obtained. The results are not constant, but such could hardly be expected, since molalities instead of activities were used. There is indication, however, that a constant value will be approached in a very dilute solution.

Summary

1. Using cells of the type In(s), $In_2(SO_4)_3$-(m), Hg_2SO_4-Hg electromotive force measurements have been made at 0, 15, 25 and 35°.

2. The freezing points of dilute solutions of indium sulfate were investigated.

3. Calculations have been made of the activity coefficients of indium sulfate in aqueous solution, and of the partial molal heat contents relative to the 0.01 M solution.

4. pH values of solutions of indium sulfate have been determined at room temperature, using the quinhydrone electrode.

5. The constant for the hydrolysis of indium sulfate has been calculated assuming the reaction to be
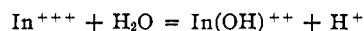
$$In^{+++} + H_2O = In(OH)^{++} + H^+$$

The Presence of Free Radicals in the Thermal Decomposition of Diethyl Ether

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The decomposition of diethyl ether is a reaction for which a chain mechanism involving free radicals has been postulated.[1] The experimental results of previous investigations,[2-6] except for the recent results on the inhibition of the rate of reaction by small quantities of nitric oxide,[7] do not enable any decision to be made between the alternative theories of molecular rearrangement and such a chain mechanism. The present investigation provides definite evidence for the presence of free radicals since small amounts of ether are found to catalyze the decomposition of acetaldehyde. Quantitative estimations of the aldehydes, which are formed as intermediates, and a more detailed study of the kinetics of the over-all reaction have enabled the kinetics of the ether decomposition to be separated from those of secondary reactions.

Experimental Details.—The thermal reactions were studied in a Pyrex bulb, approximately 500 cc. in volume, placed in an electrically heated furnace. Fluctuations of the voltage were reduced by the use of Radiatron ballast tubes (U. V. 886 and 876), and the temperature was controlled by hand to within one degree. Pressures greater than 20 mm. were measured on a mercury manometer made from capillary tubing and heated by nicrome wire to prevent the condensation of organic vapors. The dead-

space outside the furnace did not amount to more than 2% of the volume of the bulb. Pressures of less than 20 mm. were measured with a sulfuric acid manometer separated from the reaction by a click-gage. It was found that pressure equilibrium between the bulb and click-gage was not established instantaneously, so that the time lag was estimated with different pressures of air and a correction applied.

The reaction vessel was evacuated through a liquid air trap by a mercury vapor pump and oil pump to pressures of less than 10^{-3} mm. If at any time air was admitted to the reaction vessel, it was well washed out with the vapor of the substance in use.

The substances used were stored, if liquids, in small bulbs attached to the system; if gases, in a reservoir over mercury. Mixtures were made in a reservoir over mercury, and could be thoroughly mixed by changing the mercury level.

Gas analyses were carried out according to the micro methods of Blacet and Leighton.[8] The greater part of any aldehyde or ether present was removed in a trap at $-70°$. As it was found that the beads slowly absorb other gases than that for which they are used (e. g., fuming sulfuric acid slowly absorbs carbon monoxide), the times of contact were carefully controlled.

In order to determine the amounts of aldehydes present the gas was withdrawn, shaken with water and (a) the total aldehydes found by titration with sodium bisulfite; (b) the formaldehyde estimated by the potassium cyanide method.[9] The bisulfite solution was stabilized with ethyl alcohol and frequently standardized against iodine. Blank experiments with acetaldehyde showed that it also slowly reacts with potassium cyanide for which interaction a correction was applied. Experiments with undecomposed acetaldehyde vapor withdrawn from the furnace showed the bisulfite method to be accurate.

(1) F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(2) Hinshelwood, Proc. Roy. Soc. (London), **A114**, 84 (1927).

(3) Newitt and Vernon. ibid., **A135**, 307 (1932).

(4) Steacie and Solomon, J. Chem. Phys., **2**, 503 (1934).

(5) O. K. Rice and Sickman, THIS JOURNAL, **56**, 1444 (1934).

