CCXXXVII.—*The Unimolecular Decomposition of Some Ethers in the Gaseous State.*

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CERTAIN chemical reactions take place in gases at rates which are independent of pressure when this is high, but diminish at lower pressures. This behaviour is explained by the theory that at higher pressures the rate of activation and deactivation of molecules by collision is much greater than the rate of chemical transformation : thus an almost constant fraction of the molecules are in the activated condition at all pressures, and a constant fraction of these undergo chemical change in unit time. The reaction is therefore unimolecular. As the pressure decreases, this condition ceases to be satisfied, and finally a state of affairs must be reached where the rate of reaction is governed by the rate of activation, giving a bimolecular reaction. Unimolecular reactions are characteristic of molecules with a complex structure such as diethyl ether and azomethane. The region of pressure in which the falling off of the velocity coefficient occurs depends upon the number of degrees of freedom involved in the activation process : the greater this number, the greater is the possible rate of activation, and hence the lower the pressure at which the condition for a unimolecular reaction begins to fail. A comparison of the behaviour of a series of related substances might, therefore, be expected to reveal a decrease in this pressure with an increase in the size of the molecule.

The decompositions of three ethers in the gaseous state, *viz.*, methyl ethyl, methyl propyl, and di*iso*propyl ethers, have been examined with the object of comparing them with the decompositions of dimethyl (*Proc. Roy. Soc.*, 1927, *A*, **115**, 215), diethyl (*ibid.*, **114**, 84), and dipropyl ethers previously investigated, and incidentally of obtaining further information about certain matters of general theoretical importance.

The experimental methods employed were precisely the same as in the previous investigations.

The behaviour of methyl ethyl and methyl propyl ethers closely resembles that of dimethyl and diethyl ether. At pressures above a certain value, the velocity coefficients are independent of the pressure, but at lower pressures they fall off, but are restored to the normal value by the presence of sufficient hydrogen. This action of hydrogen has hitherto appeared to be peculiarly specific, a fact which is a little surprising, since the function of the hydrogen is simply to maintain the rate of activation by collision. Its efficiency in this respect is probably due to the high molecular velocity.

Helium, the only gas comparable with hydrogen in this respect, suffers from the disadvantage of possessing no energy except that of translational motion. If the effectiveness of a foreign gas in maintaining the rate of activation is a function both of the speed of its molecules, which determines the number of collisions they make, and of the amount of energy available for transfer, then the advantage possessed in the second respect by a gas with many atoms in the molecule may compensate for its disadvantage in the first respect. Methyl propyl ether gives considerable quantities of ethane in its decomposition, and there appears to be significance in the fact that the reaction products are even more effective than hydrogen in preventing the falling off of the reaction velocity at low pressures. The methane formed in the decomposition of methyl ethyl ether has a similar, but much less marked, influence.

Di*iso*propyl ether possesses a more complex molecule than the other two ethers, and no falling off in rate is, in fact, observed down to about 30 mm. It would be interesting to know where the falling off actually begins, but the determination of this is made almost impossible by the fact that the ether decomposes by several different reactions, including a surface reaction which is bound to exert a greater disturbing action the lower the pressure.

If k_∞ is the velocity coefficient at high pressures, and k that at some pressure p, the question arises how the curve obtained by plotting k/k_∞ against p is affected by temperature. According to the simplest theory of activation, *viz.*, that the molecule must contain a total energy greater than E, and that the probability of transformation is independent of the actual amount in excess of E, the curve should be almost unaffected by the temperature. If the probability of transformation is assumed to be a function of the excess energy, then the curves are displaced with changing temperature. For the decomposition of azomethane (Rice and Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 617; 1927, **49**, 1617) a displacement is observed in the sense that the coefficients begin to fall off at a higher pressure the higher the temperature. For the decomposition of methyl propyl ether the curves are displaced in a similar way, but for that of methyl ethyl ether they appear hardly to be displaced at all. It is unsafe, however, to draw from these results theoretical conclusions about the activation process itself, since the influence of the reaction products and other secondary effects must distort the picture to some extent.

