[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Homogeneous Decomposition of Diethyl Ether at Low Pressures; with Some Remarks on the Theory of Unimolecular Reactions[1]

BY O. K. RICE AND D. V. SICKMAN

In the theory of unimolecular gas reactions, as developed by Hinshelwood,[2] Rice and Ramsperger,[3] and Kassel,[4] the pressure at which the rate constant first shows a falling off from its high pressure value depends upon the number of degrees of freedom possessed by the molecule in its internal vibrations. It has been customary to use the reaction rate data to calculate what may be called the effective number of degrees of freedom in the case of a given reaction. It was pointed out by Rice and Ramsperger[3b] and by Rice[5] that in many cases the effective number of degrees of freedom is much smaller than one would expect by noting the number of atoms, and hence the number of possible types of vibrations in the molecules decomposing, even allowing for the fact that the classical model, on which the calculation of the effective number of degrees of freedom is based, cannot in the light of the quantum theory be strictly correct. In other words, in these reactions the rate constant begins to fall below its high pressure value at a higher pressure than would normally be expected. It thus appears probable that only a limited number of the actual degrees of freedom of the molecule can transmit energy readily to the particular bond or bonds of the decomposing molecule which break or rearrange in the decomposition; if, however, the inactive degrees of freedom can transmit energy slowly to the bond which breaks, either directly or, as is rather to be expected, through the active degrees of freedom (a process which we shall call "internal activation"), one might expect that at lower pressures, where the time necessary for this transfer to take place is less than the time between collisions, the unimolecular rate constant would again approach a constant value, which is less than its high pressure value.[6]

Ethyl ether is a molecule in which the smallness of the number of effective degrees of freedom is particularly marked. The number of effective degrees of freedom, as determined by Hinshelwood,[7] is about four; contrast this for example with azomethane, actually a simpler molecule, which has an effective number of degrees of freedom of about twelve.[3b] It seems, therefore, particularly appropriate to carry the experimental data in this case to lower pressures.

The decomposition of gaseous ethyl ether was first studied by Hinshelwood,[7] who carried it from around 500 mm. down to 25 mm. at 525°. This pressure range was not sufficient to show whether there is a second unimolecular region at low pressures, though there was some slight indication that one might occur. Further experiments in the same pressure range have been performed by Steacie[8] and by Kassel,[9] while Newitt and Vernon[10] have performed experiments at pressures up to several atmospheres. Instead of approaching a limiting high pressure value, the rate constant keeps on increasing as one goes to pressures of several atmospheres. This gives one the impression that a bimolecular reaction is coming in at high pressures, but the rate of this reaction is faster than can be accounted for on the usual theory of bimolecular reactions, and, as we shall see, there seems to be no real reason to think that a different reaction is coming in. It may be the low pressure end of a unimolecular stage of the reaction whose limiting rate would occur only at still higher pressures.

Experimental Method

The decomposition of the ether was followed by noting the change of pressure with the time as the reaction proceeded. The ether was allowed to pass into a Pyrex bulb kept at the desired temperature and the pressure was measured either by means of a mercury manometer, or a McLeod gage, the latter having several bulbs so that it could be used over a considerable range of pressures at

---

[1] Preliminary report, THIS JOURNAL, **54**, 3778 (1932).

[2] Hinshelwood, *Proc. Roy. Soc.* (London), **A113**, 230 (1926).

[3] O. K. Rice and Ramsperger, (a) THIS JOURNAL, **49**, 1617 (1927); (b) *ibid.*, **50**, 617 (1928).

[4] Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928).

[5] O. K. Rice, *Z. physik. Chem.*, **7B**, 226 (1930).

[6] This assumes, of course, that there are sufficient collisions to keep up to their Maxwell-Boltzmann equilibrium quota the molecules which have, in their active and inactive parts, combined a total energy of the order of the energy of activation. At still lower pressures the rate constant of this second unimolecular stage will fall off. See Rice, Ref. 5, p. 233.

[7] Hinshelwood, *Proc. Roy. Soc.* (London), **A114**, 84 (1927).

[8] Steacie, (a) *J. Phys. Chem.*, **36**, 1562 (1932); (b) *J. Chem. Phys.*, **1**, 313 (1933).

[9] Kassel, THIS JOURNAL, **54**, 3641 (1932).

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

the low pressure end. Two separate pieces of apparatus were used.

Apparatus I consisted of a liter Pyrex bulb immersed in a vigorously stirred bath of an equimolecular mixture of sodium and potassium nitrate mounted on an automobile jack so that it could be removed from the reaction vessel when desired. The temperature of this salt bath was regulated to ±0.2°. The necessary correction for the external volume[11] (about 6% when the McLeod gage was used; about 3% for the manometer) has been made in the results. The ether supply was shut off by mercury traps, and did not come into contact with stopcocks except at the moment of admission to the reaction vessel, and was immediately followed by mercury, so that no leakage could occur.

Apparatus II was designed so as to avoid stopcock grease, entirely. While the same backing-up pump was used as for Apparatus I it was connected through 3 meters or more of tubing, and no stopcocks whatever were used to handle either mercury or ether.

During some of the experiments a gold trap was placed in the connection to the reaction vessel to prevent diffusion of mercury into it. The reaction vessel was filled with ether vapor by allowing liquid ether to evaporate into it. Now, although the part of the system containing the liquid ether was in contact with mercury, since the ether was evaporated rather rapidly and had a direct path to the reaction vessel, it is not likely that it would pick up much mercury vapor, and part of that would be removed by the gold trap. So we had a means of varying the concentration of mercury vapor in the reaction vessel, and thus testing any possible effect it might have on the reaction. In some experiments in which the pressure of ether was not too high, the gold trap was replaced by a trap immersed in melting phenyl chloride (−47°) which should condense out most of the mercury, and did not have the disadvantage of introducing a finely divided metal into the apparatus.

The thermostat in Apparatus II was an air-bath. The windings were made in sections so that by properly adjusting the resistance of the sections it was possible to avoid temperature gradients in the furnace. The temperature was controlled with an accuracy comparable to that of Apparatus I. The temperature was read by means of a thermocouple placed in a well which went inside the reaction flask. The reaction vessel in this case was a 500-cc. instead of a 1000-cc. bulb. In this case the volume of the McLeod gage and connections was about 30 cc. and the correction for external volume will be about 15%. The correction when the McLeod gage is not used will be about 10%. The necessary corrections have been made.

The Preparation of the Ether.—The ether used in all but four of the experiments made at 478°, tabulated below, was prepared as follows. Commercial C. P. ether was shaken several times with water, 5 times with calcium chloride solution, 5 times with water, 3 times with potassium bicarbonate–mercuric chloride mixture, with strongly alakaline permanganate until no reduction took place (about 15 times), and finally with more water. It was left overnight with calcium chloride, then for three weeks with sodium wire. It was fractionated 6 times in vacuum, discarding first and last portions, and boiled freely to remove dissolved gases. The ether thus purified was stored in contact with mercury.

The ether with which the other four experiments at 478° and the experiments at 462 and 525° were performed was an earlier sample, prepared in essentially the same way, except that it was not treated with potassium bicarbonate–mercuric chloride mixture.

