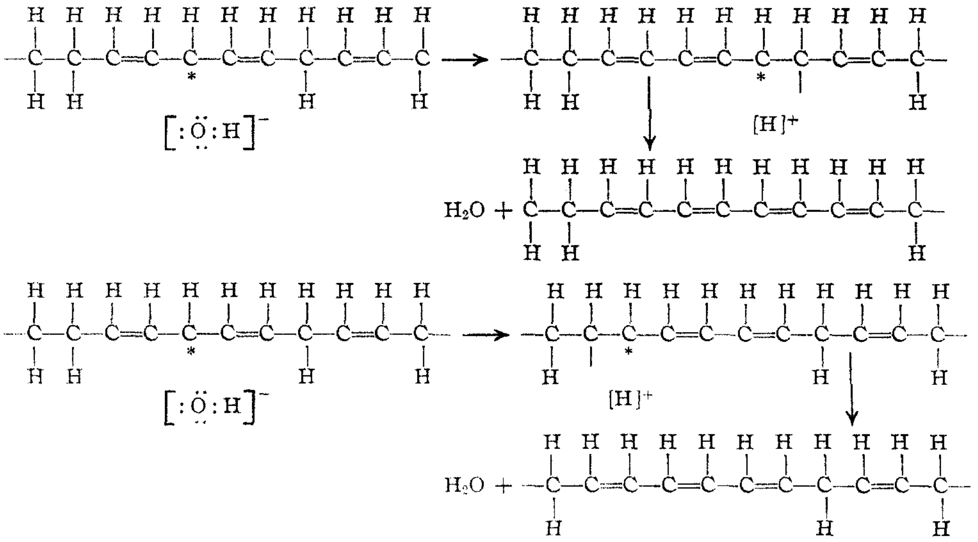

3. By low temperature crystallization from solvents, the most unsaturated fraction of bleached linseed oil fatty acids was obtained. This process removed the substance causing a band at 2680 Å., leaving the highly unsaturated fraction with a spectrum similar in character to that obtained for the four double bond conjugated system in decatetraene and in parinaric acid.

4. Oxidation of the oil or fatty acid esters is a necessary intermediate step in the formation of the conjugated systems which may be produced by dehydration.

5. Pure non-conjugated linoleic and linolenic acids would show no absorption bands in the region of wave length longer than 2200 Å. Any bands found in regions of longer wave length are due to the presence of traces of conjugated materials.

6. There was no evidence for diene conjugation in linoleic and linolenic acids prepared by debromination.

7. In the bleached oils examined, the amounts of conjugated material were very small, about 0.1 or 0.2%.

8. Deodorization results in a lowering of these bands due to polymerization of the conjugated systems at elevated temperatures. The bands are removed in the processes of bodying linseed oil by heating *in vacuo* or by oxidation.

LAFAYETTE, INDIANA RECEIVED JANUARY 2, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetics of Gaseous Reactions by Means of the Mass Spectrometer. The Thermal Decomposition of Dimethyl Ether and Acetaldehyde*

BY EDGAR LEIFER AND HAROLD C. UREY

The kinetics of gaseous reactions have been the subject of a great many investigations not only because of their intrinsic interest, but also with the hope of securing a clearer insight into the mechanisms of the reactions. These studies have been made principally by two methods, namely, by the measurement of pressure and by detailed analyses of the reaction mixture by chemical and physical means. Most of the data reported in the literature for kinetics of gaseous reactions have been found by pressure measurements because of the ease with which they may be made. If one then assumes an appropriate mechanism consistent with the data, a rate constant may be calculated. The obvious disadvantage of the pressure method is that it gives no insight into the nature of the reactions, which actually take place; that is, any intermediates, which are formed, may not be detected. Because of this, the tendency in recent work in gas reactions has

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* Presented at the Atlantic City Meeting of the American Chemical Society.

been to perform detailed analyses on samples withdrawn from the reaction vessel at definite time intervals. The number of reactions so studied has been few and in fewer cases have complete analyses been made. This is especially true in reactions involving organic molecules, where separations are very difficult. The following disadvantages are inherent in this method. Small amounts of some substances are extremely difficult to determine. Errors such as those arising from polymerization reactions may appear during analyses. A third disadvantage is that one can generally obtain only one point from a particular reaction mixture. The great deal of controversy and confusion which exists in this field indicates the need for new approaches to these problems. It, therefore, seemed that a mass spectrometer, which heretofore has been used mainly for isotopic abundance ratios, might be used to advantage. One could then follow the course of any gaseous reactant, product, or stable intermediate by tracing the intensity of the mass spectrometer peak with time. In addition, by using isotopes as tracers, many interesting features of the reaction may be disclosed. Small amounts of products which are formed in quantities as small as 0.1% can be detected.