By assuming that at the pressure where the reaction velocity begins to fall the rate of activation is of the same order of magnitude as the rate of reaction, the number of " square terms," n, among which the energy of activation is shared, can be calculated in the manner already described (*Proc. Roy. Soc.*, 1926, *A*, **113**, 230). The values of n now found are : for dimethyl ether 11, for diethyl ether 8, for methyl ethyl ether 9, and for methyl propyl ether 12. Since there are two " square terms " to each internal vibration this means that 4—6 such degrees of freedom are involved. There is, however, no simple relation between n and the chemical formula of the molecule. For di*iso*propyl ether n cannot be calculated, but it is not less than 26, and thus differs greatly from the values given by the other ethers. This reflects the considerable difference in structure, and it is interesting to note that the value of n which must be assumed for azo*iso*propane (Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 714) is very much greater than the value for azomethane. A series of experiments made some time ago by P. J. Askey, although incomplete, showed that the behaviour of dipropyl ether was much more similar to that of the lower ethers.

The Decomposition of Methyl Ethyl Ether.

A sample, obtained from Poulenc Frères and carefully fractionated in a well-dried apparatus, had b. p. 11—12°.

This ether decomposes according to the equation $CH_3{\cdot}O{\cdot}C_2H_5 = CO + 2CH_4$. The total increase of pressure is, however, not 200% as the equation indicates, but 168—171%. Some condensation product is formed, and a slight tarry deposit is observed. This must come, not from the final or any intermediate decomposition products, but from the original ether, since the analysis of the gaseous products corresponds quite closely to the above equation. If the condensation product is assumed to occupy a negligible volume, 8% of the ether condenses and 92% decomposes in accordance with the equation. Analysis of the products of decomposition at two different temperatures, carried out in a Bone and Wheeler apparatus, gave the following results :

	CH_4.	CO.	CO_2.	Unsat. hydrocarbons.
Products at 430°, %	64·5	33·0	—	2·5
,, ,, 444°, %	63·6	33·8	1·2	1·4

The saturated hydrocarbon was shown to consist of $(2CH_4)$ and not $(C_2H_6 + H_2)$ by first leaving it in contact with copper oxide at 275° for 10 minutes, which would cause preferential combustion of any hydrogen, and then carrying out a combustion of the residue. The ratios for this residue were : gas used : CO_2 formed : contraction : oxygen used $= 1{\cdot}00 : 1{\cdot}04 : 1{\cdot}95 : 1{\cdot}99$, the theoretical values for methane being $1 : 1 : 2 : 2$ and for ethane $1 : 2 : 2{\cdot}5 : 3{\cdot}5$.

The reaction is predominantly homogeneous, although at lower temperatures the surface reaction is not entirely absent. In the following table t_{50} and t_{100} are the times (in secs.) required for the pressure to increase by 50% and 100% respectively of the initial value. Bulb 1 was a silica bulb, and bulb 2 a similar one packed with small silica balls, having a ratio surface/volume about 16 times greater. Bulb 3 was somewhat larger and packed with open lengths of silica tubing.

Temp.	Bulb No.	Initial press. (mm.).	t_{50}.	t_{100}.	Temp.	Bulb No.	Initial press. (mm.).	t_{50}.	t_{100}.
460°	1	540	39	135	430°	1	248	171	—
460	2	458	41	117	430	3	223	136	—
460	1	122	66	210	400	1	449	670	—
460	2	135	57	143	400	3	488	407	—
430	1	531	143	509	400	1	77	1020	—
430	2	540	127	346	400	3	77	680	—

The reaction as measured by the increase of pressure does not follow a simple unimolecular course. The coefficients increase for the first 25% of the reaction and then fall again. Two causes can lead to this initial increase: first, the accelerating influence of the products, and secondly, a certain intermediate formation of aldehyde, analogous to the formation of formaldehyde which occurs with dimethyl ether. In the following table details are given of a typical experiment; a is the total pressure increase, x the increase at time t, and k the value of $1/t \cdot \log_{10}a/(a-x)$.

$T = 460°$. $a = 862$ mm.

t (secs.)	11	15·5	20·5	27	45	91	135	203	285	518	601	733
x (mm.)	50	100	150	200	303	453	540	623	688	788	818	838
$k \times 10^3$	2·35	3·45	4·05	4·24	4·18	3·56	3·16	2·75	2·44	2·06	2·05	2·17

In spite of the fact that the reaction is far from being an ideal example of a unimolecular change, it satisfies the most important criterion of such a reaction, *viz.*, that t_{50} and t_{100} are independent of pressure over a considerable range. At low pressures these values increase, but the increase does not occur in presence of sufficient hydrogen, nor of a sufficient quantity of the reaction products, as shown below.