Calculation of the Results

It seemed desirable in the reduction of the experimental data to use a method which, while not too complicated, would not depend too strongly on the personal judgment of the person making the calculations. A somewhat modified least squares method was therefore adopted.

If we subtract two successive readings of the pressure, p, and divide by the time interval we have an approximate value of $\mathrm{d}p/\mathrm{d}t$ for the mean time, t, of the interval. We thus can readily obtain from our measurements the value of $\mathrm{d}p/\mathrm{d}t$ as a function of t, and, for the first part of a run, we may to a good approximation write $\mathrm{d}p/\mathrm{d}t = a + bt$, where a and b are constants. We have now taken the readings from the first part of the run, and determined the best values of a and b by the method of least squares. The value of a is just the value of $\mathrm{d}p/\mathrm{d}t$ for $t = 0$, from which we can get the initial value of $(\mathrm{d}p/\mathrm{d}t)/p$. This is proportional to the initial rate constant, K, which is what we desire to get; the constant of proportionality being unimportant we shall simply write $K = a/p$ (where p is the *initial* pressure).

In making these calculations we have taken the readings up to the point at which the pressure had increased to 1.5 times its initial value for the experiments at 525°. For the lower temperatures we have taken the readings up to 1.25 times the initial pressure in order to make the least squares calculations. The reason for this difference of procedure was that the reaction ran so fast at 525° that it was impossible to make enough readings by the time the pressure had increased to 1.25 times its initial value for the averaging to have much significance; while at the lower temperatures the reaction was so slow that it was not in general followed for a sufficiently long time to allow the pressure to increase to 1.5 its initial value. From an inspection of the data at 525° it did not seem likely that this difference in procedure would introduce any appreciable systematic errors which would be of significance when comparing the data at different temperatures.

It was assumed throughout in making the calculations that equal time intervals were to be weighted equally. In most cases the readings were taken at equal time intervals; in some cases where a few pressure readings were taken at smaller time intervals the intermediate readings were ignored and only those taken at the end of equal intervals were used in getting the differences. In other cases differences over some longer time intervals were given weights roughly proportional to the length of the interval. Since these weights can make only a very small difference in the final result they were done only roughly. It is also true that it would be better to weight equal pressure

---

(11) The McLeod gage is left open to the flask during the run. Under these conditions the observed rate must be increased by $V_eT_i/100\ V_iT_e$ per cent. where V_e, T_e, V_i, T_i are external volume, external temperature, volume of the reaction flask, temperature of the reaction flask, respectively.

intervals equally rather than equal time intervals, but in this case either way would come to practically the same thing.

The Experimental Results

In Table I we present the initial values of the rate constant, $K = (\mathrm{d}p/\mathrm{d}t)/p$, and $[\mathrm{d}\ \log_e(\mathrm{d}p/\mathrm{d}t)/\mathrm{d}t]/K$, for runs done at various values of the initial pressure, p. When the rate of change of pressure during the course of a run is expressible as a function of the time by a linear expression, $\mathrm{d}p/\mathrm{d}t = a + bt$, as has been assumed in making the calculations, K is equal to a/p, while $[\mathrm{d}\ \log_e(\mathrm{d}p/\mathrm{d}t)/\mathrm{d}t]/K$ is given by b/aK. (Unless otherwise stated, all quantities always have their initial values.) In Fig. 1 we have plotted the values of $\log_{10} K$ as a function of $\log_{10} p$, together with the results of other investigators.[12] The curves are theoretical curves, to be explained later. In the inset of Fig. 1, we have plotted the values of b/aK for the experiments at 462° and for those experiments at 478° which were done in Apparatus I. The values of b/aK at 525° are all zero within the limits of experimental error, as may readily be seen. The deviations of b/aK in Fig. 1 indicate the extent of lack of reproducibility of the trend of the reaction during a run at the lower temperatures. The value of b/aK or $[\mathrm{d}\ \log_e(\mathrm{d}p/\mathrm{d}t)/\mathrm{d}t]/K$ represents the change of $\log_e(\mathrm{d}p/\mathrm{d}t)$ in a time equal to $1/K$. Most of the runs at 478 and 462° took about one-fourth this long, so the variation in $\log_e(\mathrm{d}p/\mathrm{d}t)$ during the course of a run will only be about one-quarter the value of b/aK. This variation, as may be seen from Fig. 1, is subject to an average experimental error of about $\pm {}^1/_4 \times 0.5 = \pm 0.13$. The error which could be due to fluctuations in temperature, assuming the temperature changed as much as ±0.4° during a run, sometimes in one direction, sometimes in the other, would only be about one-sixth this large. The deviations in the value of b/aK seem, therefore, a little larger than should be expected;[13] it may be remarked, however, that

Table I

525°C.—Apparatus I

p, mm.	K(sec.$^{-1}$) × 10^3	b/aK
191.0	1.65	0.28
139.5	1.61	− .01
89.6	1.43	− .07
81.5	1.28	.06
38.6	1.06	− .12
29.4	1.00	− .18
11.59	0.718	− .08
5.86	.529	.05
5.49	.623	$.13^a$
5.27	.915	− .47
2.69	.477	− .14
1.79	.466	− .30
1.290	.346	$.16^a$
0.844	.330	− .09
.230	.254	$.18^a$
.197	.258	$.38^a$
.146	.202	− .04

462°C.—Apparatus I

p, mm.	K(sec.$^{-1}$) × 10^5	b/aK
447	9.25	1.9
429	10.5	0.1
210	7.35	.8
107.3	5.40	1.0
33.5	3.74	−0.1
9.63	2.15	.3
3.11	1.44	1.1
1.208	1.22	-0.3^a
0.820	1.21	− .5
.236	1.16	1.1

478°C.—Apparatus 1

p, mm.	K(sec.$^{-1}$) × 10^4	b/aK
468.0	2.31	1.6
365.0	2.20	1.0
267.0	2.02	0.5
231.0	1.59	1.7^b
221.0	1.73	1.2
181.4	1.69	0.6
174.7	1.58	1.0
101.2	1.28	0.8
88.7	1.28	.7
87.7	1.12	1.4^b
64.7	1.08	1.1
52.9	1.27	−0.2
52.8	0.951	.2
30.8	.769	1.5
17.5	.739	0.3
10.2	.591	.5
5.68	.504	− .1
3.37	.527	− .9
1.773	.307	.5
1.174	.261	.4
0.962	.408	$.5^b$
.842	.316	− .5
.541	.300	− .6
.233	.242	.0
.127	.139	3.2

478°C.—Apparatus II

p, mm.	K(sec.$^{-1}$) × 10^4	b/aK	p, mm.	K(sec.$^{-1}$) × 10^4	b/aK
493	2.58	$-0.8^{b,c}$	37.6	0.778	0.0^c
363	2.19	$.8^{b,c}$	32.8	.576	$4.5^{c,d}$
338	2.00	1.2^c	21.3	.646	1.6
304	2.14	0.6^c	15.57	.561	1.7^d
299	1.94	$1.8^{b,c}$	13.38	.685	0.1^c
265	1.74	$1.7^{b,c}$	11.23	.444	$.0^c$
258	1.91	1.1^c	9.99	.530	$.5^c$
204	1.65	1.2^c	6.93	.481	$.6^e$
203	1.73	0.9^c	5.76	.432	.7
161	1.45	$1.1^{b,c}$	3.88	.415	.4
148	1.29	1.9^c	2.16	.535	-2.1^f
144.6	1.40	$0.9^{b,c}$	1.006	.264	0.4^e
130.5	1.26	$.9^c$	0.843	.296	− .2
117.5	1.29	1.0^c	.465	.121	$5.6^{d,e}$
94.5	1.17	1.4^c	.433	.279	$-0.8^{c,d}$
39.4	1.07	-0.7^c	.309	.201	.8

[a] Packed flask. [b] Temperature control not good. [c] Gold trap, [d] Early pressure readings erratic. [e] Phenyl chloride trap. [f] This run was stopped when the pressure had increased by only 10%.