Method of Analysis

In this work a mass spectrometer of the Bleakney[1] type was used. The thermal decomposition of dimethyl ether, where a stable intermediate is formed, and also the decomposition of acetaldehyde, were studied by this method. These substances were selected because it was thought that they were typical—neither too simple nor too complicated.

There are several factors which must be considered before this method can be applied. In the absence of any change in concentration the peak intensity for a particular mass must remain constant. In Table I the intensity of the mass 46 peak (CH_3OCH_3) is shown as a function of time at a constant electron beam intensity, when no decomposition is taking place.

TABLE I

Time, hr.	Peak intensity (Arbitrary Units)
0	59.2
1	57.7
2	57.0

These results immediately place a limitation of about 5% on the accuracy obtainable with this method. Peak intensities must be compared at constant electron beam intensities. In the present research, this was accomplished by adjusting the filament current while measurements were being made.[2] Not only is it necessary to control the electron intensity, but also it has been found necessary to control the energy of the electron beam so that the products of reaction, which are measured, will be those formed in the reaction vessel and not those produced by electron bombardment. In order to maintain a high intensity of electrons and yet adjust their energies to the proper values, the electrons emitted by the heated filament were first accelerated through 44 volts between the filament and the first slit, and then decelerated between the next two plates before entering the ionizing region.[3] Listed in Table II are the accelerating voltages below which the peaks corresponding to stable intermediates and products could not be formed by electron bombardment of dimethyl ether and acetaldehyde molecules.

TABLE II

Dimethyl ether			Acetaldehyde		
Mass	Ion	Acc. voltage, volts	Mass	Ion	Acc. voltage, volts
30	$HCHO^+$	14.5	28	CO^+	16.0
28	CO^+	18.5	16	CH_4^+	14.5
16	CH_4^+	18.0			
2	H_2^+	20.0			

For any given ion the peak intensity corresponding to formation by electron bombardment drops off rapidly with the accelerating voltage. For example, the results for carbon monoxide formed from cold dimethyl ether by electron bombardment are illustrated in Fig. 1. It was always found possible to find such an accelerating voltage. The appearance potentials listed in Table II are purely empirical. Even with these accelerating voltages, the electron energies were still sufficient to ionize the decomposition products and reactant molecules for mass analyses. In order to be certain that no error arises from this source, cold reacting substances were placed behind another leak and, simply by reversing a stopcock, one could allow this unreacted gas, rather than the reacted gases, to flow into the spectrometer.

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(1) Bleakney, *Phys. Review*, **40**, 496 (1932).

(2) A circuit recently devised by Professor A. O. Nier for heating the filament with an alternating current, controls the current automatically to give a constant electron beam intensity. This is a great advantage for this type of work.

(3) Bleakney, ref. 1, Fig. 1, for arrangement of accelerating plates.

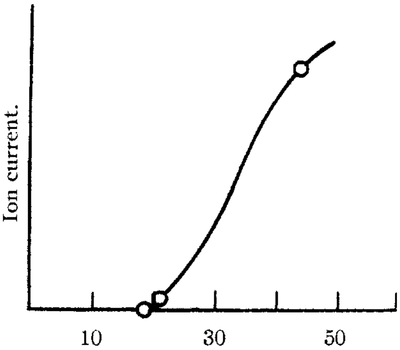

Fig. 1.

Another difficulty may arise from thermal molecular decomposition on the heated filament inside the spectrometer. In a Bleakney spectrometer the filament is close to the pumping lead, and any decomposition products so formed were pumped out and could not be detected. With other mass spectrometers, where the filament is larger and not so conveniently placed near the pumping lead, *e. g.*, Nier[4] type, it may be necessary to introduce an extra pumping lead around the filament chamber to avoid this decomposition.[5]

The next problem of importance is to determine the relation between the peak intensities and the pressure inside the reaction vessel. The rate of gas flow from the reaction vessel into the mass spectrometer was 0.01–0.05 ml. per hour. When a sample of gas was placed behind the leak, this rate of flow was found to give peak intensity readings which were directly proportional to the pressure over a range of several hundred millimeters. These intensities were within the measurable range.