(6) Steacie, Hatcher and Rosenberg, J. Chem. Phys., **4**, 220 (1936).

(7) Staveley and Hinshelwood, Proc. Roy. Soc. (London), **A154**, 335 (1935).

(8) Blacet and Leighton, Ind. Eng. Chem., Anal. Ed., **3**, 266 (1931).

(9) Romijn, Z. anal. Chem., **36**, 19 (1897).

Diethyl ether (99.5%) was dried over sodium and freshly distilled in an all-glass apparatus. Acetaldehyde (Eastman Kodak) was distilled and the fraction boiling between 20.5 and 21° collected for use. A particularly pure specimen of helium, prepared for cryogenic work, was used. Ethylene was purified by fractionation at liquid air temperatures.

Experimental Results.—Analyses of the gaseous reaction products were made on samples for which the initial pressure, p_0, was 200 mm. at 507°, and which were allowed to proceed to various stages of completion, $\Delta p/\Delta p_\infty$. The results are given in Table I.

TABLE I

Gas Analyses: p_0 = 200 mm., Temp. = 507°

$\dfrac{\Delta p}{\Delta p_\infty}$	Hydrocarbons, % Unsatd.	Satd.	H_2, %	CO (obsd.), %	CO (calcd.), %
0.05	7.6	77.4	7.4	7.6	10
.075	10.0	74.8	7.0	8.2	12
.25	9.5	68.2	5.3	17.0	20
.40	8.5	68.5	4.0	19.0	24
.50	10.5	60.9	4.3	24.3	25
.90	8.5	57.9	4.3	29.3	32

It is known that formaldehyde and acetaldehyde are formed during the decomposition of diethyl ether,[3] and as their rates of decomposition are of the same order of magnitude as that of the ether, considerable quantities of the aldehydes are built up in the system. Quantitative estimations were carried out (a) at 507 and 552° for an initial pressure of 200 mm., and (b) at 552° for an initial pressure of 20 mm. In Fig. 1 the percentages of total aldehydes relative to the amount of ether originally present are plotted for comparable stages of completion. The ratio of formaldehyde
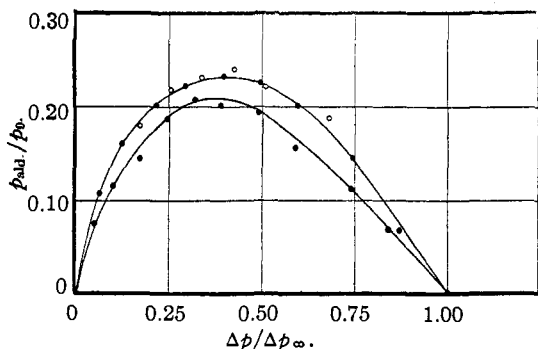

Fig. 1.—Amounts of aldehydes built up at different stages of completion: ●, p_0 200 mm., temp., 552°; ☉, p_0 20 mm., temp., 552°; ◉, p_0 200 mm., temp., 521°.

to the total aldehydes is in each case from 20 to 25%. The almost exact agreement between the two curves for 200 and 20 mm. means that the

order of the reaction that produces the aldehyde is the same as that by which it decomposes: results to be described later show that the former is 1.4. The amounts of aldehyde present do, however, show a definite increase with temperature (Table II) for which allowance must be made in deriving the energy of activation of the ether decomposition from pressure measurements.

TABLE II

Aldehydes Present at $\Delta p/\Delta p_\infty$ = 0.40

Temp., °C.	p_0, mm.	$p_{ald.}/p_0$ × 100	$p_{form.}/p_{ald.}$ × 100
552	380	22.9	23
552	200	23.4	24
552	53	23.5	..
552	20	23.6	23
507	200	21.0	21
490.5	200	21.0	19
473.5	200	20.4	..
442	200	18.8	18
490	4636	18.0	32 (Newitt and Vernon)