This tabulation includes all the runs which were made except five at 520°, and one in which mercury got by accident into the reaction flask.

---

(12) We have made estimates of the initial value of $(\mathrm{d}p/\mathrm{d}t)/p$ in each case from the data given, by assuming that $\mathrm{d}p/\mathrm{d}t$ is constant over the time necessary for the pressure to increase by 50% in the case of Hinshelwood's data,[7] and over the twenty-minute interval used by Steacie.[8b] Steacie's earlier data[8a] were not used. In the case of Kassel's data,[9] his values for the change in pressure in ten minutes were used, making the same assumption about the constancy of $\mathrm{d}p/\mathrm{d}t$. In the case of Newitt and Vernon's data the constants given by them (Table III and Table IV)[10] were used. It was verified from their Table II that their k has the same meaning as our K.

(13) There is a noticeable correlation between irregularities in the values of b/aK and K. Of the seven points which had the most irregular values of K, six had markedly irregular values of b/aK. When an average value of b/aK was substituted for the observed, and the calculations carried through on that basis, all six values of K were improved, some quite considerably. It seems probable

an error in one or two readings near the beginning or end of a run has a rather large effect on b/aK. For some reason the values of b/aK at the higher temperature seem to be much more reproducible. We may remark that, were the reaction truly first order, b/aK would be negative. If, as seems probable (see below), about two molecules of product are produced from one molecule of ether, then for a truly first order reaction we should have $b/aK = -0.5$.

The data from Apparatus II, at least when the McLeod gage was used, were somewhat more erratic than those obtained from Apparatus I, and a few of the points in Fig. 1 are very far off. In a few runs, as noted in Table I, the initial readings were erratic, in a couple of instances the pressure actually decreasing after the initial readings. We are at a loss to explain this, but it may have been due in part to the fact that the tube connecting the reaction vessel to the McLeod gage was rather long and narrow, so that pressure equilibrium was probably not immediately attained, though why this should not have occurred in all the experiments is not clear. There was also some tendency for the mercury to stick in the gage. But whatever the cause of these irregularities, we may conclude with considerable certainty that there is no systematic error due to stopcock grease or mercury.

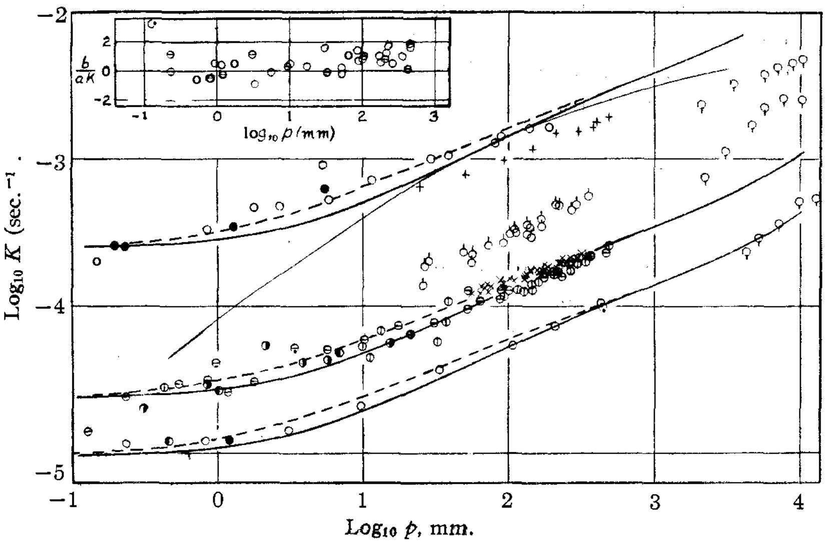

Fig. 1.—Diethyl ether. 462° and 525°: O; with packed flask: ●. 478°, Apparatus I: ⊖; Apparatus II: ◑; Apparatus II with gold trap: ⦶; Apparatus II with phenyl chloride trap: ◐. Hinshelwood, 525°, +. Kassel, 487°, ȯ. Steacie, 478°, ×. Newitt and Vernon, 462°, 490°, and 510°, ♀. In inset, 478°, O; 462°, ⊖.

The homogeneity of the reaction was tested by experiments using bulbs packed with Pyrex tubing to increase the surface about seven-fold. It was found that if the packed bulb was left empty of ether vapor at the temperatures used sufficient material, probably water vapor, would distil out, in the time necessary for a run, to affect the results appreciably. However, since the rate at which this material appeared was very approximately constant over long periods of time and did not appear to vary before and after a run was made in the bulb, it was possible to correct for it.[14] In the worst cases, at the lowest pressures used, this correction amounted to about 35% of the rate constant. When the correction was made, the runs in the packed flasks agreed with runs in unpacked flasks, so we conclude that the reaction is homogeneous even at the lowest pressures studied.

From our results we are able to get the energy of activation, E (defined by the equation $K = Ae^{-E/RT}$). At high pressures, or rather, we should say, moderate pressures of around 100 mm. we estimate E to be 62,000 calories per mole. (In getting this we considered the change in K with temperature at constant concentration, and measured from the curves actually shown in Fig. 1.) This does not agree well with the result of Hinshelwood, which is 53,000; we would have to decrease the rate at the highest temperature by around 40% while that at the lowest remained fixed, in order to agree with Hinshelwood.

Theoretical Considerations

The most interesting characteristic of the experimental results presented in Fig. 1 is the fact that the log K-log p curve is concave upward instead of concave downward, as demanded by the usual theory. Though, as already noted, the experiments were made to test one definite

---

that many of these irregularities would be avoided by more usual methods of calculation, but we believe that the least squares method described is, nevertheless, preferable when the quantity which one wishes to calculate is the initial value of K.

[14] A small correction was also made for some of the runs in the unpacked flask.

hypothesis, several possibilities suggest themselves.

Hypothesis A.—There may be two entirely separate unimolecular reactions, one with a rate constant which begins to fall off from its high pressure value in the pressure region investigated, and another whose rate constant does not fall off till one gets to much lower pressures. In the pressure range used, then, the observed rate constant would not fall below the value characteristic of this second unimolecular reaction, and the curves would have the form actually exhibited.

Hypothesis B.—Some kind of "internal activation," such as suggested in the introductory paragraphs, may become important at low pressures, and account for the fact that the rate constant does not fall off as rapidly as expected.

Hypothesis C.—The reaction may be a chain reaction with the pressure dependence of the rate determined in some unknown way by the kinetics of the chain. This possibility we shall not consider in any detail, though it is by no means entirely excluded. We may remark, however, that the fact that hydrogen accelerates the ether decomposition is more easily interpreted on the basis of the usual theory of unimolecular reactions, involving activation by collision and no chains. Furthermore the chain mechanisms recently proposed by F. O. Rice and Herzfeld[15] do not give rate pressure curves of the type actually obtained in the particular case of diethyl ether, but it might be possible to invent a mechanism that would.

