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The decomposition of diethyl ether has been investigated with considerable accuracy at pressures up to 260 atmospheres at 426°C. The results confirm the previous approximate values found by Steacie and Solomon. The rate of the reaction is still increasing at the highest pressures investigated. The results may be qualitatively explained by the Rice-Herzfeld mechanism, and support the idea that the reaction is not a simple unimolecular change.

INTRODUCTION

AN investigation of the kinetics of the decomposition of ethyl ether at high pressures was described in a previous paper by Solomon and one of us.[1] In that investigation the rate of reaction was inferred from the rate of change of pressure, and on account of gas law aberrations, etc., it was only possible to claim an accuracy of about a factor of 2. In the present work the accuracy has been greatly improved by eliminating this source of error.

EXPERIMENTAL

Only minor changes were made in the apparatus previously described. The method of following the reaction, however, was completely altered, the rate being inferred from analyses rather than from the rate of change of pressure. The method used was as follows:

In making an experiment the procedure was identical with that previously described, except that pressure readings were taken merely to give the initial pressure and a rough indication of the extent of reaction. After the reaction had progressed to the desired extent, the bomb was cooled to room temperature and all the gaseous products were blown off into a large calibrated volume connected to a mercury manometer. The products were then analyzed in a Burrell gas analysis apparatus. It was thus possible to calculate the absolute amount of any gaseous product formed in the reaction. This could then be compared with the amount of the same product formed when the reaction went to completion, small differences in the initial pressure being corrected for on the assumption that

the ideal gas law held. The extent to which the reaction had progressed during a given time could thus be inferred, and each experiment thus gave one point on the percent reaction-time curve. In practice the rate was inferred from the amount of saturated hydrocarbons produced, since this was the most reproducible value.

THE REACTION PRODUCTS

Analyses of the gaseous products at completion are given in Table I. It will be seen that saturated

TABLE I. *The products of reaction.*

INI-TIAL PRES-SURE (cm)	PRESSURE INCREASE AT COM-PLETION (%)	GASEOUS PRODUCTS (Percent)				REMARKS
		CO_2	C=C	CO	SATURATED HYDRO-CARBONS (+H_2)	
1860	154	12.5	7.0	9.5	70.1	
1840	153	8.6	4.3	21.5	66.0	
2380	121	13.9	5.8	13.2	67.1	
2480	135	11.5	6.6	15.6	65.9	Packed with steel turnings
1900	160	11.2	2.7	17.7	68.4	
2430	176	5.6	1.9	26.1	66.4	
7080	232	3.7	3.4	22.4	70.5	Packed with steel turnings
7280	221	6.7	3.0	18.5	71.6	Left overnight before samp-ling
6980	238	4.3	2.4	26.8	66.5	Coated with KCl
15300	268	5.8	13.6	16.1	64.5	
14580	270	5.7	13.7	19.4	61.2	
19020	266	6.8	10.9	19.5	62.8	
18100	281	5.2	13.9	20.2	60.7	

hydrocarbons are the main product of the reaction, as found in previous investigations. The amount produced is sufficiently constant to serve as a measure of the rate. With the exception of one or two low pressure experiments, the amount of carbon monoxide produced is also satisfactorily constant. The amount of unsaturated hydrocarbons is, in general, small. The large increase in the experiments at the highest pressures may be fictitious, since in these runs the gas was

[1] Steacie and Solomon, J. Chem. Phys. **2**, 503 (1934).

absorbed by fuming sulphuric acid much more slowly than usual. It is therefore possible that some condensation product is formed at high pressures, which is absorbed by fuming sulphuric acid.

The comparatively large amounts of carbon dioxide are difficult to explain. It seems certain that it really is carbon dioxide, since it was not condensable at $-80°C$. A few experiments were made at an initial pressure of 3 atmos. These gave erratic results, and showed that the reaction is largely heterogeneous (in a stainless steel vessel) at low pressures. In these experiments the CO_2 was very high and variable. The CO_2 produced at higher pressures, however, cannot be ascribed to a heterogeneous decomposition of the ether, since at higher pressures the reaction is not appreciably heterogeneous. The carbon dioxide cannot arise from the reaction

$$2CO = CO_2 + C,$$
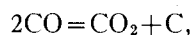
since large amounts of CO are left at completion, and are not diminished on standing overnight. This also seems to rule out the possible attack of the bomb by CO,

$$3Fe + 2CO = Fe_3C + CO_2.$$
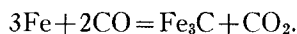
A small amount of some carbonaceous material is, however, produced. In any event, the production of CO_2 does not seem to affect appreciably the amount of saturated hydrocarbons produced, and hence should be without effect on the calculated rates of reaction.