Irrespective of the mechanism by which the ether decomposes, it is possible, *a priori*, (a) that the ether decomposes directly to carbon monoxide, *e. g.*

$$C_2H_5OC_2H_5 \longrightarrow C_2H_4 + CH_4 + CO$$
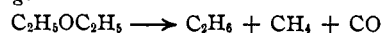
or (b) that an aldehyde is formed as an intermediate, *e. g.*

$$C_2H_5OC_2H_5 \longrightarrow CH_3CHO + C_2H_6$$

and that the aldehyde subsequently decomposes to carbon monoxide and methane. If all the ether decomposes in the former manner, the percentage of carbon monoxide in the products would be constant throughout the reaction; if all in the latter manner, the percentage would be very small in the early stages and increase as the reaction proceeds. Further, assuming that all the ether does actually form an aldehyde as an intermediate, it is possible, knowing the amounts of aldehyde present (Fig. 1), to calculate at any stage of the reaction the amount of aldehyde which has decomposed and therefore the percentage of carbon monoxide in the reaction products. The agreement between the calculated and observed amounts of carbon monoxide (Table I) justifies the conclusion that virtually all the ether forms an aldehyde as an intermediate step in its decomposition.

The question arises as to whether the aldehydes decompose at the same rate as in the pure state. At 552°, the maximum amounts of aldehyde are present when the pressure increase is 40% complete: at this stage the rate of production of alde-

hyde equals its rate of destruction. For an initial ether pressure of 197 mm. the rate of destruction of ether, which equals the rate of formation of aldehyde, is 0.374 mm./sec. From Fig. 1 it is seen that $p_{ald.}/p_0$ is 0.234, so that the aldehyde pressure is 46.1 mm. For this temperature and pressure it may be calculated from the results on the decomposition of pure acetaldehyde[10] that the rate of aldehyde disappearance is 0.122 mm./sec.; for formaldehyde the value is very similar.[11] When, therefore, these aldehydes are formed as intermediates in the decomposition of ether they react at a rate approximately three times greater than in its absence. This is too great a difference to be accounted for by cross activation by collisions with ether, and indicates a definite catalytic action of ether which has been confirmed by comparing the rates of decomposition of pure acetaldehyde with those of mixtures containing small percentages of ether.

The Decomposition of Acetaldehyde Catalyzed by Diethyl Ether.—Experiments with acetaldehyde were alternated with those of the aldehyde–ether mixtures. In both cases, after allowing for the ether decomposition, the shapes of the pressure–time curve were similar, and the endpoint was nearly double the initial pressure. The rates have, therefore, been compared from the half-times, after applying a correction for the rate of decomposition of the ether: this is comparatively small as the rates of reaction of ether and acetaldehyde are similar (at 552° and 200 mm. they are 0.79 mm./sec. for ether and 1.15 mm./sec. for acetaldehyde). Table III gives the temperature, the percentage of ether to the total gas, the initial acetaldehyde pressure and the ratio of $1/t_{1/2}$ to that for the same initial pressure of pure

TABLE III

THE CATALYSIS OF ACETALDEHYDE BY DIETHYL ETHER

Temp., °C.	% Ether	$p_{ald.}$, mm.	% increase $1/t_{1/2}$
552	1.9	179	5.3
	5.2	161	15.5
	5.2	90	21.7
	5.2	20.3	25.0
	18.5	156	55.2
507	5.2	178	15.8
	11.3	164	32.2
	11.3	85	38.9
	11.3	23.2	40.0
490.5	5.2	174	16.1

(10) Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

(11) Fletcher, *ibid.*, **A146**, 357 (1934).

acetaldehyde. The increase in $1/t_{1/2}$, which represents the catalyzed reaction, is independent of temperature, and nearly proportional to the percentage of ether. It may be noted that the addition of 5% of acetaldehyde does not change the initial rate of the ether decomposition.