$T = 460°$.

Initial press. (mm.)	540	410	298	219	176	122	88	63	42
t_{100} (secs.)	135	142	151	165	175	210	256	302	336

Initial press. (mm.)	91	120	175	282	103	110
Press. of hydrogen	610	292	306	394	—	—
Initial press. of reaction products	—	—	—	—	200	400
t_{100} (secs.)	159	164	177	163	188	159

$T = 430°$.

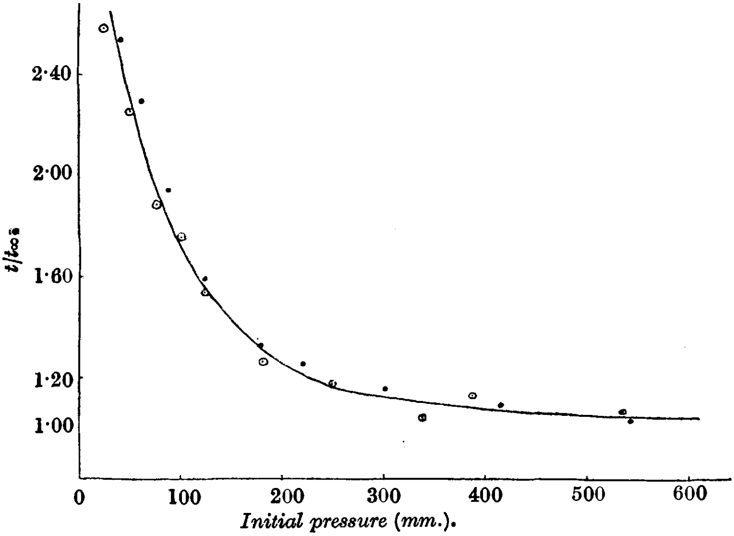
Initial press. (mm.)	531	384	335	248	180	124	102	77	54	52	26
t_{50} (secs.)	153	163	151	171	184	223	257	274	314	328	378

In Fig. 1, t/t_∞ is plotted for 430° and 460°, t_∞ being the limiting value of t at high pressures.

From the following values of t_{50} for a series of temperatures, the heat of activation is calculated in the usual way from the Arrhenius equation, and found to be 47,000 cals. per g.-mol.

Temp. (Abs.)	733°	703°	673°	659°
t_{50} (secs.)	39	155	670	1564

FIG. 1.



Decomposition of methyl ethyl ether.

● t/t_∞ *for* t_{100} *at* 460°. ⊙ t/t_∞ *for* t_{50} *at* 430°.

From the heat of activation, the number of "square terms" between which the energy is shared (*viz.*, n) is calculated from the expression

$$N = \frac{Z \, . \, e^{-\left\{\frac{47{,}000+(\frac{1}{2}n-1)RT}{RT}\right\}} \left\{\frac{47{,}000 + (\frac{1}{2}n - 1)RT}{RT}\right\}^{\frac{1}{2}n-1}}{\underline{|\tfrac{1}{2}n - 1}}$$

where, as an approximation, it is assumed that N, the number of molecules reacting in one second in 1 c.c., is equal to the number of activating collisions at $\frac{1}{4}$ atmosphere, where the reaction rate begins to fall off. At 700° Abs. and at this pressure, $N = 5{\cdot}1 \times 10^{15}$. The total number of collisions, Z, is $\sqrt{2}\pi\bar{u}\sigma^2\nu^2$, ν being the number of molecules per c.c., and σ the molecular diameter (say, 5×10^{-8} cm.); at the same temperature and pressure Z is found to be $4{\cdot}2 \times 10^{27}$. Hence the value of n is found to be 9.

The Decomposition of Methyl Propyl Ether.

The ether, obtained from Poulenc Frères, dried over sodium, and carefully fractionated, had b. p. 38·8°/761 mm. Its decomposition occurs according to the equation $CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CO + CH_4 + C_2H_6$, a small fraction, not exceeding 10%, following the equation $CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 = CO + H_2 + C_3H_8$.

Analysis of the decomposition products at 450° and at 400° showed :

	CO.	CO_2.	Unsatd. hydrocarbons.	Satd. hydrocarbons + H_2.
Products at 450°, %	35·1	1·0	1·9	62·0
,, ,, 400°, %	34·0	0·1	2·1	63·8

The combustion of the "saturated hydrocarbons + hydrogen" gave the following results.