Detailed Discussion of Hypothesis A.—Put in slightly more general form than that given above, this hypothesis states that the observed rate constant is simply the sum of the rate constants of a series of separate elementary unimolecular reactions which occur simultaneously. The dependence on pressure of the resultant rate constant (K) will ultimately be determined by the pressure dependence of the separate rate constants (K^i). The simplest case will occur if all these separate reactions follow Theory I of Rice and Ramsperger,[3a] that is, if $K^i_\infty = b^iW^i$, where W^i is the equilibrium fraction of activated molecules, and b^i is the probability that an activated molecule decomposes in unit time, b^i being the same for all activated molecules, and K^i_∞ is the limiting value of K^i at high pressures. It may then be shown that

$$K^i = K^i_\infty\,(1 + K^i_\infty kT/a^iW^ip)^{-1} = K^i_\infty\,(1 + \beta^i/p)^{-1} \quad (1)$$

where p is the pressure and a^i a constant from the kinetic theory of gases, such that $a^iW^i(p/kT)^2$ is the total number of collisions per unit volume per unit time which result in deactivation of an activated molecule; a^i thus depends on an effective collision cross section. β^i is defined by Equation 1, and it gives the pressure at which $K^i = K^i_\infty/2$. (Again we refer to *initial* pressures, etc.)

If now we have a composite reaction, built up from elementary reactions whose K^i are given by expressions like (1), we may write for the over-all rate constant[16]

$$K = \Sigma_iK^i = \Sigma_iK^i_\infty\,(1 + \beta^i/p)^{-1} \qquad (2)$$

In order for the log K–log p curve to be concave upward rather than downward, or at least to have a trend in that direction as compared with the curves given by the more usual theory, the small β^i must go with the small K^i_∞. In general we shall distinguish the separate i's as $i = 1$, $i = 2$, etc., where $\beta^1 > \beta^2 > \beta^3 > \ldots$

Equation 2 is based on the assumption that the activated states of the various reactions are independent of each other, so that the number of molecules in the activated state for any one of the elementary reactions is independent of how fast any of the others may be proceeding. If this is not true, then (2) can be only a rough approximation.

The elementary reactions may be of various types. Thus we could imagine that there were several successive excited vibrational levels in a molecule, from which transitions to a repulsive electronic state could occur (predissociation). There would be different transition probability for each of the successive vibrational levels and elementary reaction would be the reaction involving any *one* of these vibrational levels. Or each of the elementary reactions could involve the rupture of a specific bond of the molecule. Or, again, each of the elementary reactions could involve a different type of decomposition, each type of decomposition having concerned in it some specific number of degrees of freedom, or modes of vibration of the molecule. If this were the case, then a better expression would be obtained by replacing each K^i by one defined by the general expression of Rice and Ramsperger;[17] namely, we would have

---

[15] F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[16] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933), have used an equation equivalent to this.

[17] Ref. 3a, Eq. 8.

$$K^i = \int_{\epsilon_0^i}^{\infty} K_\epsilon^i \, \mathrm{d}\epsilon^i = \int_{\epsilon_0^i}^{\infty} W_\epsilon^i b_\epsilon^i \,(1 + b_\epsilon^i kT/a^i p)^{-1} \, \mathrm{d}\epsilon^i \quad (3)$$

In this equation $K_\epsilon^i d\epsilon^i$ is the contribution to the elementary reaction from molecules whose energy[18] lies between ϵ^i and $\epsilon^i + \mathrm{d}\epsilon^i$, $W_\epsilon^i d\epsilon^i$ is the equilibrium fraction of such molecules, b_ϵ^i their probability of reaction in unit time, and ϵ_0^i is the least energy a molecule may have in order to react in the specified manner. It is in general assumed that reaction occurs when this amount of energy, ϵ_0^i, becomes localized in a special part of the molecule. W_ϵ^i depends upon s^i, the number of modes of oscillation involved in the particular elementary reaction. In place of (2) we get[19]

$$K = \Sigma_i \int_{\epsilon_0^i}^{\infty} K_\epsilon^i \, \mathrm{d}\epsilon^i \qquad (4)$$

Detailed Discussion of Hypothesis B.[20]—Let us first consider the simplest possible case. We suppose a very small number of degrees of freedom to be concerned directly in the reaction, so that were it not for the internal activation the reaction would obey Equation 1. The internal activation, present because energy can leak over slowly between the active and inactive degrees of freedom, simply provides a source of activation which is independent of pressure. (We consider the molecule to be activated only if the requisite energy is in the active degrees of freedom.) At least this is true as long as there are enough collisions to keep up to its equilibrium value the fraction of molecules which have, in their active and inactive parts together, sufficient energy to cause reaction to occur. There is likewise, of course, the internal deactivation which is independent of pressure. One may show, in a manner similar to that used by Rice and Ramsperger in their development of Theory I, that the result does not differ in form[21] from that obtained from Equation 2 by setting $\beta^2 = 0$ and $K_\infty^3 = K_\infty^4 = \ldots = 0$. We may thus write

$$K = K_\infty^1 \,(1 + \beta^1/p)^{-1} + K_\infty^2 \qquad (5)$$

It is to be noted that we have thus made the superscript 1 refer to the active part of the molecule. This convention will also be used in the following paragraphs.

The treatment of Hypothesis B, in the case where Equation 3 rather than Equation 1 would be used were there no internal activation, is much more difficult. We shall essay no more than a rough approximation.

This approximation is based upon the observation that internal activation differs in an important respect from activation by collision. In the latter all the energy exchange takes place suddenly at the moment of collision, whereas internal activation is a slow process which is going on all the time. We can imagine a slow transference of energy back and forth between the parts of the molecule, perhaps with a certain periodic character.

We can treat this type of internal activation, assuming that the pressure is so low that collisions may be neglected, roughly as follows. Suppose a molecule with energy in its active part equal to ϵ_1^1 has just an even chance to decompose before it loses enough energy by fluctuation back to the other part of the molecule to render its rate of decomposition negligible. At greater energies than ϵ_1^1 the rate of activation will be increasingly inadequate to keep up the rate of reaction, but at lower energies the internal activation will serve to keep the supply of activated molecules nearly at its equilibrium value. We can thus get a rough idea of the rate by integrating $W_\epsilon^1 b_\epsilon^1$ up to ϵ_1^1. We thus get

$$K_0 = \int_{\epsilon_0^1}^{\epsilon_1^1} W_\epsilon^1 b_\epsilon^1 \mathrm{d}\epsilon^1 \qquad (6)$$

and K_0 will be the limiting low pressure value of K.

In order now to take care of collisions we may assume as a first approximation that for energies less than ϵ_1^1 the effective means of activation is internal transfer of energy, while for energies greater than ϵ_1^1 it is collision. This is naturally a very rough approximation, but should give us some idea of the course of the reaction with pressure. Our final expression becomes

---

(18) This will include, of course, only such part of the energy as is available, in the sense of the Rice–Ramsperger theory, for the *i*th mode of decomposition.