The catalysis of acetaldehyde by ether may be explained on the hypothesis that the decomposition of ether produces free radicals which then set up a chain in acetaldehyde. The uncatalyzed reaction of acetaldehyde cannot involve free radicals to any appreciable extent or the introduction of a few free radicals from ether, at temperatures at which the acetaldehyde is already decomposing as fast as the ether, would not increase the rate appreciably. At temperatures around 550°, therefore, the uncatalyzed reaction is

$$CH_3CHO \longrightarrow CH_4 + CO$$
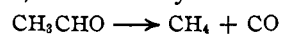
If free radicals are present, however, the chain decomposition

$$CH_3CHO + R \longrightarrow CH_4 + CH_3CO$$
$$CH_3CO \longrightarrow CH_3 + CO$$
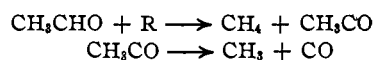
can also occur.

The chain length, λ, can be found in terms of the fraction of free radicals, x, produced from ether. At 552° the addition of 9 mm. of ether to 161 mm. of aldehyde causes an increase in $1/t_{1/2}$ of 15.5%: the initial rate may be assumed to increase by the same amount. In the absence of ether this rate is 0.82 mm./sec., so that the increase is 0.13 mm./sec. The initial rate of disappearance of ether, assuming no cross activation by acetaldehyde, is 0.011 mm./sec.; if collisions with acetaldehyde are equally as effective as collisions with ether in causing activation, the rate of disappearance is 0.031 mm./sec. The value of λ therefore lies between $12/x$ and $4/x$. The results with nitric oxide on ether[7] indicate that at this temperature the inhibited reaction is about 0.3 of the total reaction, so that for ether the chain length is $0.7/x$. The value of x may be very considerably smaller than 0.3 as ether molecules not only produce free radicals but also decompose directly to molecules without the formation of such radicals.

The Rate of Pressure Increase.—Deductions about the rate of disappearance of ether can only be made from measurements on the rate of pressure increase if (a) the final pressure increase at any temperature and pressure is known, and if (b) allowance is made for the undecomposed aldehydes present. Newitt and Vernon[3] at pressures

greater than atmospheric have estimated the aldehydes and corrected for them.

The final pressure increase, Δp_∞, at any initial ether pressure, p_0, does not vary with temperature, but at any temperature there is a marked decrease with pressure. The values obtained at different pressures at temperatures from 495 to 565° are plotted in Fig. 2. A similar variation has been found for other molecules[11] and has been correlated with condensation reactions.
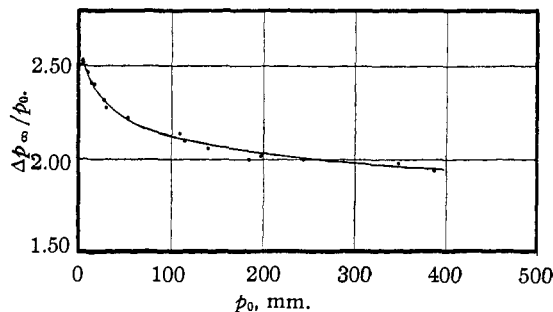

Fig. 2.—Variation of end-point with initial pressure.

The rates at different initial pressures were compared by taking the times, $t_{1/4}$ and $t_{1/2}$, in seconds, for one-quarter and one-half of the pressure increase at completion. The variations of $1/t_{1/4}$ with p_0 at 552 and 521° are plotted in Fig. 3.
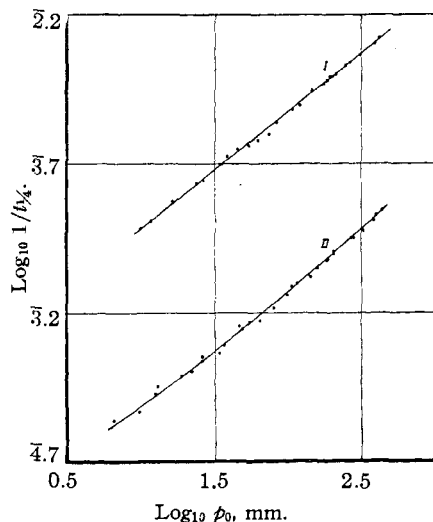

Fig. 3.—I, 552°; II, 507°.

