) to $26 \times 3/5 = 15.6$ % of the ethylene oxide decomposed.

On the other hand, if RH is wholly or in part a radical whose concentration is decreased by the addition of nitric oxide (a H atom, for example) then the amount of methane formed in reaction (1) will be greater than 10.4 %, by an amount depending on the decrease of the concentration of RH.

The addition of nitric oxide decreased the methyl concentration by 22.9 % and 28.6 % in two separate experiments. On the simple assumption that RH is wholly ethylene oxide we can calculate the expected degree of inhibition of the reaction to be $\frac{15.6 \times 22.9}{100} = 3.6$ % and $\frac{15.6 \times 28.6}{100} = 4.4$ % respectively.

These results are in good agreement with the experimental measurements given in table 4, i.e. 3.8 % and 3.5 % respectively.

REACTION MECHANISM.—An elaboration of Sickman's ²² free radical mechanism for the decomposition of ethylene oxide has been put forward by Fletcher and Rollefson.^{15b} It involves induced decomposition by a methylene radical formed in the primary reaction

$$(CH_2)_2O \rightarrow H \cdot CHO + CH_2$$

to two methyl radicals and carbon monoxide,

$$CH_2 + (CH_2)_2O \rightarrow 2CH_3 + CO.$$

Although the methylene radical should be susceptible to detection by the present method ³ none was in fact found among the decomposition products of ethylene oxide. Moreover, Fletcher and Rollefson's mechanism does not postulate any reaction between methyl radicals and ethylene oxide. It has recently been shown, however, by both thermal ¹⁹ and photochemical ²³ studies, that the reaction

$$CH_3 + (CH_2)_2O \rightarrow products$$

occurs readily. This, in conjunction with our own experiments in which methyl radicals were the only free radicals to be detected, leads us to the view that not only do methyl radicals induce the decomposition of ethylene oxide, but also the primary split of the parent molecule gives a methyl radical

$$(CH_2)_2O \rightarrow CH_3 + CHO.$$
 (3)

The number of methyl radicals formed per ethylene oxide molecule decomposed appears to be considerably greater than under Fletcher and Rollefson's experimental conditions (see table 3). Fletcher and Rollefson reported a value of 0.28. In the calculation of our values it is assumed that all the ethane arises from the recombination of two methyl radicals. This assumption is almost certainly true, but since the ethane concentration is only 13-15 % of the methyl concentration, if a part of the ethane arises in some other way the values given in table 3 will not be greatly affected. It should be noted that the sensitized decomposition of ethylene oxide will not appreciably affect the radical concentration, since apart from the small amount of side reaction to ketene, each methyl radical removed by reaction is regenerated. This will become clear from an examination of the proposed reaction mechanism. In actual fact the values given in table 3 are minimum values since some of the methyl radicals will disappear by reaction with other free radicals, e.g.

$$CH_3 + H(+M) \rightarrow CH_4(+M). \tag{4}$$

The mechanism proposed below is similar in many respects to that proposed by Gomer and Noyes 23 for the photochemical decomposition of ethylene oxide at 175°, the major differences being that no formaldehyde 18 or acetaldehyde was found. Moreover the C₂H₃O radical, if it exists at all as a separate entity at our elevated temperatures, has too short a life to combine with other atoms or radicals. Thus we find no products of greater molecular weight than ethylene oxide and in particular we find no propionaldehyde.

The most important primary reactions and most of the possible radical removing steps are listed below:

$$(CH_2)_2 O \rightarrow CH_4 + CO$$
 (1)

$$(CH_2)_2O \rightarrow CH_3 + CHO$$
 (3)

$$CHO \rightarrow CO + H$$
 (5)

 $CH_3 + (CH_2)_2O \rightarrow CH_4 + C_2H_3O$ (6)

$$H + (CH_2)_2 O \rightarrow H_2 + C_2 H_3 O \tag{7}$$

$$C_2H_3O \rightarrow CH_3 + CO$$
 (8)

(15)

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 $C_2H_3O \rightarrow CH_2CO + H$ (9)

$$CHO + CHO \rightarrow 2CO + H_2$$
(10)

- $H + CHO \rightarrow CO + H_2 \tag{11}$
- $CH_3 + CHO \rightarrow CO + CH_4$ (12)
- $CH_3 + CH_3 \rightarrow C_2H_6 \tag{13}$

$$(M+)H + CH_3 \rightarrow CH_4(+M) \tag{4}$$

$$(M+)H + H \rightarrow H_2(+M) \tag{14}$$

$$(CH_2)_2O \rightarrow CH_2CO + H_2$$

The radicals H, CHO and C_2H_3O were not detected experimentally and therefore, if they exist in the free state, have a shorter life than the methyl radical. The CHO radical has become quite popular in reaction kinetics; its heat of dissociation to CO and H is not large. Its detailed reactions are not known, but all those postulated are quite probable.