	$\frac{CO_2 \text{ formed}}{\text{Gas burnt}}$.	$\frac{\text{Contraction}}{\text{Gas burnt}}$.	$\frac{\text{Oxygen used}}{\text{Gas burnt}}$.
450°	1·54	2·21	2·76
400°	1·53	2·24	2·76
Theoretical for $CH_4 + C_2H_6$	1·50	2·25	2·75

The mixture $(C_3H_8 + H_2)$ would give the same ratios as $(CH_4 + C_2H_6)$, but a number of experiments on the fractional combustion of the residue with copper oxide showed that the proportion of propane and hydrogen was not more than about 10% of the whole residue.

The pressure of the decomposition products varied from 2·5 to 2·6 times the initial pressure instead of being 3·0 times as the equation requires. Condensation therefore occurs, but since the relative amounts of the gaseous products correspond to the equation, it is evidently the ether itself and not some intermediate product which condenses. Since propaldehyde, if formed, would be stable in this temperature region, and, moreover, tests for aldehydes gave negative results, the reaction does not appear to involve the intermediate stage $CH_3{\cdot}O{\cdot}C_3H_7 = CH_4 + C_2H_5{\cdot}CHO$.

The reaction in an empty silica bulb is mainly homogeneous. In a bulb packed with silica balls, having a surface/volume ratio 16 times greater, there was some acceleration of the condensation reaction, which actually gives the appearance at low pressures of a deceleration of the normal decomposition, and distorts the curves of pressure increase plotted against time. At higher pressures, t_{50} was the same in both bulbs : the later stages of the reaction were somewhat faster in the packed bulb, but the total pressure increase was less. The disturbances were, however, in no way comparable with the 16-fold increase of surface/volume ratio.

About 100 experiments were made at different temperatures and pressures. The curves obtained by plotting increase of pressure against time are generally similar to those obtained with methyl ethyl ether, and need not be given in detail. The following table shows the variation of t_{50} with initial pressure.

$T = 425°$.

Press. (mm.)	336	281·5	228	195·5	181	142·5
t_{50} (secs.)	216	210	207	216	201	213
Press. (mm.)	137	118	111	77	46·5	22
t_{50} (secs.)	216	219	230	270	345	393

The pressure at which the falling-off of the reaction rate takes place varies with temperature. This is best shown by quoting the pressure, p', at which t_{50} attains double the limiting value for high pressures.

T	458°	437°	425°
p' (mm.)	95	50	20

Hydrogen had the usual effect of accelerating the low-pressure reactions to the normal high-pressure rates. The action of the reaction products was very marked and analogous to that of hydrogen as the following table shows; carbon monoxide has little, if any, influence: it would thus appear to be the ethane which exerts the marked effect.

$T = 450°$.

	t_{50} (secs.).
64·5 mm. Ether alone	164
67 mm. Ether + 228 mm. reaction products	70
62 mm. Ether + 220 mm. reaction products	67
213 mm. Ether alone	70
56 mm. Ether + 220 mm. carbon monoxide	176

The heat of activation, obtained in the usual way from the following data, is 49,000 calories.

Temp. (Abs.)	723°	713°	703°	698°	693°	683°	673°
t_{50} (high-pressure values)	62	94	149	195	255	416	846

By taking about 100 mm. as the point at which the velocity begins to fall off at 700° Abs., n is found to be 12.

The Decomposition of Diïsopropyl Ether.

The ether was prepared according to the details given by Erlenmeyer, by boiling *iso*propyl iodide with moist silver oxide. It was found advisable to use some 20% excess of silver oxide, and to reflux the crude ether with a further quantity of the oxide to remove any remaining traces of iodide. The ether was dried over sodium and carefully fractionated, the boiling point of the fraction used being 67·8—68·1°/760 mm. (Found: C, 70·3; H, 13·58. Calc.: C, 70·6; H, 13·7%).

The study of the decomposition was complicated by the fact that in different circumstances it occurs according to different mechanisms :

(*a*) $C_3H_7{\cdot}O{\cdot}C_3H_7 = CO + 3CH_4 + \frac{1}{2}C_2H_4 + C$;
(*b*) $C_3H_7{\cdot}O{\cdot}C_3H_7 = 2CH_3{\cdot}CH{:}CH_2 + H_2O$;
(*c*) $C_3H_7{\cdot}O{\cdot}C_3H_7 = CH_3{\cdot}CO{\cdot}CH_3 + C_3H_8$.