Experimental

The reaction vessel, which was a tube of Pyrex glass 4.0 cm. in diameter and 20 cm. long, having a volume of approximately 250 ml. (A in Fig. 2), was placed in the well of a sulfur thermostat equipped with a barostat and a vacuum tube relay control.[6] This device maintained the temperature at 503.8 ± 0.3°. The temperature was measured with a Pt:Pt–Rh thermocouple calibrated at the melting points of Bureau of Standards samples of tin, zinc, and aluminum. A capillary leak (F) drawn from Pyrex tubing extended 9 cm. into the inside of the reaction vessel.

In addition to determining the peak intensities of the products and the reactants, the progress of the reaction was also followed by observing the increase in pressure by means of a capillary mercury manometer (G).

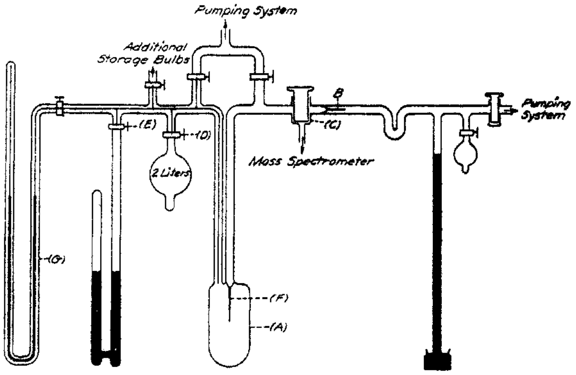

Fig. 2.—Diagram of apparatus.

Figure 2 describes the apparatus used. Preliminary to making a run, the mass spectrometer was baked free of adsorbed gases, if this was found necessary. A sample of cold dimethyl ether gas was placed behind leak (B) and the decelerating voltages were adjusted until the appearance potentials for the ions were reached. At this time the ion-accelerating voltages necessary to bring the molecular ions into focus were determined. The mass spectrometer was now assumed to be ready for a run and stopcock (C) was turned to allow gas to leak from the reaction vessel into the mass spectrometer. The presence of stopcock (C) was found to be very useful since, by reversing it at any time, it could be determined whether a measured peak was formed from thermal decomposition in the reaction vessel or from other sources inside the spectrometer. By opening stopcock (D), a sample of gas was admitted to the reaction vessel (A), which was already well pumped out and at the working temperature. After closing stopcock (D), the initial pressure was determined by closing stopcock (E) and reading the barometer. This was taken as the initial time of the reaction. The entire operation of admitting the gas and closing stopcocks took about fifteen seconds. The connections between the reaction vessel and the storage bulbs were of capillary tubing, and the dead space amounted to about 1% of the total volume of the reaction vessel. Measurements were taken every three minutes in the early stages of reaction and less frequently as reaction progressed. All stopcocks were lubricated with Apiezon-N grease.

If the reaction follows the stoichiometric equation, as in the case of acetaldehyde, the agreement between the mass spectrometer and pressure methods has been found to be good to about 3%, when the reaction is followed for about sixty minutes. However, generally over longer time periods and in cases where the exact extent of reaction cannot be calculated from the increase of pressure, as in the case of dimethyl ether where small amounts of formaldehyde are present as an intermediate, the over-all agreement between the two methods is about 10%. Too much weight should not be placed upon results during the first twelve minutes, as it was found that it takes this time before equilibrium conditions are established in the flow of gases through the spectrometer. In calculating the results it is assumed that there is zero time lag between reaction and ionization.

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(4) Nier, *Rev. Scientific Instr.*, **11**, 212 (1940).

(5) Hustrulid, Kusch and Tate [*Phys. Review*, **54**, 1037 (1938)] in studying ionization potentials by means of a mass spectrometer found that by enclosing the filament in a housing and by introducing a separate pumping lead, the products of decomposition at the filament were prevented from diffusing into the ionizing region.

(6) Rittenberg and Urey, THIS JOURNAL, **56**, 1885 (1934).