As the amounts of aldehydes present throughout the reaction have been estimated, a pressure–time curve, such as would be obtained if the aldehyde present were completely decomposed, can be constructed (it has been assumed that unit pressure of aldehyde gives 1.95 units of products). This has been done in Fig. 4 for $p_0 = 198$ mm. at

552°, and it is seen that the induction period noticeable in the uncorrected curve is in this way removed. The uncorrected values of $t_{1/4}$ and $t_{1/2}$ are 102 and 232.5 sec., respectively; from the corrected curve they are 68.2 and 167 sec., so that as the correction for the aldehydes at this temperature is the same at all pressures (Fig. 1), the observed values of $t_{1/4}$ at 552° must all be decreased by the factor $68.2/102 = 0.669$. The corrected value of $t_{1/2}/t_{1/4}$ is 2.45, which is very close to that for a unimolecular reaction (2.41). The unimolecular constant, $k_{uni.}$, is connected at 552° with $t_{1/4}$ by the relation, $k_{uni.} = 0.43/t_{1/4}$.
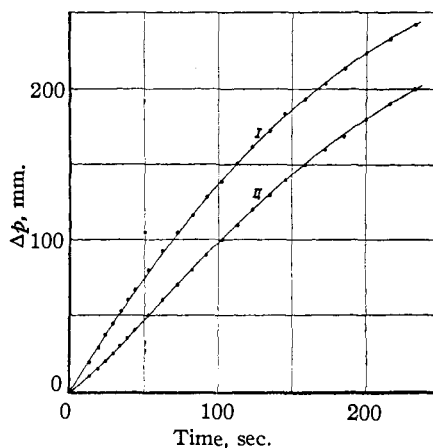

Fig. 4.—Pressure–time curve: p_0 197 mm., temp. 552°; I, corrected for aldehydes present; II, uncorrected for aldehydes.

The slope of log $1/t_{1/4}$: log p_0 (Fig. 3) gives directly the order of the ether decomposition with respect to the initial pressure, as the correction to be applied for the aldehydes is the same at all pressures. This gives an order of 1.40 at 552°, and at 521° a similar value, though at this temperature the order increases somewhat with pressure, as has been found by Rice and Sickman at lower temperatures and pressures.[5] It is known that the non-chain reaction, i. e., that in which small quantities of nitric oxide eliminate the chain reaction, varies with the initial pressure from 50 to 500 mm. in the same manner as the uninhibited reaction.[7] It follows, therefore, that the orders of both the chain and non-chain reactions are approximately 1.4. At much higher pressures (30 to 300 atm.), Steacie, Hatcher and Rosenberg[6] derive an order of 1.35, though they make no allowance for any variation in the end-points.

The Variation of the Energy of Activation with Pressure.—Theories of quasi-unimolecular re-

actions predict an increase in the energy of activation with pressure, which have been verified for azomethane.[12] In other cases, e. g., the aldehydes,[13] the reverse has, however, been found, and has been correlated with chemical and physical complexities of the reactions. For diethyl ether, in which the greater number of molecules decompose by a chain mechanism, our results show that the energy of activation, E_1, decreases slightly but definitely with pressure (Table IV). The values of E are those derived directly from the slopes of log $1/t_{1/4}$ against $1/T$; the quarter times for constant concentrations were compared (Fig. 5). These energies of activation represent composites of the individual energies of activation of the reactions which contribute to the pressure increase. The smaller amounts of aldehydes formed at lower temperatures indicate a lower energy of activation for their destruction than for their formation. At 552° it has been found that $k = 0.43/t_{1/4}$; a similar calculation for $p_0 = 200$ mm. at 507° gives $k = 0.412/t_{1/4}$. If $k = x/t_{1/4}$, the energy of activation, E_1, for the initial decomposition of ether is

$$E_1 = (E + R) \, d \ln x/d(1/T)$$
$$= E + 1200 \text{ cal.}$$

and at 200 mm., $k = 1.6 \times 10^{13} \, e^{-58,600/RT}$

TABLE IV

The Energy of Activation of Diethyl Ether

p_0, mm.	E, cal.	E_1, cal.
400	56,900	58,100
200	57,400	58,600
100	58,200	59,400
50	58,700	59,900
25	59,000	60,200
12	58,700	59,900

Our results lie between those of Hinshelwood[2] (53,000 cal.), and those of Rice and Sickman[5] (62,000 cal.).