Reaction (*a*) represents the final result of the homogeneous unimolecular decomposition, (*b*) is a surface reaction, and (*c*) is a reaction, probably homogeneous, which normally accompanies (*a*) to a slight extent and may become the predominating mode of decomposition under the catalytic influence of *iso*propyl iodide. Reaction (*a*) takes place with conveniently measurable velocity in a silica bulb from 500° to 570°. The following are typical analyses of the gaseous products :

	CO.	CO_2.	CH_4.	Unsatd. hydrocarbons.
At 550°, %	18·0	1·3	67·4	13·3
At 566°, %	20·1	—	65·0	14·9

The saturated hydrocarbon is almost entirely methane, since in the first of the above analyses it gave 1·06 vols. of carbon dioxide, a contraction ratio of 1·94, and used up 2·00 vols. of oxygen.

In the course of the reaction, the surface of the bulb became coated with a coherent shiny deposit of carbon. The unsaturated hydrocarbon was found, by comparing the combustion of the total hydrocarbon with that of the saturated fraction, to be mainly ethylene with a little propylene, presumably from reaction (*b*).

The increase in pressure on decomposition varied from 220 to 245%.

The following figures show the course of a reaction at 551°, and the homogeneous nature of the change, the pressure increase being given as % of the initial pressure. Bulb 1 is the empty silica bulb, bulb 2 that packed with silica balls.

Bulb 1. Initial press., 230 mm.				Bulb 2. Initial press., 311 mm.			
Time (secs.).	Increase.	Time (secs.).	Increase.	Time (secs.).	Increase.	Time (secs.).	Increase.
38	20·0	610	111·2	32	16·1	373	93·4
78	37·4	826	120·0	61	29·0	445	100·0
147	59·2	1095	128·6	130	51·5	641	112·6
230	76·5	1465	137·4	214	70·7	1242	128·6
287	85·3	2505	159·0	293	83·7	14940	220·0
360	94·0	3720	169·0				
460	102·7	14340	236·0				

It is clear from the table that the later stages of the reaction are long drawn out, suggesting the possibility of intermediate reactions. This will be discussed later.

Unlike methyl ethyl and methyl propyl ethers, di*iso*propyl ether gives values of t_{50} and t_{100} which are independent of pressure down at least to 30 mm., as may be seen from the following data.

	Initial press. (mm.).	t_{50} (secs.).	t_{100} (secs.).
At 566°.	327	57	225
	284	63	230
	255	63	216
	146	58	206

	Initial press. (mm.).	t_{50} (secs.).	t_{100} (secs.).
At 551°.	230	110	426
	109	110	465
	78	114	420
	53	115	448
	29	118	467

The heat of activation is derived from the following data : from t_{50} a value 63,000 cals. is found, and from t_{100} a value 66,500 :

Temp. (Abs.) …………	839°	832°	824°	816°	805°
t_{50} (secs.) ……………	60	87	127	168	225
t_{100} (secs.) ……………	220	315	460	665	862

An entirely independent series of experiments gave a value of 64,000 cals. from t_{50}. There are apparently consecutive reactions involved, and if the value of E is extrapolated to $t = 0$, we find 60,500 cals. for the heat of activation of the initial decomposition. The value of n cannot of course be calculated, since the point at which the reaction velocity begins to fall off is not known. It is, however, not less than 26, and thus appears to be considerably greater than that for the other ethers.

The first experiments in which a packed bulb was substituted for the empty bulb showed a very considerable increase in velocity, thus suggesting that the reaction in the empty bulb was largely heterogeneous; but analysis showed that the reaction thus accelerated by the increased surface was quite a different one, being in fact reaction (*b*). In an experiment at 450°, where the reaction took place about 20 times as fast as in the empty bulb, 96·2% of the gaseous product was an unsaturated hydrocarbon, the combustion of which gave 3·08 vols. of carbon dioxide for 1 vol. of gas and a contraction of 2·65 vols. The amount of carbon dioxide shows that the molecule contains 3 carbon atoms, and thus corresponds to propylene. At higher temperatures the propylene begins to decompose into methane as the following analyses show.

	CH_4.	CO.	CO_2.	Unsatd. hydrocarbons.
Products at 515°, % ……	27·4	2·9	—	69·7
,, ,, 566°, % ……	46·8	4·1	0·4	48·7

The unsaturated hydrocarbon was in every case proved to be propylene by first absorbing the unsaturated part of the gas with mercuric acetate and combusting the methane alone, and then combusting the whole gas mixture. By deducting the effect due to the methane, that due to the unsaturated part was found to correspond to propylene.