TABLE III

ACETALDEHYDE—503.8°

	CH_3CHO			CO			CH_4	
Time, min.	Pressure mass sp., mm.	Calculated pressure manometer, mm.	Time, min.	Pressure mass sp., mm.	Calculated pressure manometer, mm.	Time, min.	Pressure mass sp., mm.	Calculatd pressure manometer, mm.
0	..	225	3.0	42	37	4.0	53	49
10.0	144	145	5.0	69	60	8.0	86	83
12.0	132	135	7.0	82	78	11.5	106	111
15.0	121	123	13.0	115	120	18.0	145	143
19.5	108	107	17.0	132	137	22.0	157	157
23.0	98	97.5	23.0	155	160	29.5	183	175
26.0	92	91.5	27.5	165	165	34.5	189	185
31.0	82	82	37.0	182	186	41.5	200	192
36.0	74	75	40.0	189	190	43.5	203	194
41.0	70	70	45.0	194	194			

That this is so within the experimental error has been verified by reversing stopcock C during a run and then again reversing it to its initial condition.

Dimethyl ether was prepared by three successive distillations from a 40% solution of dimethyl ether in sulfuric acid obtained from Eastman Kodak Company, and only the middle third was taken. Eastman Kodak acetaldehyde was twice distilled through a tube of anhydrous calcium sulfate and the middle third was again distilled into the storage bulb. Nitric oxide was prepared from potassium nitrite and potassium iodide by the method of Johnston and Giauque.[7] Hydrogen and deuterium were purified from electrolytically prepared samples by repeated circulation over platinized asbestos at 450° and through traps immersed in liquid nitrogen on either side of the storage bulb. Tank helium, containing nitrogen as the main impurity according to the manufacturers, was circulated over magnesium at 550° and through traps immersed in liquid nitrogen. Nitrogen gas, about 99.9% pure, was prepared from ammonia by oxidation with copper oxide. Formaldehyde was prepared from paraformaldehyde by heating and distilling.

Results

Acetaldehyde.—The results for a typical run of the thermal decomposition of acetaldehyde are shown in Table III. The mass spectrometer data for the progress of the reaction are compared with the pressure of the various constituents calculated from the increase of pressure assuming the stoichiometric reaction

$$CH_3CHO = CH_4 + CO \qquad (1)$$

From this table it is apparent that the mass spectrometer readings are a direct measure of the pressure within the reaction vessel. The rates of the individual reactions are approximately second order in agreement with the work of Kassel[8] and proceed according to Eq. (1). As with many other organic decompositions, the rate coefficient is a function of the initial pressure and the rate coefficient in a given run falls off as the extent of decomposition proceeds. These effects will be discussed in greater detail in the case of dimethyl ether.

In addition to the products already mentioned, approximately 0.5% of acetylene is produced in the decomposition probably according to

$$CH_3CHO = C_2H_2 + H_2O \qquad (2)$$

It was impossible to determine the amount of water formed by Eq. (2) in the spectrometer as it is always present to that extent from other sources.

Dimethyl Ether.—In Table IV results are given for a typical run of dimethyl ether. In this case a stable intermediate is formed. To evaluate the pressure of formaldehyde standard samples of dimethyl ether and formaldehyde were prepared and their peak intensities were measured. From an inspection of the results in this table, it can be seen that formaldehyde is an intermediate in the reaction and that the reaction takes place according to the stoichiometric equations

$$(CH_3)_2O = CH_4 + HCHO \qquad (3)$$
$$HCHO = CO + H_2 \qquad (4)$$

These equations have been postulated previously by Hinshelwood and Askey.[9]

In addition to the products already discussed, 0.8% of ethane is also formed. The ethane was identified by heating a reaction mixture for twenty hours and determining the masses of the remaining constituents. Since ethane has a mass of 30 which is also that of formaldehyde, it was impossible to distinguish between them owing to the small peak intensities. To verify the nature of this peak, separate sample tubes containing dimethyl ether at a pressure of 350 mm. were heated for thirty-five hours at 503.8°. The

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(7) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

(8) Kassel, *J. Phys. Chem.*, **34**, 1166 (1930).