If all the methane comes from reactions (1) and (6) and all the hydrogen atoms are removed by reaction (7),²⁴ a minimum value to the extent of reaction (3) can be given. At 975° this will be $\frac{1}{2}(100 - 26) = 37$ %. The half arises because effectively all the C₂H₃O produced in (7) gives a methyl radical by reaction (8). The amount of ethylene oxide decomposing by reaction (3) will be increased above 37 % in the event that either of the following reactions occur; that some CHO disappears by reactions not forming hydrogen atoms or that hydrogen atoms are removed by reactions not regenerating CH₃.

COLLISION EFFICIENCY OF REACTION BETWEEN METHYL RADICALS AND NITRIC OXIDE.—The collision efficiency for the reaction $CH_3 + NO \rightarrow$ products is given by the number of collisions between methyl radicals and nitric oxide which lead to reaction, divided by the total number of collisions. The pressure of nitric oxide was converted to molecules cm⁻³ and then substituted in the equation

$$Z = n_1 \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \left(\frac{8\pi RT(M_1 + M_2)}{M_1 M_2}\right)^{\frac{1}{2}}$$

which gives the number of collisions each methyl has with nitric oxide per cm³ per sec. The mean molecular diameter was taken as 3.75×10^{-8} cm.²⁵ The collision efficiency was obtained by multiplying the collision number Z by the contact time and dividing into the proportion of methyls which react (see table 4). The results obtained in the two experiments and the values obtained by earlier workers are given in table 5. The close agreement obtained over such a large temperature range may indicate that the activation energy of the reaction is small, or zero.

TABLE 5.—Collision efficiency of reaction $CH_3 + NO \rightarrow PRODUCTS$

workers	temp. (°C)	collision efficiency	
Forsyth 25	800	$1.4 imes 10^{-5}$	
Staveley and Hinshelwood ²⁶	540	$6.6 imes 10^{-4}$	
Durham and Steacie 27	25	$1.5 imes 10^{-4}$	
present experiment (1) $[CH_3] = 6.0 \mu$	950	$2.6 imes10^{-4}$	
present experiment (2) [CH ₃] = $5 \cdot 2 \mu$	950	$1.4 imes 10^{-4}$	

COLLISION EFFICIENCY OF METHYL RECOMBINATION.—If it is assumed that all the ethane formed in the ethylene oxide decomposition arises from methyl recombination, the data for the partial pressure of methyl and ethane given in table 2 can be used to calculate a collision efficiency for the recombination. The calculated values are $2 \cdot 1 \times 10^{-2}$ at 975° and $2 \cdot 9 \times 10^{-2}$ at 925°. These are in good agreement with the average value of $2 \cdot 9 \times 10^{-2}$ previously calculated in the same way from the data for mercury dimethyl decomposition.⁷

and possibly

PROPYLENE OXIDE.—The major products of the thermal decomposition of 3.2μ of propylene oxide at a temperature where decomposition is essentially complete (950°) are shown in table 6.16c The partial pressures of the products are given in microns. In addition to the products listed, traces of water, ketene, propylene and allene were found. Since the only important oxygenated product was carbon monoxide it was assumed that under these conditions of complete decomposition the amount of propylene oxide originally present was equal to the amount of carbon monoxide formed. The carbon and hydrogen balances were worked out from this basis. The activation energy of the reaction was 31.8 kcal, and the rate constant at 650° was 165.1 sec^{-1} .

Table 6.—The thermal decomposition of 3.2 μ propylene oxide at 950° C in 10 mm helium

		(Contact tir	$ne = 1.85 \times$	10-3 sec)		
C_2H_6	C_2H_4	C ₂ H ₂	CH4	CH3	H ₂	CO
0.50	1'93	% C found % H found	in products in products in products	= 103 = 113	5.25	5.21

It is apparent from the large quantity of methyl radicals present in the products that a free radical mechanism is of importance in the decomposition of propylene oxide. The compound was, however, not examined in sufficient detail for this mechanism to be thoroughly elucidated; it will, however, probably be quite similar to that for ethylene oxide, and the following is suggested:

$$CH_{3}CHCH_{2}O \rightarrow C_{2}H_{4} + H.CHO$$
(1)

$$H. CHO \rightarrow H_2 + CO$$
 (2)

$$CH_{3}CHCH_{2}O \rightarrow CH_{3} + C_{2}H_{3}O.$$
(3)