Discussion

The decomposition of diethyl ether was at first thought to be a simple quasi-unimolecular reaction;[2] later Rice and Sickman[5] postulated the existence of two or more unimolecular reactions or selective types of internal activation. The chain mechanism of Rice and Herzfeld[1] can now in part be accepted as the present work has demonstrated the existence of free radicals, and the retardation by nitric oxide shows that chains are

(12) O. K. Rice and Ramsperger, This Journal, 50, 617 (1928).
(13) Hinshelwood, Fletcher, Verhoek and Winkler, Proc. Roy. Soc. (London), A146, 327 (1934).

set up by the radicals.[7] We have also found that the retardation of the rate by the reaction products[2] is due to ethylene, which can act as a chain breaker. Further, it is known that free radicals produced photochemically from acetone[14] or thermally from ethylene oxide[15] can also set up chains in diethyl ether at lower temperatures.
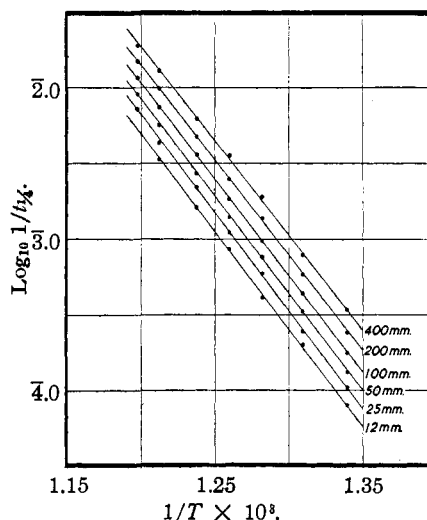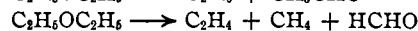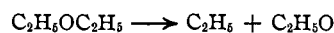

Fig. 5.—Variation of energy of activation with initial pressure.

Although the chain mechanism is thus firmly established, there is evidence that a certain fraction of ether molecules decompose by an intramolecular rearrangement directly to an aldehyde and other molecules.[15] Thus there are three general ways in which ether molecules may break down:
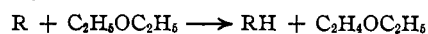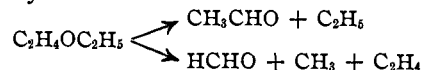
(1) By rearrangement to molecules

$$C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_3CHO$$
$$C_2H_5OC_2H_5 \longrightarrow C_2H_4 + CH_4 + HCHO$$

(2) By the formation of free radicals

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5 + C_2H_5O$$

(3) By interaction with free radicals (R)

$$R + C_2H_5OC_2H_5 \longrightarrow RH + C_2H_4OC_2H_5$$

followed by

$$C_2H_4OC_2H_5 \begin{cases} CH_3CHO + C_2H_5 \\ HCHO + CH_3 + C_2H_4 \end{cases}$$

and subsequent chain decomposition of the aldehydes. Our results indicate that an aldehyde is always formed as an intermediate, so that there is no direct production of carbon monoxide from such a reaction as

$$C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_4 + CO$$
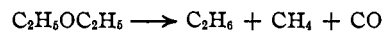
(14) Leermakers, This Journal, 56, 1899 (1934).
(15) Fletcher and Rollefson, ibid., 58, 2135 (1936).