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

TABLE IV

DIMETHYL ETHER—503.8°

	CH_3OCH_3			CH_4			CO			H_2			CH_2O
Time, min.	Pressure mass sp., mm.	Calcd. pressure manometer, mm.	Time, min.	Pressure mass sp., mm.	Calcd. pressure manometer, mm.	Time, min.	Pressure mass sp., mm.	Calcd. pressure manometer, mm.	Time, min.	Pressure mass sp., mm.	Calcd. pressure manometer, mm.	Time, min.	Pressure mass sp., mm.
0	..	245	0	0	0	0	0	0	0	0	0	0	0
12.0	186	195	4.0	12	15	7.5	13	26	3.0	9	13	4.0	9
15.0	180	184	10.0	32	38	12.0	26	45	7.0	22	32	8.5	15
19.0	173	171	14.0	48	53	18.0	47	66	10.0	28	41	17.0	23
20.5	168	161	17.0	54	64	23.0	63	82	14.0	39	51	21.5	27
27.0	150	148	25.0	82	87	30.0	86	100	18.0	50	69	26.0	28
31.5	140	136	29.0	96	98	35.0	101	113	24.0	71	88	32.0	26
36.0	126	128	36.0	120	116	41.0	121	125	29.0	83	102	35.0	26
38.0	122	121	40.0	130	124	47.0	135	139	36.5	100	119	42.0	24
41.0	117	115	49.0	148	139	57.0	149	149	41.3	113	128	47.0	23
48.0	106	102	55.0	160	147	69.0	150	159	46.0	118	139	52.0	22
51.0	100	99	72.0	163	162	81.0	155	167	54.0	127	146	61.0	20
62.5	84	85	80.0	166	167	90.0	161	170	63.0	133	157	70.0	18
69.0	76	80	95.0	170	171	105.0	169	174	74.0	140	163	77.0	17
78.0	72	76	104.0	172	174	118.0	176	178	84.0	150	168	88.0	15
86.0	70	73	120.0	181	179	133.0	180	183	97.0	160	173	96.0	14
97.0	65	69	130.0	183	182	148.0	184	187	109.0	169	178	104.0	13
103.0	63	67	150.0	189	188	162.0	190	190	118.0	173	181	116.0	11
117.0	60	63	161.0	192	191				128.5	181	184	130.0	10
129.0	59	60							138.0	186	187	140.0	9
141.0	58	56							150.0	190	191	152.5	8
152.0	54	53											

products of reaction were cooled to the temperature of liquid nitrogen and the permanent gases were pumped away. Upon warming to the temperature of dry-ice, a gas pressure of 2 mm. was obtained. An isotopic analysis of this gas proved it to be ethane. The ratio of mass 30/31 was found to be 35.8. The difference between this value and the value calculated from the accepted value for the carbon and hydrogen isotope ratios, which is 43.3, is explained by the overlapping of peaks. Formaldehyde, on the other hand, has a mass 30/31 ratio twice that of ethane. In addition peaks were observed during these analyses corresponding to C_2^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ which could under no circumstances come from formaldehyde. No higher masses which might be produced by polymerization of formaldehyde or dimethyl ether were found in the spectrometer.

In order to correlate the kinetic data for the dimethyl ether decomposition, it is desirable to consider the process as composed of two parts, the initial reaction and the final reaction. The effects of surface–volume ratio, initial dimethyl ether

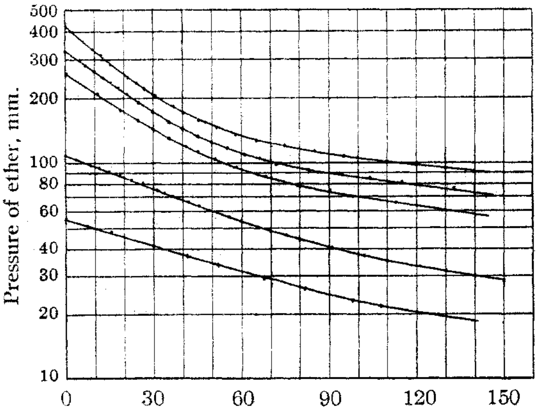

Fig. 3.—Unpacked reaction vessel.

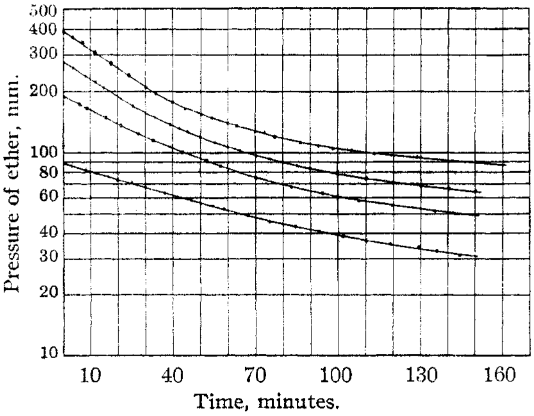

Fig. 4.—Partially packed reaction vessel.