Since no formaldehyde was detected reaction (2) must be very fast at this temperature. The two radicals formed in reaction (3) will follow the same paths as in ethylene oxide. The acetylene probably arises from dehydrogenation of ethylene. Calculations based on the collision efficiency of the $CH_3 + CH_3$ reaction show that only 0.05μ of ethane arises from this reaction, the remaining ethane must arise from the hydrogenation of ethylene. The minimum value for the number of methyl radicals formed per propylene oxide molecule decomposed is therefore $(1.04 + 2 \times 0.05)/3.2 = 0.36$. If it is assumed, as is quite probable, that all the methane arises from the reaction of methyl radicals with propylene oxide a value of 0.48 is obtained.

$$CH_3 + CH_3CHCH_2O \rightarrow CH_4 + C_3H_5O \tag{4}$$

$$C_{3}H_{5}O \rightarrow C_{2}H_{4} + CHO.$$
 (5)

On the basis of these simplifying assumptions, the extent of reaction (1) is then 64 %, reaction (3) 24 % (i.e. $\frac{1}{2} \times 0.48 \times 100$, since two methyl radicals are formed for every propylene oxide molecule decomposing by reaction (3)), and reaction (4) 12 %.

DIMETHYL ETHER.—The products of the thermal decomposition of 2.23μ of dimethyl ether are shown in fig. 3 as a function of temperature, together with the decrease in the amount of dimethyl ether remaining. In table 7 these results are summed up in the carbon and oxygen balances. The oxygen balance approaches 100 at the higher temperatures, but it is apparent from the carbon balances that about 20 % of the carbon is disappearing to compounds we have not detected. This result we have so far been unable to account for satisfactorily. At the lower temperatures it might be due to polymerization of the formaldehyde.

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The activation energy of the reaction was found to be 32.4 kcal with a rate constant at 650° of 8.7 sec^{-1} . An activation energy of 17.8 kcal was obtained for methane production, using the results at the lower temperatures where secondary reactions are comparatively unimportant. This compares favourably with a value of 16 kcal obtained by Leermakers²⁸ (who, by photolyzing acetone as a source of methyl radicals, sensitized the decomposition of dimethyl ether at temperatures from 270° to 400°).

There is abundant evidence 2^{9-31} for the existence of free radicals and chain reactions in the decomposition. The build up and subsequent decay of the intermediate formaldehyde during the decomposition at 500° has been studied previously by Leifer and Urey ¹ using a mass spectrometer, which was not, however,



FIG. 3.—Formation of products from the decomposition of 2.23 μ of dimethyl ether,

designed to study free radicals. The same build up and decay of formaldehyde is apparent in fig. 3. The formaldehyde decomposes to hydrogen and carbon monoxide, as is clearly shown by the rapid increase of these two products. The concentration of ethane and methyl radicals also pass through a maximum, the former because of some decomposition to ethylene and hydrogen (at the highest temperature, 1050°, the ethylene has increased to an amount equal to the ethane). The decrease of the methyl concentration may be due in part to reaction with the rapidly increasing concentration of hydrogen. Except for the absence of the CH₃O radical, which may well be unstable at these temperatures, our results appear to be in accord with the mechanism of Rice and Herzfeld.³²

TABLE	7.—CARB	ON AND	OXYGEN	BALANCES	IN	DECOMPOSITION	OF	DIMETHYL	ETHER
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temp. (°C)	775	850	00	950	1000
contact time (sec \times 10 ⁻³)	2.16	2.01	1.93	1.85	1.78
% decomposition	32.0	62.0	79.0	92·0	99.0
% C found in products	75.0	80.0	80.0	83·0	82.0
% O found in products	87.0	94·0	95.0	98·0	104.0

DIOXANE.—The main products of decomposition of dioxane at 915° were carbon monoxide, hydrogen and ethane, with smaller amounts of water, formaldehyde, ketene, ethylene and acetylene. Methyl radicals were present only in

amounts corresponding to about 1 % of the dioxane composed. This quantity may well arise merely from the decomposition of ethane. No methylene or other radicals were detected. This is interesting in view of the strongly inhibiting action of nitric oxide reported by Küchler and Lambert.³³ However, these workers report the reaction to be not catalyzed by methyl radicals from the decomposition of azomethane, and moreover, the para-ortho hydrogen method gave negative results. The radicals reported by Forsyth ²⁵ are undoubtedly methyl.

The activation energy of the decomposition was 43.5 kcal, and a value of 9.8 sec⁻¹ was obtained for the rate constant at 650° . Since practically no radicals were found, this compound was not studied in detail.

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