(19) It must be stated that the necessity of writing K as a sum of a number of integrals depends upon the exact definition of "elementary reaction." It is quite obvious that in the limiting case when there is a continuous range of activated states, each one of which can give rise to an elementary reaction, then the sum in (2) goes over into a single integral which is of exactly the form (3), provided the particular activated state is completely defined by the energy of the molecule (see, *e. g.*, Fletcher and Hinshelwood, Ref. 16). It is really the fact that this last condition is not fulfilled that necessitates writing K as the sum of several integrals. Also, writing K in the form (4) implies a rather definite determination of b_ϵ^i, namely, that of Theory II of Rice and Ramsperger, or what comes to practically the same thing, that of Theory III of Kassel.

(20) Some theoretical considerations of a general nature bearing on this material have been set forth by Gershinowitz and Rice, *J. Chem. Phys.*, **2**, 281 (1934).

(21) It differs only in that K_∞^2 has a slightly different significance in the two equations.

$$K = \int_{\epsilon_0^1}^{\epsilon_1^1} W_\epsilon^1 b_\epsilon^1 \mathrm{d}\epsilon^1 + \int_{\epsilon_1^1}^{\infty} W_\epsilon^1 b_\epsilon^1 (1 + b_\epsilon^1 kT/a^1 p)^{-1} \mathrm{d}\epsilon^1 \quad (7)$$

For very large pressures, we can of course write

$$K_\infty = \int_{\epsilon_0^1}^{\infty} W_\epsilon^1 b_\epsilon^1 \mathrm{d}\epsilon^1 \qquad (8)$$

We shall use only classical statistical mechanics in evaluating the various terms of Equation 7, it not being worth while to attempt to use the complicated expressions resulting from the introduction of quantum theory. Of the various forms of the classical theory considered by Rice and Ramsperger and by Kassel, the one developed by Kassel, in which it is assumed that the reaction of a complex molecule takes place when an energy ϵ_0^1 or greater has accumulated in one bond, is the simplest from an arithmetical point of view and gives results essentially similar to Theory II of Rice and Ramsperger. We shall accordingly use Kassel's form of the theory.

According to classical statistical mechanics, if s^1 is the number of active degrees of freedom of a molecule

$$W_\epsilon^1 = (\epsilon^1/kT)^{s^1-1} e^{-\epsilon^1/kT} [kT\Gamma(s^1)]^{-1} \qquad (9)$$

On the basis of Kassel's theory[22]

$$b_\epsilon^1 = A[(\epsilon^1 - \epsilon_0^1)/\epsilon^1]^{s^1-1} \qquad (10)$$

where A is a constant.

From (9), (10) and (8) we get

$$K_\infty = Ae^{-\epsilon_0^1/kT} \qquad (11)$$

and from (6), (9), (10) and (11) we may determine ϵ_1^1 if K_0 and K_∞ are known.

Discussion of Special Cases

Before we attempt to apply the theory to diethyl ether we shall consider several reactions which have been studied by others. In some of these cases theories similar to the above have already been applied, but some further discussion appears desirable.

Acetaldehyde.—Fletcher and Hinshelwood[16] have recently extended the earlier work of Hinshelwood and Hutchison[23] and of Kassel[24] on acetaldehyde, and made measurements over a large range of pressures. They have considered the possibility of explaining their results on the basis of an equation equivalent to (2) based on Hypothesis A. After some discussion, however, they eventually arrived at a theory essentially identical with the earlier suggestion of Rice, namely, hypothesis B. However, the energy of activation of the reaction shows a difference at high and low pressures,[25] far greater than seems likely to occur on the basis of Hypothesis B; this will be sufficiently evident from the subsequent discussion of diethyl ether, but did not appear from Fletcher and Hinshelwood's work, as they did not give a sufficiently detailed discussion of the theory.

Furthermore, since this paper was originally submitted for publication, evidence has been obtained in this Laboratory[26] which rather indicates that the thermal decomposition of acetaldehyde is really a chain reaction, with a mechanism similar to that suggested by F. O. Rice and Herzfeld.[15] The difference in energy of activation at high and low pressures suggests that this is not the whole story, but it must be said that at the present time it seems quite unlikely that Equation 2 may be applied to acetaldehyde.

Nitrous Oxide.—Musgrave and Hinshelwood,[27] and, since this paper was originally submitted, Hunter[28] have discussed the decomposition of nitrous oxide and have concluded that Hypothesis A is applicable to the experimental results. They believe that there are at least two elementary reactions,[29] all with different energies of activation. It seems to us that in this case the general conclusions they have drawn from their data are correct.

Nitryl Chloride.—The decomposition of this substance has been studied by Schumacher and

---

[22] For the special assumptions necessary to get this result see Ref. 4, or Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., 1932, Chap. V.

[23] Hinshelwood and Hutchison, *Proc. Roy. Soc.* (London), **A111**, 380 (1926).

[24] Kassel, *J. Phys. Chem.*, **34**, 1166 (1930).

[25] It is 55,000 calories per mole at 25 mm., and 47,700 at 450 mm.

[26] Sickman and Allen, This Journal, **56**, 1251 (1934); Leermakers, *ibid.*, **56**, 1537 (1934).

[27] Musgrave and Hinshelwood, *Proc. Roy. Soc.* (London), **A135**, 23 (1932).

[28] Hunter, *ibid.*, **A144**, 386 (1934).

[29] It should be stated, however, that the results of Musgrave and Hinshelwood and Hunter do not agree particularly well with those of Nagasako and Volmer, *Z. physik. Chem.*, **10B**, 414 (1930). If the large change in temperature coefficient with pressure found by Musgrave and Hinshelwood and by Hunter is correct, then it would seem almost certain that at least two reactions are involved. We have not investigated the newer data in detail and the conclusions of Hinshelwood and his co-workers are not based on any attempt to fit the rate pressure curve exactly, but only on certain breaks in the curve which are noted when K is plotted against p, without reducing to logarithmic form. It is the considered opinion of Hinshelwood and his co-workers that this method of presenting the data is better than the logarithmic graph which we use. The latter reduces any breaks which may appear in the non-logarithmic graph to very small humps, but it is our opinion that this gives a truer representation of their actual importance. The breaks are greatly emphasized by the non-logarithmic plot, on account of the steadily increasing curvature as one goes to lower pressures. The logarithmic curve, on the contrary, does not change rapidly in curvature. It has the further advantage that the separate log K^i of Equation 2 have, when plotted as a function of log p, a shape which is independent of β^i. Furthermore, deviations from the expected shape are easily detected in the logarithmic plot, even though no breaks occur in the curve, and in this respect we believe it to be much superior to the non-logarithmic curve. It may not be amiss to remark that the arithmetic can be conveniently handled by the use of addition logarithms. See, *e. g.*, Milne-Thomson and Comrie, "Standard Four-Figure Mathematical Tables," The Macmillan Co., 1931, p. 10.