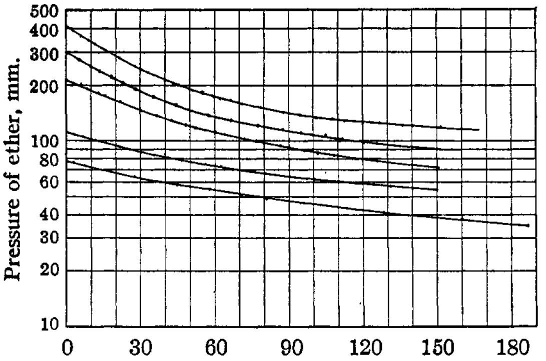

Fig. 5.—Fully packed reaction vessel.

pressures, and added gases on the rate coefficients of both parts will be discussed.

Figures 3, 4, 5 show the logarithm of the dimethyl ether pressure as a function of time for packed and unpacked vessels. In Tables V, VI, VII the corresponding rate coefficients are tabulated. These were obtained by graphically determining the slopes.

TABLE V

UNPACKED PYREX VESSEL—503.8°

Initial pressure dimethyl ether, mm.	Added gas and its pressure, mm.	k initial, min.$^{-1}$	k final, min.$^{-1}$
54	0	0.00889	0.0042
109	0	.0120	.0041
258	0	.0190	.0043
326	0	.0214	.0042
389	0	.0231	..
415	0	.0239	..
422	0	.0241	.0046

TABLE VI

PARTIALLY PACKED[a] PYREX VESSEL—503.8°

Initial pressure dimethyl ether, mm.	Added gas and its pressure, mm.	k initial, min.$^{-1}$	k final, min.$^{-1}$
89	0	0.00923	0.0034
175	0	.0139	.0032
189	0	.0148	.0031
280	0	.0186	.0032
390	0	.0216	.0029
438	0	.0224	..
240	N_2-153	.0176	..
337	N_2-167	.0207	.0032
260	HCHO-30	.0178	..
159	He-194	.0134	..
198	D_2- 52	.0165	..
194	H_2- 52	.0169	..
195	D_2-107	.0182	..
196	H_2-107	.0185	..
183	H_2-184	.0208	.0033
220	H_2-274	.0230	.0031
193	D_2-182	.0211	.0031
290	D_2-153	.0230	..

[a] Vessel was packed to one-third of its height with 2-mm. tubing, in lengths of 2 cm.

TABLE VII

FULLY PACKED[a] PYREX VESSEL—503.8°

Initial pressure dimethyl ether, mm.	Added gas and its pressure, mm.	k initial, min.$^{-1}$	k final, min.$^{-1}$
78	0	0.0066	0.0021
112	0	.0085	.0024
216	0	.0132	.0020
298	0	.0164	.0019
410	0	.0184	.0020
509	0	.0196	..

[a] Vessel was fully packed with 6-mm. tubing, in lengths of 2 cm.

From the data in these tables, the following conclusions may be drawn. Both the initial and final portions of the reaction are inhibited by increasing the surface volume ratio as shown in Fig. 6. The initial rate coefficient, k_i, is a function of the initial dimethyl ether pressure (Fig. 6). That the initial rate coefficient is a function of the initial pressure has been observed in the thermal decomposition of many organic substances. This effect is shown by ethers, acetone and acetaldehyde[10] regardless of the order of the reaction. In all cases cited, when the initial rate coefficients were plotted against the initial pressure, it was assumed that k_i went to zero at zero initial concentrations. If one inspects Fig. 6, however, it is observed that in each of the three curves, the intercept is not zero but is finite and has the value of k_f, the final rate coefficient. Dimethyl ether is not unique in showing a falling off in the rate during a run. The previously men-

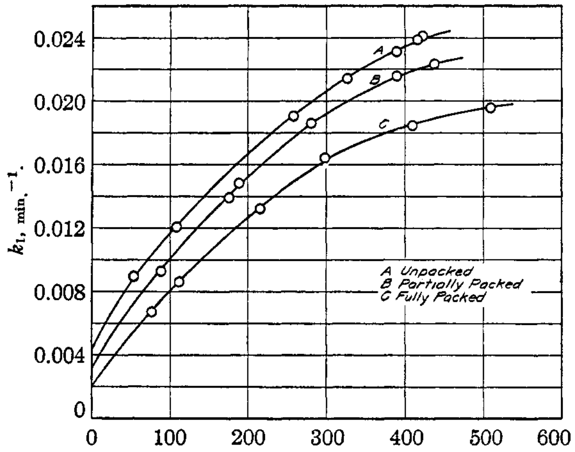

Fig. 6.