As successive experiments were made in the packed bulb, the reaction velocity was observed to fall steadily and finally become equal to that in the unpacked bulb—as shown in the table already given. The surface had evidently become poisoned, and, since it could be rendered active again by burning off the shiny carbon deposit which had been formed, it seems natural to suppose that this deposit was the cause of the poisoning. The reaction in the poisoned packed bulb gave the normal products of the homogeneous reaction.

The question arises whether the formation and subsequent decomposition of propylene occurs in the homogeneous reaction. The following experiment is evidence against such an idea. An unpoisoned surface reaction was allowed to take place at 450°, and the products were then heated to 566° for three hours and analysed (Found : C_3H_6, 27·8; CH_4, 68·8; CO, 3·4%). When the small amount of carbon monoxide is compared with the 18% yielded by the homogeneous reaction, it becomes evident that the products of the latter cannot be formed entirely by way of propylene.

Reaction (*c*) makes its appearance in rather curious circumstances. A sample of di*iso*propyl ether with which some preliminary experiments were tried decomposed rapidly in the neighbourhood of 400°, by a reaction which had a low temperature coefficient and was affected by pressure approximately in the manner of a bimolecular reaction. The increase of pressure on decomposition was almost exactly 100%; the gaseous products consisted principally of propane, and large quantities of acetone were found by the iodoform test. After the acetone vapour had been frozen out, the gas had the following composition : CO_2, 1·1; CO, 5·0; C_3H_8, 81·6; unsatd. hydrocarbons, 12·3%. The saturated hydrocarbon gave the following ratios on explosion : Gas used : CO_2 formed : contraction : O_2 used = 1 : 2·92 : 3·02 : 4·95. The values required for propane are 1 : 3 : 3 : 5. At higher temperatures the ratios were between those required for propane and those for ethane, indicating some decomposition of the propane.

As experiments proceeded, it soon became evident that this reaction was of a quite abnormal character, since the rate increased steadily as the supply of liquid ether in the small bulb from which vapour was admitted to the reaction vessel grew smaller. This proved to be due to the presence of a catalyst somewhat less volatile than the ether, which increased in proportion as fractionation proceeded. The fact that samples of the ether refluxed with excess of silver oxide failed to give this reaction, or, indeed, to show any behaviour depending on the extent of fractionation, suggested that the substance catalysing reaction (*c*) was *iso*propyl iodide. This supposition was shown to be correct by adding to some ether which did not show the abnormal behaviour small quantities of water, which produced no effect, and of *iso*propyl iodide, which once more caused the rapid decomposition into acetone and propane. This catalytic reaction is further discussed in the succeeding paper.

An attempt to settle the question whether reaction (*a*) involves the intermediate production of acetone and propane was made by withdrawing a sample of gas during the course of the reaction and estimating the acetone quantitatively by the usual iodoform method. When the initial pressure of 312 mm. at 515° had increased by 165 mm., the amount of acetone present was found to be 50 mm. Taking into account the rate of decomposition of acetone, which is rather slow at this temperature, the maximum amount which is likely to have been formed is 55 mm. The result seems to indicate that, at all events, about one-third of the decomposition proceeds by way of acetone. But as far as this evidence goes there may also be direct decomposition into the final products of reaction (*c*). When it is borne in mind, however, that part of the products of (*a*) could have been formed by subsequent decomposition of those formed in reaction (*b*), the initial act of decomposition of the molecule, which ultimately leads to the formation of the substances given by equation (*c*), cannot be regarded as definitely known. The conclusions that have been drawn regarding the kinetics of the reaction are, however, not affected by this uncertainty.

Summary.

The decompositions of gaseous methyl ethyl ether and methyl propyl ether are homogeneous reactions, the rates of which are independent of pressure at higher pressures and fall off at lower pressures.

With methyl ethyl ether, the pressure at which this falling off occurs is independent of temperature, whilst with methyl propyl ether it is greater the higher the temperature.

Not only hydrogen, but also the products of reaction, prevent this falling off, the effect of the products being much more marked with methyl propyl ether.

Di*iso*propyl ether has various modes of decomposition, of which one is a homogeneous reaction, independent of the pressure over the range investigated.

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