Sprenger.[30] Their experiments with inert gases seem to indicate that this is a quasi-unimolecular reaction of the ordinary type, nevertheless, the log K–log p curves appear to be almost exactly straight lines with a slope of $^1/_2$, which on the basis of the ordinary theories is quite unexpected. As a matter of fact, however, Equation 5 fits the experimental results very well, as is shown in Fig. 2. This, of course, does not allow us to distinguish between Hypothesis A and Hypothesis B, but the fact that the temperature coefficient varies very little if any with pressure would seem to make Hypothesis B very reasonable, and we shall show later that it is at least quite consistent with what is known about the reaction. In making our calculations we have set $K^2 = K^1/99$ for all temperatures. In order to have the rate constant fall off at the right pressure, using effective collision diameters of kinetic theory size, it is necessary to assume[31] that $s^1 = 2$. We have, nevertheless, made the calculations on the basis of Equation 5 rather than use the more complicated Equation 7. This does not make any great difference in the shape of the curves, and may indeed be correct if the reaction mechanism proposed by Schumacher and Sprenger, involving the splitting off of a chlorine atom, is correct, and if the chlorine splits off when it receives enough vibrational energy in a direction *transverse* to its bond. For the transverse vibration really involves *two* oscillators, and one might expect that the probability of reaction would be independent of the way the energy is divided between these two oscillators, which would call for Theory I. In any event, it would not be possible to fit the data, assuming $s^1 = 2$, without bringing in another reaction at low pressures. If, however, we should make the assumption that transfer of energy at collision was not very efficient, thus assigning the molecule a smaller effective radius and should compensate for this by setting $s^1 = 4$ or $s^1 = 5$, then the ordinary Theory II of Rice and Ramsperger, or Theory III of Kassel, could be made to fit the data within the limits of error without assuming any low pressure unimolecular stage coming in. This would assume that the slight upward trend at the low pressures of the curves of data at the high temperatures was due to experimental error. Though only experiments at lower pressures could definitely settle this question, we are inclined to believe that another unimolecular stage is actually coming in at low pressures, and shall proceed to discuss the reaction on that basis.

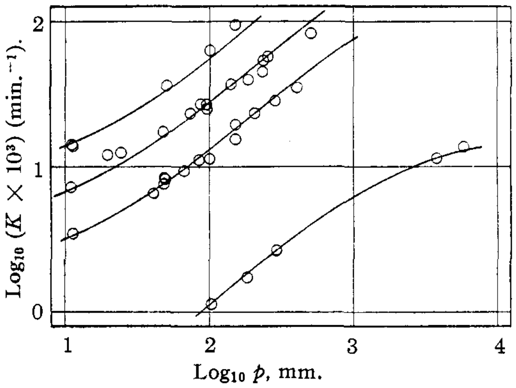

Fig. 2.—Nitryl chloride (temperatures, 100, 130, 140, 150°).

The calculations with Equation 5 are, as we have noted, equivalent to using Equation 2 and setting $K^3_\infty = K^4_\infty = \ldots = 0$ and $\beta^2 = 0$. This gives good agreement with experiment which is destroyed if β^2 is taken to be greater than $^1/_{500}$ to $^1/_{1000}$ the value of β^1. Since $\beta^i = K^i_\infty kT/a^iW^i$ and K^2_∞ is about $K^1_\infty/100$ we see that a good part but not all of the difference in the β^i may be referred to the K^i_∞. It might be possible to refer the rest of the difference between β^1 and β^2 to the a^i, the quantities which determine the number of effective collisions. It seems quite probable, however, that it is to be ascribed to a larger value of W^2, on account of a larger number of degrees of freedom being active at low pressures. We believe it likely that the reaction mechanism is similar to that postulated by Herzberg[32] to explain the decomposition of nitrous oxide, namely, the molecules must first be excited to some rather definite higher vibrational level, and from this level dissociation may take place through a radiationless transition, involving an electronic shift. It seems probable that at high pressures the vibrational level must be excited directly by collision, but at low pressures excitation by energy transfer from the rest of the molecule becomes important. There is at

---

(30) Schumacher and Sprenger, *Z. physik. Chem.*, **12B**, 115 (1931).

(31) In making this calculation we have used the value 24,900 calories per mole for the activation energy. Schumacher and Sprenger give the value 20,500, which recalculation from their data shows to be in error.

(32) Herzberg, *Z. physik. Chem.*, **17B**, 68 (1932). That an electron transition of some kind is involved is indicated by the rather low value of the absolute rate of reaction; if we express the rate constant, K^1_∞, in the form $Ae^{-E/kT}$, A has a value of about 10^{11} sec.$^{-1}$.

least no evidence against this hypothesis in this case, and it seems to fit in quite well with the reaction mechanism proposed by Schumacher and Sprenger which involves a splitting off of the chlorine atom. It is very likely that the vibration of the chlorine atom would have frequencies sufficiently different from the others in the molecule so that there would be slow exchange of energy with the rest of the molecule.

Diethyl Ether.—In Fig. 1 we have included theoretical curves to compare with the experimental data on diethyl ether. These curves were obtained from the equations developed above, together with the assumption that the high pressure data of Newitt and Vernon are to be accounted for by simply adding a bimolecular reaction which becomes increasingly important at the higher pressures. The solid curves of Fig. 1 are the result of making the calculation from Equation 7, adding the bimolecular part; at 525° the curve for the ordinary Rice–Ramsperger–Kassel theory is also given as a solid line. The broken curves are obtained from Equation 4, using the same constants to evaluate K_ϵ^1 that were used to evaluate the second term of Equation 7, assuming that K_∞^2 is equal at each temperature to the K_0 of Hypothesis B, and letting $\beta^2 = 0$ and $K_\infty^3 = K_\infty^4 = \ldots = 0$. The high pressure bimolecular reaction is added in, as for Hypothesis B. In proceeding thus, it is seen that we have used Hypothesis B to determine any difference in the temperature coefficients exhibited by the theoretical curves at the high and low pressure ends; the exact way this has been done will be explained immediately. Our curves for Hypothesis A have merely been fitted on to those for Hypothesis B in such a way that they coincide at each temperature for very high pressures and very low pressures. In the calculations we have assumed $\epsilon_0^1 = 59{,}700$ calories per mole,[33] $\epsilon_1^1 = 63{,}430$ calories per mole, K_∞ as shown, and the effective number of degrees of freedom, $s^1 = 6$. This is somewhat larger than Hinshelwood's value of s^1, but still much less than the total number of degrees of freedom in the molecule. A (Equation 10) was of course simply given the value necessary to place the curve in such a position along the pressure axis that it would fit the data. The value of A thus chosen made the effective diameter of kinetic theory order of magnitude. The constant for the high pressure bimolecular part was such as to give a specific rate equal to 2.16 times K_∞ at a pressure of 10^4 mm. That this is not a bimolecular reaction of the ordinary type is seen by computing the number of collisions and multiplying by $e^{-E/kT}$, giving E, the activation energy, the value of 59,700 (which seems about right for the reaction at high as well as at moderate pressures, though this is not very certain). The rate thus calculated is about 10^{-4} times too small.[34] The particular way that we have divided up the reaction into bimolecular and unimolecular parts at high pressures is thus rather arbitrary; nevertheless, it seems reasonable enough to do this in order to discuss the reaction at low pressures.