Table I also gives the percent pressure increase at completion, although with the present experimental method this is no longer of great importance. The pressure increase rises greatly at high pressures. Since the products of the reaction do not change greatly with changing pressure, it is apparent that the change in the pressure increase at completion is mainly due to increasing gas law aberrations. It is to be noted that the pressure increases at high pressures are much higher than those previously reported by Steacie and Solomon. On account of the much larger number of experiments reported here, and of the improvement of the technique as the work progressed, the present values are certainly the

more accurate. In any case, however, the error introduced into Steacie and Solomon's velocity constants from this cause is well within the factor of 2 which they claimed as their experimental accuracy.

THE RATE OF REACTION

The reaction rate data are given in Table II.

TABLE II. *Reaction rate data.*

Ini- tial Pres- sure (cm)	Time (min.)	% Re- acted	$K \times 10^4$ (sec.$^{-1}$)	Ini- tial Pres- sure (cm)	Time (min.)	% Re- acted	$K \times 10^4$ (sec.$^{-1}$)
2350	11.0	18.7	3.14	7280	38.0	46.5	2.72
2460	46.5	44.9	2.13	7030	57.0	60.4	2.71
				6980	87.0	78.2	2.91
7080	13.0	34.4	5.45	7180	100.0	61.2	1.58
6800	18.0	35.3	4.00	7140	116.0	75.6	2.02
7030	32.0	50.2	3.64	6930	137.0	82.6	2.12
14480	26.0	56.1	5.53	16320	56.5	73.2	3.88
				17160	90.0	82.8	3.26
20700	17.5	42.1	5.19				
				21200	56.5	74.3	4.00
2370	76.0	57.5	1.87	19630	90.0	74.8	2.55
1910	105.5	60.1	1.45				
2340	146.0	76.1	1.63				

The values of K given in the last column are first-order constants. It is apparent that K drifts largely as the reaction progresses. The results at any pressure would agree, in fact with an order of about 1.8. To determine the effect of pressure upon the rate, the most unobjectionable method would be to extrapolate the K's to zero time and obtain the initial rates. Such an extrapolation, however, is very indefinite in view of the scattering of the values of K. It is therefore preferable to compare the values of K corresponding to some definite amount of reaction. For the sake of uniformity we have adopted 20 percent reaction for this purpose, as did Newitt and Vernon[2] and Steacie and Solomon. We thus obtain the values given in Table III. These are probably accurate to within 10 percent.

TABLE III. *The effect of pressure on the rate.*

INITIAL PRESSURE (cm)		
2300	7000	15000–20000
$K_{20} \times 10^4$ (sec.$^{-1}$)		
3.0	4.9	6.2

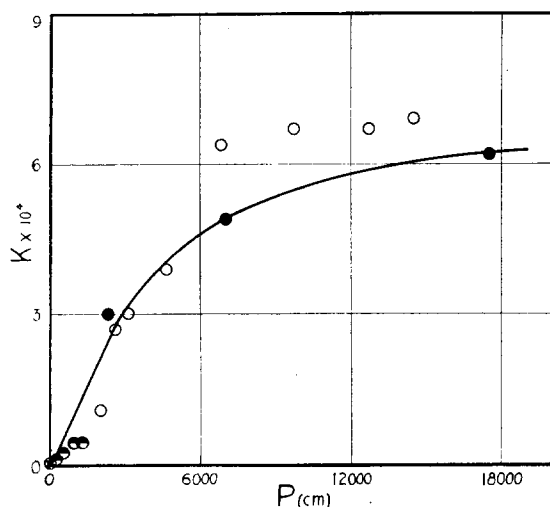[2] Newitt and Vernon, Proc. Roy. Soc. **A135**, 307 (1932).

FIG. 1. The rate of reaction at 426°K. Black circles, this investigation; open circles, Steacie and Solomon; half-black circles, Newitt and Vernon; circle and cross, average low pressure value of Hinshelwood, Rice and Sickman, Kassel, and Steacie.

The data are plotted in Fig. 1, and are compared with the results of other investigations, as recalculated in the previous paper. The excellent agreement with the results of Steacie and Solomon is noteworthy, since the method of determining the rate was entirely different in the two investigations.

THE EFFECT OF SURFACE

A number of experiments were made with the reaction vessel packed with stainless steel turnings, and others with the reaction vessel coated with potassium chloride. It was found that such treatment had no measurable effect on the rate, and the reaction may therefore be considered to be homogeneous in a stainless steel vessel at high pressures.

It was obviously desirable to tie-in the results of the present investigation with those obtained at low pressures, and an attempt was made to determine the rate at 3 atmos. by the same method. It was found, however, that at these pressures the results were very erratic, and the rate was considerably increased by packing the reaction vessel. The results at this pressure have therefore been discarded.