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(10) Hinshelwood, "Kinetics of Chemical Change," Oxford Press, New York, N. Y., 1940.

tioned substances behave in a similar manner. It seems likely, therefore, that most of the curves in the literature for the decomposition of organic substances made by plotting k_i as a function of the initial concentration are erroneous if extrapolated to zero. This might indicate that k_i may be defined by $k_i = k_a + k_f$. As the reaction proceeds, k_a falls off to zero and k_i approaches k_f. The drop in k_a may be due to a chain breaking process presumably taking place at the wall. This is shown by the fact that deviations from the initial rate become more apparent in the earlier stages of the reaction as the surface–volume ratio is increased (Figs. 3, 4, 5).

Efforts which were made to explain the data on the basis of concurrent reactions of different orders were unsuccessful.

From Table VI it is apparent that k_i is a function of the added hydrogen and deuterium concentrations, is slightly accelerated by formaldehyde and is independent of other added gases. The specific effect of hydrogen on k_i, that is, in bringing the low pressure k_i back to the high pressure value, has been attributed to the ease with which hydrogen can exchange its energy. On the other hand, it is very significant that helium, nitrogen, carbon monoxide, carbon dioxide have practically no effect. This is in contrast to decomposition reactions, such as that of nitrous oxide,[11] where such gases have an effect and where the energy transfer is significant. We, therefore, determined the effect of deuterium gas, and from Table VI we see that within the experimental error the effect is the same as for hydrogen. These results seem to point to the conclusion that energy transfer is not significant in these experiments. At the same time it is interesting to note that k_f is independent of added hydrogen or deuterium.

To get some insight into the nature of the reactions taking place, we have investigated the reactions

$$D_2 + H_2 = 2HD \qquad (5)$$

$$CH_3OCH_3 + D_2 = CH_3OCH_2D + HD \qquad (6)$$

Both these reactions were found to occur with a measurable rate at 503.8°. One and one-half hours after 100 mm. of deuterium (96%) were mixed with 275 mm. of ether, 10% of the remaining ether contained one deuterium atom per molecule. These reactions probably take place on the surface of the reaction vessel by means of a mechanism involving atomic hydrogen. This is one of the mechanisms which has been proposed by Bonhoeffer and Harteck[12] for *o–p* hydrogen conversion at temperatures above 300° in similar reaction vessels. Furthermore, Williamson[13] has shown that above 480° both Pyrex and silica glasses adsorb appreciable amounts of hydrogen.

The exchange reaction between CH_3OCH_3 and D_2 can take place by either of two mechanisms, if our postulates are correct.

$$\begin{array}{lll} \text{I.} & CH_3OCH_3(g) + D(s) & = CH_3OCH_2(g) + HD(s) \\ & CH_3OCH_2(g) + D_2(g) & = CH_3OCH_2D(g) + D(g) \end{array}$$

or

$$\begin{array}{lll} \text{II.} & CH_3OCH_3(s) & = CH_3OCH_2(s) + H(s) \\ & D_2(s) & = 2D(s) \\ & CH_3OCH_2(s) + D(s) & = CH_3OCH_2D(s) \\ & CH_3OCH_2D(s) & = CH_3OCH_2D(g) \end{array}$$

or both. Mechanism II involves dissociative adsorption on the surface, and was used by Taylor and co-workers[14] to explain the exchange reaction between CH_4 and CD_4 on metallic surfaces. If reactions occur by mechanism II, then, for the thermal decomposition reaction, we may have chains starting at the surface and in the gas phase, as well as chains being broken on the wall. Since, in our experiments, we observe an inhibition by packing, the probability of chain breaking at the walls must be greater than chain initiation at the walls.