The curves for the various temperatures, shown in Fig. 1, were obtained in the following way. First the curve for 478° was constructed and it was assumed that the temperature coefficient was independent of pressure above about 100 mm. On the other hand, at the low pressures the curves were calculated directly from (7) for the various temperatures, and it is thus found that the energy of activation should, according to the theory, be about 3000 calories less at the low range of pressures than it is around 100 or 200 mm. It is readily seen that something of this sort must be the case since the average energy of the molecules which actually react is less at the low pressures than at the high pressures, according to the theory. However, this average energy is the average energy only of the part of the molecule most directly concerned with the reaction. The theory therefore implicitly contains the assumption that the average energy of the rest of the molecule will be independent of the energy of the part most directly concerned with the decomposition. This assumption might well be unjustified, as would be the case, for example, if the time required to transfer energy back and forth from the active to the inactive part of the molecule decreased as the total energy (*i. e.*, the sum of the energies of the active and inactive parts) increased. The effect of this may be seen from Equation 6, as it would mean that the average or effective value of

---

(33) Our final best value was slightly larger than this, but the difference is of no great significance. Using the correct value of ϵ_0^1 would make the necessary effective value of the collision diameter slightly larger, but not sufficiently to make it worth while to repeat the calculation using a larger value of s^1.

(34) Thus we are apparently not observing the effect predicted by Kassel, This Journal, **50**, 1344 (1928).

ϵ_1^1 would increase with the temperature, thus increasing the relative rate at the higher temperature and so making the low pressure temperature coefficient higher than it otherwise would be.

It is not surprising, therefore, that the experimental temperature coefficients at various pressures should not follow exactly the prediction from our theoretical curves, even if we assume Hypothesis B is correct. As a matter of fact we find that, at least within the limit of experimental error, the apparent activation energy at the very lowest pressures is about the same as at 100 mm. In our preliminary note[1] we stated that the temperature coefficient appeared to be slightly higher at the low pressures, and this is true except at the very lowest pressure. In other words the curve for 525° appears to have slightly less curvature than the curves at 478 and 462°. The greatest difference in activation energy along the range is about 3000 calories. It is not certain that this is beyond the experimental error.

As far as regards the shape of the log K–log p curve at any one temperature, it is seen from Fig. 1 that the experimental data fit the broken curve, based on the assumption that a distinct and separate reaction comes in at low pressures, at least as well as it fits the solid curve based on the assumption of internal activation. It is fairly obvious, however, that no unequivocal decision between the two hypotheses can be obtained by comparison of the experimental points with the theoretical curves, and the agreement in either case is about as good as one could expect. One certainly could not expect the rather crude development of Hypothesis B to give better than semi-quantitative results. Furthermore, complications can come into the process of internal activation which were not taken into account in the theory. It was noted in the paper of Rice[5] that at a sufficiently low pressure the rate constant for the low pressure unimolecular stage would begin to fall off; this might be followed by another unimolecular stage at still lower pressures, and so on. If, however, the various rate constants for the different unimolecular stages did not differ very much from each other they would all be mixed up together; the curve, as noted by Kassel,[35] would assume a complex and unpredictable form, but its curvature should certainly be lessened, and so it would become more like the experimental curve. In any event, as we have already suggested in the introductory paragraphs, some such explanation would seem to be necessary to account for the reaction at high pressures. That the latter is not just the ordinary type of bimolecular reaction, merely superimposed upon the unimolecular reaction, has been noted. In this connection we may note that Newitt and Vernon report that the course of the reaction during a run is not second order, but roughly first order; and as we shall see in the next section there is no sufficient evidence for supposing that we have an absolutely separate and distinct reaction at high pressures. However, on account of the complexity of the various reactions that may follow the initial one, we should be cautious in drawing conclusions from the trend of the rate constant during a run, and there is still unexplained the observation of Newitt and Vernon that the presence of hydrogen or acetaldehyde does not affect the rate of decomposition of the ether.[36] This is very peculiar since at moderate pressures hydrogen has been shown by Hinshelwood to accelerate the reaction, hydrogen acting as an activating agent, an observation which we, also, have confirmed.[1]

We may sum up our discussion on diethyl ether by saying that the reaction rate data do not allow us to distinguish between Hypothesis A and Hypothesis B, but either seems satisfactory for the low and moderate pressure region.

Analysis of the Reaction Products

In order to throw further light on the question as to whether Hypothesis A or Hypothesis B is to be preferred, some analyses of the products of reaction were made. Unfortunately the results are not capable of unambiguous interpretation, and have only the status of preliminary experiments. To exhaust the possibilities would require another research in itself. Nevertheless, what has been done is of some interest, and will be presented here.

Since there seems to be no doubt that the initial decomposition of diethyl ether is followed by other reactions, and since we are primarily interested in the initial reaction, it follows that gas analyses will be of greatest interest if made early in the course of a run. We, therefore, made two runs at 478°, at pressures of 170 mm. and 5 mm., respectively, which were allowed to go until the pressure had

---

(35) Kassel, Ref. 22, p. 107.

(36) We have stated there is no reason to suppose that the high pressure reaction involves any process essentially different from the reaction at moderate pressures. This appears in the next section, and is based on the analyses of the reaction products. In view of this different behavior with hydrogen, however, one may not rule out the possibility that it might be of somewhat different character. It is possible that a chain reaction of the type postulated by F. O. Rice and Herzfeld[15] comes in at the high pressures.

increased by only 5%. The gas in the reaction vessel was withdrawn with a Toepler pump through a trap cooled in carbon dioxide snow to remove excess ether vapor. The remaining ether was absorbed in concentrated sulfuric acid, and the rest of the gas, representing the reaction products, was analyzed by the method of Christiansen and Huffman,[37] for carbon dioxide (by absorption in potassium hydroxide solution), ethylene or other unsaturated products (by absorption in fuming sulfuric acid), and carbon monoxide (by absorption in ammoniacal cuprous chloride solution). Several check analyses made on the two samples of gas gave results as follows. Initial pressure, 170 mm.: CO_2, 0.0%; C_2H_4, 0.5%; CO, 18.5%. Initial pressure, 5 mm.: CO_2, 0.0%; C_2H_4, 0.7%; CO, 29.8%. The results are given as volume percentages of the gas left after the ether was removed. The gas unaccounted for presumably consists of saturated hydrocarbons. These differ from the results of Hinshelwood.[7]

The performance of these analyses is rendered difficult by the presence of the large amount of undecomposed ether which must be removed. In removing it, it is not impossible that other gases will be also removed by solution in it. It seems very unlikely that any appreciable amount of carbon monoxide will dissolve in the ether at the temperature at which it is removed; on the other hand, ethane may well do so. This effect will be of most importance at the higher pressures, and it is therefore seen that if a correction for it is necessary it can only increase the difference between the analyses for the two pressures.

Since Newitt and Vernon found aldehydes to be present in the partially completed experiments, and since formaldehyde is known to be an intermediate product in the decomposition of dimethyl ether it seemed to us that it would be desirable to test for aldehydes in the reaction products. Accordingly we made two runs at 478°, one at 150 mm. and one at 10 mm. pressure, allowing these to go until the pressure had increased by about 20%. We got definite positive tests for aldehyde in both cases, using fuchsin solution as an indicator. These experiments were performed several months after the experiments at 478° with the last of the ether which had been prepared for these experiments. As the ether had been standing in vacuum over mercury in diffuse light there seemed no likelihood that there could be any aldehyde or aldehyde-like substances in the ether itself. Nevertheless, it seemed desirable to make a blank test; it was possible to get only an amount of ether equivalent to that used in a run at 12 mm.; however, on standing for two hours in the solution no slightest change of color could be observed, which seemed to be satisfactory evidence that there was no aldehyde in the ether itself.