The proportion of the three types of reaction will vary with the pressure and temperature; thus from the relative energies of activation the chain reaction predominates more at lower temperatures.[7] The formation of free radicals by a unimolecular process, and chain termination by the recombination of two small (ethyl and methyl) radicals best accounts for the observed order of the chain reaction of approximately 1.4.[16] The inhibited reaction is probably composed of a number of quasi-unimolecular components of types 1 and 2, so that the order with respect to the initial pressure will, as in the aldehydes,[10] have no simple value. It is at first sight surprising that the order during the course of a run is first order, as the ethylene produced, which retards the rate of reaction, would be expected to raise the order. However, as the reaction proceeds there will be an increase in the relative proportions of methyl to ethyl radicals due to such a reaction as

$$C_2H_5 + CH_3CHO \longrightarrow C_2H_6 + CO + CH_3$$

and methyl radicals may react more easily with ether than do ethyl radicals.

The indecisive influence of inert gases is in agreement with the complex nature of the reaction. Such gases have been found slightly to retard the rate of chain reactions,[15] while they accelerate that of quasi-unimolecular reactions.[17] We have found that helium, when present in a 2:1 ratio, does not change the rate by more than ±2%.

The Evidence for Chains in Related Compounds.—The decomposition of dimethyl ether has been studied by Hinshelwood and Askey,[18] and the results justify a chain mechanism. Formaldehyde is formed as an intermediate (CH_3-$OCH_3 \longrightarrow CH_4 + HCHO$) and its rate of decomposition is considerably faster than that of the pure substance. Making a calculation similar to that for diethyl ether, it is found that for an initial ether pressure of 312 mm. at 504°, the rate of disappearance of formaldehyde when its pressure is 38 mm. is 0.10 mm./sec. If it is assumed that there is no cross-activation by other molecules, the value extrapolated from the data on pure formaldehyde[11] is 6.8×10^{-3} mm./sec., *i. e.*, some fifteen times slower. Free radicals will account for the catalysis of the formaldehyde decomposition which does not normally involve a

chain mechanism: part of the dimethyl ether reacts therefore through a chain mechanism, as it has been found that chains exist in the presence of free radicals.[14] As in other chain reactions the rate is retarded by inert gases.

Quantitative analyses of the amounts of acetaldehyde present at different stages of the reaction have not been made for methyl ethyl ether. Ure and Young[19] assumed that 65% of the ether decomposed to acetaldehyde, and in this way obtained a rate constant for the aldehyde decomposition similar to that from direct measurement. If, as in the other simple ethers, virtually all the ether forms an aldehyde as an intermediate, the velocity constant for the aldehyde will be greater than in the absence of ether, in agreement with a free radical mechanism. Glass and Hinshelwood[20] found that both methyl ethyl and methyl propyl ether decompose more rapidly in the presence of their respective reaction products. This effect may not have been due to inert gases but rather to traces of iodine compounds, introduced during the preparation of the ethers.

Methyl alcohol bears a structural resemblance to the methyl ethers, and formaldehyde is formed in the course of its decomposition.[21] Its rate of reaction has, however, been explained without postulating the existence of free radicals. The reaction of methyl alcohol in the presence of ethylene oxide shows that the alcohol does not easily form chains even in the presence of comparatively large concentrations of free radicals:[15] further, the decomposition of methyl alcohol is not retarded by nitric oxide and decomposes faster in the presence of its reaction products.[22] There is no evidence, therefore, for a chain mechanism though the formation of free radicals has not been disproved definitely.

The kinetics of the individual reactions which constitute the different steps in the chain decompositions of the ethers must await the determination of the chain-lengths and the percentage of molecules which produce free radicals. In view of the considerable proportion of molecules which decompose without interacting with free radicals, the values assumed by Rice and Herzfeld for the separate steps may need considerable modification.

(16) F. O. Rice, *Chem. Rev.*, **17**, 53 (1935).

(17) O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

(18) Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A115**, 215 (1927).

(19) Ure and Young, *J. Phys. Chem.*, **37**, 1169 (1933).

(20) Glass and Hinshelwood, *J. Chem. Soc.*, 1804 (1929).

(21) Fletcher, *Proc. Roy. Soc.* (London), **A147**, 119 (1934).