Further evidence supporting the fact that the surface plays an important role in starting reaction is found in the behavior of the vessel after being in contact with nitric oxide. Nitric oxide at a pressure of a few millimeters has been found to inhibit the reaction very strongly. After making several runs with nitric oxide, it was found that even after pumping the vessel for several hours with a diffusion pump, enough nitric oxide was left on the surface to cause some inhibition, and it was only after the introduction of oxygen and again pumping that the surface was restored to its original condition.

We have indicated in our discussion that the reaction follows a complicated course. We do not believe that an extensive discussion of the mechanism for such a reaction is desirable in the absence of considerably more data than are available. However, the following conclusions may be drawn.

1. The presence of ethane produced during the

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(11) M. Volmer, *et al.*, *Z. physik. Chem.*, **B25**, 81 (1934).

(12) Bonhoeffer and Harteck, *ibid.*, **B4**, 113 (1929).

(13) Williamson, THIS JOURNAL, **55**, 1437 (1933).

(14) Morikawa, Benedict and Taylor, *ibid.*, **58**, 1445, 1795 (1936).

reaction indicates a chain mechanism involving a free methyl group as a chain carrier. From our experimentally measured ethane concentration, further, a chain length of 10^2 may be calculated.

2. Unwarranted emphasis should not be placed upon the initial phases of the reaction, especially since the initial process appears to be more complicated than the final stage of the reaction. We believe that the entire course of the reactions should be studied rather than that conclusions should be drawn from a study of any one part.

Summary

1. A mass spectrometer has been used in a new method for following the course of kinetic reactions. This method has the advantages of direct identification and concentration measurements of all stable substances involved, including intermediates.

2. The thermal decompositions of dimethyl ether and acetaldehyde have been studied by this method.

3. A chain mechanism for the decomposition of dimethyl ether has been postulated and a chain length of 10^2 calculated. The initial rate constant is a function of the initial dimethyl ether pressure. However, the initial rate has been shown to approach the final rate at zero initial concentration.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polarographic Investigation of Rhenium Compounds. I. Reduction of Perrhenate Ion at the Dropping Mercury Electrode

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Since its discovery in 1925 by Walter and Ida Noddack and O. Berg, the chemistry of rhenium has been investigated diligently by numerous investigators, and compounds have been reported corresponding to all the possible oxidation states between + 7 (perrhenate ion) and − 1 (rhenide ion).[1] However, very few quantitative data are available concerning the oxidation–reduction potentials connecting the various oxidation states of rhenium compounds in aqueous solution. In the present investigation a start in the direction of obtaining such information has been made by employing the polarographic technique to study the reduction of perrhenate ion at the dropping mercury electrode.

Experimental Technique

Polarograms were recorded according to the usual technique[2] with a Heyrovsky Polarograph, Model XI.[3] For most of the measurements the H-type cell with saturated calomel anode and the dropping electrode assembly described by Lingane and Laitinen[4] were used. In some experiments a Heyrovsky-type cell with a pool of mercury as anode was used, and in these cases proper correction was made for the anode potential in order to refer the potential of the dropping electrode to the saturated calomel electrode. Except as otherwise noted the experiments were run with the cells in a water thermostat at 25°. Nitrogen was used to remove air from the solutions under investigation. The drop time and rate of flow of mercury from the dropping electrode were determined in the usual manner.[2]

The sample of potassium perrhenate used was kindly furnished by Dr. Max Mosesman. It was known to be of high purity and was used without further purification. Since the amount of the sample was quite small (0.5 g.) the experiments were performed with solutions as dilute as was consistent with satisfactory accuracy of measurement.

Diffusion Current Constant of Perrhenate Ion.—The oxidation states to which perrhenate ion is reduced under various conditions were determined from the observed diffusion currents by means of the Ilkovic equation in the form[5]

$$\frac{i_d}{C} = 605nD^{1/2}m^{2/3}t^{1/6} \quad (25°) \qquad (1)$$

where i_d is the diffusion current (microamperes), D is the diffusion coefficient (cm.^{2} sec.$^{-1}$) and C

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(1) W. Noddack and I. Noddack, "Das Rhenium," Leopold Voss, Leipzig, 1933.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, 1941.

(3) Manufactured by E. H. Sargent and Co., Chicago, Ill.

(4) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(5) For a detailed discussion of the Ilkovic equation and its applications, see Ref. 2.