According to the results of our analyses we feel that the most likely mechanism of the initial reaction is

$$C_2H_5OC_2H_5 \longrightarrow CH_3CHO + C_2H_6$$
$$CH_3CHO \longrightarrow CH_4 + CO$$

This mechanism has been suggested by Newitt and Vernon to account for the major part of the high pressure reaction. It seems, therefore, very likely that at least as far as the initial part of the reaction is concerned the mechanism is the same at all pressures.

Our method of detecting the presence of aldehydes will not, of course, distinguish between acetaldehyde and formaldehyde. Newitt and Vernon have determined formaldehyde and acetaldehyde separately. They find that there is formaldehyde present in increasing amounts as the reaction goes on. They also found a certain amount of ethylene to be present, and suggest the supplementary mechanism of decomposition

$$C_2H_5OC_2H_5 \longrightarrow HCHO + CH_4 + C_2H_4$$
$$HCHO \longrightarrow H_2 + CO$$

Since our analyses were made earlier in the run than those of Newitt and Vernon in which a complete analysis was made, we may perhaps assume that this second mechanism of decomposition does not appreciably enter in at the initial stage of the reaction, even though Newitt and Vernon found formaldehyde present in increasingly important amounts as they lowered the pressure.

Our results differ from Hinshelwood's which may be due to the fact that his analyses were performed after completion of the reaction. The mechanism which we propose as probably accounting for the reaction at low and moderate as well as very high pressures differs from the one suggested by Hinshelwood. It may, perhaps, be worth while to point out that the mechanism of the decomposition of methyl ethyl ether, which has been proposed by Ure and Young[38] as a result of a very careful series of analyses at moderate pressures, is exactly similar to the one we believe to be correct for diethyl ether.

Some explanation is still necessary to account for the fact that more carbon monoxide is found in our analyses for the lower pressure than the higher. This difference is rather peculiar, inasmuch as the rate of decomposition of aldehyde falls off more rapidly with the pressure than that of ether. But even at the higher pressure it is too slow to account for the amount of carbon monoxide formed in so short a time. This may of course be considered to be evidence in favor of Hypothesis A, namely, it suggests that there are two distinct reactions, one of which results in the direct formation of carbon monoxide, while in the other aldehyde is an intermediate. An alternative explanation is the following.

The change from ether into ethane and aldehyde involves the shifting of a hydrogen in the molecule, as well as the breaking of a bond. It is therefore very probable that the decomposition proceeds with a twist which would cause the energy of activation to go into vibrational energy. Just how this might take place one cannot say in detail, but there may be sufficient energy available to activate the aldehyde molecule.[39] An activated aldehyde molecule would nevertheless take some little time to decompose,

---

[37] (37) Christiansen and Huffman, *Z. anal. Chem.*, **80**, 435 (1930).

[38] (38) Ure and Young, *J. Phys. Chem.*, **37**, 1169 (1933).

[39] (39) The energy of activation of the ether is available and, in addition to that, the energy of the reaction $(C_2H_5)_2O \longrightarrow C_2H_6 + CH_3CHO$, which is about 7 kg. cal. at room temperature, according to the heats of combustion of Thomsen (see Landolt–Bornstein, Tabellen, 5th Edition, 1923, pp. 1588, 1595, 1597). The energy of the reaction is probably greater at the temperature of reaction, since one may expect the specific heat of the ether to be greater than the sum of the specific heats of the other substances. Using our value of the energy of activation we thus have about 70,000 calories per mole available. Just how this would be divided between the ethane and the aldehyde we do not know, nor can we derive any information as to the amount of energy which would be needed by the aldehyde by a consideration of its thermal decomposition, since the latter is probably a chain reaction.

and its chance of being deactivated would be greater the higher the pressure. In this way the results of the gas analysis could be qualitatively explained.

If this suggestion is correct then a correction is needed in our calculation of the rate constant K from dp/dt, for it is seen that the constant of proportionality would be different at different pressures. This effect, however, would not be sufficient to affect the general character of our results, nor the conclusions which one can draw from them.

Preliminary Results on Divinyl Ether

A series of experiments over a range of pressures from 0.5 to 150 mm. has been made with divinyl ether. The log K–log p curves are very similar to those of diethyl ether, with even more pronounced upward curvature.

Acknowledgment.—We are grateful to the Milton Fund of Harvard University for a grant which made it possible to complete the experimental work reported in this paper.

Summary

The rate of decomposition of diethyl ether vapor has been studied at temperatures of 525, 478 and 462° and over pressures ranging from one- or two-tenths of a millimeter to several hundred millimeters. These results have been presented both in tables and in graphs, and have been compared with the results of other experimenters. It is found that when one plots the logarithm of the rate constant as ordinate against the logarithm of the pressure, the curve which one obtains is in this case concave upward, contrary to the usual situation with unimolecular reactions.

A detailed account is given of two possible theories, which can explain this behavior. According to Hypothesis A, in addition to the unimolecular reaction whose rate constant is beginning to fall off at moderate pressures, there is a second, distinct unimolecular reaction by way of which diethyl ether can decompose, and which becomes of importance at low pressures because of the fact that, while its rate constant is relatively small, it does not fall below its limiting high pressure value even at the lowest pressures used. According to Hypothesis B, the molecule may be divided into an active part which can transmit energy rapidly to the bond which breaks or changes in the reaction, and an inactive part. The shape of the curves is then explained on the assumption that there is a slow transfer of energy from the inactive to the active part of the molecule. Various variants and generalizations of these theories are discussed, and their application to several other reactions is considered.

Some analyses of the reaction products, as they exist toward the beginning of a run in the decomposition of the diethyl ether, are reported. These are discussed in the light of the above theories, and a tentative suggestion is made concerning the mechanism of the reaction.

CAMBRIDGE, MASS. RECEIVED MARCH 7, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochemical Gas Phase Reaction between Chlorine and Bromotrichloromethane

BY HAROLD G. VESPER AND G. K. ROLLEFSON

The photochemical reaction between chlorine and bromotrichloromethane in solution was first studied by Noddack,[1] who reported a quantum yield of one at high concentrations decreasing to about 0.2 in dilute solutions. A later study by Grüss[2] reported a quantum yield of 0.88 ± 0.25 independent of the concentration of bromotrichloromethane. The variations found by Noddack were attributed to impurities in the reagents used by him. In both these researches it was assumed that the products formed were carbon tetrachloride and bromine and the extent to which the reaction had proceeded was determined by measuring the light absorbed by the bromine. As recent investigations in this Laboratory and elsewhere[3] have shown that bromine and chlorine react to form bromine chloride, which has a markedly different absorption coefficient from bromine, it seemed probable that this reaction was not as simple as had been supposed, but involved a chain process. The results to be presented in this paper confirmed this view and a

---

(1) Noddack, *Z. Elektrochem.*, **27**, 359 (1921).

(2) Grüss, *ibid.*, **29**, 144 (1923).

(3) (a) Vesper and Rollefson, THIS JOURNAL, **56**, 620 (1934); (b) Blair and Yost, *ibid.*, **55**, 4489 (1933).