(22) Fletcher, unpublished results. The increase in rate is 21% when the reaction products are present in the ratio 2.5:1 and 60% for a 7:1 ratio.

We wish to thank Mr. D. H. Etzler for assistance with part of the experimental work, and one of us (C. J. M. F.) is grateful to the Commonwealth Fund for a Fellowship which has made this work possible.

Summary

The decomposition of diethyl ether has been studied over the pressure range of 6 to 450 mm., and at temperatures from 473 to 562°. Gas analyses indicate that an aldehyde is always formed as an intermediate, and from the amounts of aldehydes present it is found that their rates of decomposition are greater than in the pure state. In confirmation of this the decomposition of acetaldehyde is catalyzed by small amounts of ether, which is explained by the formation of free radicals from diethyl ether, and the initiation of a chain decomposition of the aldehyde. The ether decomposition is interpreted in terms of the three simultaneous processes of molecular rearrangement, free radical formation and chain decomposition, and the importance of these processes in the decomposition of analogous substances is discussed.

The Production of Free Radicals from Ethylene Oxide and the Catalysis of Other Reactions by Them

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The investigations of F. O. Rice and his co-workers have shown that free radicals are produced from a number of organic substances when they are passed through a hot tube. In the majority of cases the energy of activation for the production of the free radicals is considerably higher than that for the thermal decomposition of the substance, but for ethylene oxide the two energies of activation are similar.[1] Therefore, the fraction of free radicals present in the thermal decomposition of ethylene oxide should be relatively higher than in other compounds. In confirmation of this, we have found that small amounts are very effective in promoting the chain decomposition of other compounds,[2] and can be used to initiate chain reactions from 400 to 450°, just as azomethane has been used around 300°.[3] The catalysis of acetaldehyde by ethylene oxide is of special interest, firstly, as it is formed from ethylene oxide by isomerization and so any investigations on the decomposition of ethylene oxide must necessarily consider the chain decomposition of acetaldehyde, and secondly, because the kinetics are simplified by the fact that only one type of radical, the methyl radical, need be considered.

The kinetics of the decomposition of ethylene oxide were first studied by Heckert and Mack[4] and their results have recently been interpreted in terms of the free radical theory.[5] Thompson and Meissner[6] have shown that the decomposition is not a simple unimolecular reaction and that the variation of the rate with the initial pressure indicates a number of simultaneous reactions.

Experimental Procedure.—The reactions were followed in a manner similar to those described with diethyl ether.[7] The organic materials were purified by distillation, except for ethylene which was purified by fractionation after condensation at liquid air temperatures. Nitric oxide was formed in situ in the reaction vessel from ethyl nitrite, which under the experimental conditions decomposes instantaneously.[8]

$$2C_2H_5ONO \longrightarrow 2NO + CH_3CHO + C_2H_5OH$$
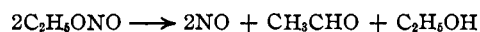
The Decomposition of Ethylene Oxide.—The pressure increase at completion is equal to the initial pressure, and the reaction is strictly homogeneous.[4] Aldehydes are formed as intermediate products of the decomposition and in order to obtain sufficiently large amounts with which to carry out tests, moderately large pressures were used and the gases removed at an early stage of the reaction. Acetaldehyde was detected by Rimini's test, formaldehyde by the resorcinol test, while a solution had a definite odor of acrolein; the ratios of unsaturated aldehydes and of formaldehyde to acetaldehyde were small. For an initial pressure of 380 mm., the total aldehyde

(1) F. O. Rice and Johnson, THIS JOURNAL, **56**, 214 (1934).
(2) Fletcher, ibid., **58**, 534 (1936).
(3) Allen and Sickman, ibid., **56**, 2031 (1934).
(4) Heckert and Mack, ibid., **51**, 2706 (1929).
(5) Sickman, J. Chem. Phys., **4**, 297 (1936).
(6) Thompson and Meissner, Nature, **137**, 870 (1936).
(7) Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).
(8) Steacie and Shaw, J. Chem. Phys., **2**, 243 (1934).