DISCUSSION

The decomposition of ethyl ether has now been investigated over a far wider range of pressure than any other reaction, viz., from 20,000 cm in this investigation to 0.01 cm in the work of Rice and Sickman.[3] It is evident that the rate of reaction increases steadily with pressure over the entire range.

Since this investigation was commenced it has become apparent that the ethyl ether decomposition is not a simple unimolecular change, but probably involves reaction chains.[4] On the basis of the Rice-Herzfeld mechanism there are two general types of free radical chain decomposition of organic compounds: (A) The chain terminates by a heavy radical combining with a light radical (CH_3 or C_2H_5). This is the mechanism proposed for the decomposition of ethyl ether, and it may be shown to lead to an approximate order of 1. (B) The chain terminates by the recombination of two light radicals, as appears to be the case in the acetaldehyde decomposition, and this leads to an order of 1.5. Which mechanism holds is governed by the activation energies of the elementary reactions, which govern the relative stationary concentrations of the various radicals.

Now it has been emphasized by Rice that free radical mechanisms of this type can only be expected to hold accurately at the start of a decomposition, before the products have accumulated to an appreciable extent. The decomposition of ethyl ether gives rise to acetaldehyde, and thus "It follows that the usual measurements of the rate of decomposition of diethyl ether are really measurements performed on mixtures with acetaldehyde and the two substances would not be expected to decompose independently since the radicals of the one enter into the decomposition of the other."[5] It follows that the decomposition of acetaldehyde will greatly increase the concentration of light radicals present, and hence the chains in the ether decomposition will in

[3] O. K. Rice and Sickman, J. Am. Chem. Soc. 56, 1444 (1934).

[4] Leermakers, J. Am. Chem. Soc. 56, 1899 (1934). F. O. Rice and Herzfeld, ibid. 56, 284 (1934). F. O. Rice and K. K. Rice, The Aliphatic Free Radicals (Baltimore, 1935), pp. 86–90.

[5] Rice and Rice, reference 4, p. 90.

part be terminated by mechanism (B) rather than by (A). The result will be to raise the order of the reaction above 1, and thus give a rate which increases steadily with increasing pressure. In the present investigation the over-all order, as inferred from the effect of pressure on the rate, is about 1.35 and the results are therefore explicable on the basis of the free radical mechan-

ism. Unfortunately the situation is far too complicated to permit a quantitative comparison with the theory.

The Decomposition of Methyl Nitrite at High Pressures

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PREVIOUS work on the decomposition of diethyl ether at high pressures[1] showed that the rate increased continually with pressure up to 260 atmos., the rate at that pressure being about 40 times the previously calculated "high pressure rate." It has since been shown by Leermakers[2] that the reaction proceeds by a chain mechanism, as had been predicted by Rice and Herzfeld.[3]

The alkyl nitrites have been shown to decompose unimolecularly[4] and it appears to be very unlikely that chains occur in these reactions.[5] Nevertheless, it seemed worth while investigating the decomposition of methyl nitrite at high pressures to see if the rate would remain constant.

The apparatus, experimental procedure, preparation of materials, etc., were as previously described, except for the substitution of an oil bath for the lead bath owing to the lower temperatures required. The rates were inferred from the change in pressure accompanying the reaction. The results are given in Table I.

TABLE I. *Temperature 217.5°C.*

RUN No.	P_0 (cm)	k(sec.$^{-1}$)	% ΔP AT COMPLETION
Steacie & Shaw	up to 65	1.0×10^{-3}	82.5
1	103	1.3	142
5	109	1.9	94
4	682	1.7	56
2	1320	1.7	118
3	2980	2.3	76
6 (Packed)	79	2.3	92

It is apparent that the pressure increase at completion is very erratic. The rate in run 6, where the surface is about double that in the empty vessel, is considerably higher than that in the corresponding unpacked runs, and the reaction is thus partly heterogeneous. Considerable error is also to be expected from gas law aberrations. In consequence the results are probably accurate only to within a factor of about 2. Furthermore most of the errors will tend to make the rate high. Hence it may be concluded that, within the rather large experimental error, there is no appreciable increase in the rate of decomposition of methyl nitrite on going from 65 cm to 35 atmos. This furnishes further support to the conclusion that the reaction is really unimolecular.

[1] Steacie and Solomon, J. Chem. Phys. **2**, 503 (1934); Steacie, Hatcher, and Rosenberg, ibid., this issue.
[2] Leermakers, J. Am. Chem. Soc. **56**, 1899 (1934).
[3] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[4] Steacie and Shaw, Proc. Roy. Soc. **A146**, 388 (1934); **A151**, 685 (1935); J. Chem. Phys. **2**, 345 (1934); **3**, 344 (1935).
[5] F. O. Rice and Radowskas, J. Am. Chem. Soc. **57**, 350 (1935).