CCCXLVII.—*Catalytic Decomposition of Some Gaseous Ethers.*

By Paul Alfred Klaus Clusius.

It was shown by Hinshelwood and Glass (J., 1929, 1815) that under the influence of iodine as a catalyst di*iso*propyl ether is decomposed into acetone and propane, $CHMe_2{\cdot}O{\cdot}CHMe_2 \longrightarrow CMe_2O + C_3H_8$, and it was subsequently found that the same homogeneous reaction takes place under the influence of various alkyl halides (Clusius and Hinshelwood, *Proc. Roy. Soc.*, 1930, *A*, **128**, 75). More interesting, however, was the fact that this catalytic decomposition, whereby a hydrogen atom adjacent to the oxygen atom is transferred to another carbon atom, is quite a general one; thus, diethyl ether and acetaldehyde undergo the following reactions (*idem, ibid.*, p. 82; Hinshelwood, Clusius, and Hadman, *ibid.*, p. 88):

$$CH_3{\cdot}CH_2{\cdot}O{\cdot}C_2H_5 \longrightarrow C_2H_6 + CH_3{\cdot}CHO$$

and

$$CH_3{\cdot}CHO \longrightarrow CH_4 + CO.$$

The heat of activation of the catalysed reaction is always smaller than that of the uncatalysed.

From a kinetic point of view it is of interest to investigate as many similar reactions as possible. Such investigations may enable us to study the influence of the structure of the molecule on the heat of activation, and to test the possibility of calculating the reaction velocity theoretically by the assumption of simple collision mechanisms. On the other hand, the general reaction is also of interest from a purely chemical point of view; a study of a mixed ether should give an idea of the strength of the hydrogen–carbon link in different groups. The results of the present investigation, however, show definitely that the behaviour of the hydrogen atoms in a radical is very much influenced by the other radical in the mixed ether. This shows distinctly that the process of activation is connected with the structure of the whole molecule and is not dependent only upon the presence of a certain group.

It seemed desirable to investigate, first, dimethyl ether, and then the series of ethers obtained by successive substitution of methyl groups for the hydrogen atoms in one of the two methyl groups, *i.e.*, $CH_3{\cdot}O{\cdot}CH_3, CH_3{\cdot}O{\cdot}CH_2{\cdot}CH_3, CH_3{\cdot}O{\cdot}CH(CH_3)_2, CH_3{\cdot}O{\cdot}C(CH_3)_3$.

The dimethyl ether gave a rather surprising result. Iodine vapour had no appreciable influence on the rate of decomposition, suggesting that the methyl group is unable to split off hydrogen catalytically. But this generalisation is not valid, because the investigation of the third ether yielded evidence of two simultaneous reactions, one of which involved the movement of a hydrogen atom of the methyl group. If the methyl group were quite stable in the presence of iodine vapour, the last ether would experience no catalytic effect at all. The fact that there is a considerable influence of the catalyst makes it clear that the result found with the simplest ether does not apply to the others.

EXPERIMENTAL.

Methyl Ethyl Ether.—The ether was prepared by heating a saturated methyl-alcoholic solution of sodium methoxide with 90% of the required amount of ethyl iodide at about 60° in a sealed tube (Williamson, *Annalen*, 1852, **81**, 77). The tube was then cooled in a freezing mixture and opened; the ether was allowed to distil, being condensed again in an all-glass apparatus, dried over sodium for several days, and carefully fractionated. There was no sign of iodine compounds in the ether, and two different preparations gave the same rate of decomposition.

The experiments were carried out in the same way as before: a certain amount of *iso*propyl iodide vapour was allowed to stream into the silica reaction vessel and to decompose; then the pressure of the products was regulated to the required magnitude, and the ether vapour added. One-third of the pressure of the decomposed iodide is due to the iodine, which is the real catalyst (compare Hinshelwood and Glass, *loc. cit.*).

The reaction takes place at a conveniently measurable rate between 460° and 550°. The total pressure increase, according to the equations $CH_3{\cdot}O{\cdot}C_2H_5 \rightarrow CH_4 + CH_3{\cdot}CHO$ and $CH_3{\cdot}CHO \rightarrow CH_4 + CO$, should be 200%. But on account of some condensation reactions the observed increase was always smaller, being about 175—180% independently of the temperature. Some tarry product is formed and a slight deposit of carbon appears on the wall of the bulb. The analysis of the gaseous products agrees very closely with the above equations; therefore it must be the unchanged ether, and not the intermediate or final products, which disappears by the side reaction. In a sample of the products withdrawn during the decomposition, the presence of acetaldehyde could easily be shown by the silver test. An analysis of the products of decomposition was carried out in a Bone and Wheeler apparatus and gave the following results:

	CH_4, %.	CO, %.	CO_2, %.	Unsat. hydrocarbons, %.
Products at 504°	65·5	33·1	—	1·4
Calculated	66·6	33·3	—	—

The explosion of the saturated hydrocarbon with an excess of oxygen gave the following relations:

	Gas used	:	contraction	:	CO_2 formed	:	oxygen used.
Found	1	:	1·97	:	1·01	:	1·98
Calc. for CH_4	1	:	2	:	1	:	2

A mixture of equal volumes of hydrogen and ethane would give the same results as methane, but it could be shown by heating the saturated hydrocarbon with copper oxide at 307° for 10 minutes, that only a very small amount of hydrogen could have been formed.

The homogeneous character of the reaction was tested in a silica bulb filled with silica beads, the surface being about 16 times greater than before. It was thereby found that only about 4% of the whole reaction velocity was due to a surface reaction.

To a sufficient approximation, the reaction may be considered to be of the first order with respect to the ether; only the primary reaction is important for the reaction velocity, because the catalytic decomposition of the acetaldehyde at this temperature takes place very rapidly. At 504°, for instance, the primary reaction is 45 times slower than the secondary.

In the following table are details of a typical experiment; a is the total pressure increase at time t, and $k = 1/t \,.\, \log_{10} a/(a-x)$:

Temp., 504°; a = 310 mm.

t (secs.)	15	53	99	127	180	225	300	360
x (mm.)	32	92	142	165	202	224	251	270
$k \,.\, 10^3$	(3·16)	2·52	2·68	2·60	2·54	2·47	2·40	2·47

The catalytic efficiency of the iodine is proportional to its own pressure, as shown by the following table, in which t_{50} and t_{75} represent the times required for 50% and 75% decomposition.

Temp., 504°; ether pressure, about 200 mm.

$3I_2$ (mm.)	40	20	10
t_{50} (secs.)	63	118	231
t_{75} (secs.)	138	260	515

On the other hand, the reaction velocity appears to be independent of the ether pressure over a large range, as shown by the following data :

Temp., 504°; iodine pressure, $\frac{20}{3}$ mm.

Initial pressure of ether, mm. ...	311	229	177	105	49
t_{50} (secs.)	121	118	116	113	95
t_{75} (secs.)	275	260	249	255	203

A series of experiments was carried out at different temperatures in order to get the heat of activation in the usual way from the Arrhenius equation. In the following table are given the observed values of t_{50} and the times corrected to a standard iodine concentration of $\frac{20}{3}$ mm. at $T = 750°$ Abs. The reaction velocity coefficient k is expressed in reciprocal seconds; $k_{\text{calc.}}$ has been found from the equation $\log_e k = 19{\cdot}7_2 - 38{,}300/RT$.

T, Abs.	t_{50}.	$\bar{t}_{50}$.	$t_{\text{corr.}}$.	$k_{\text{obs.}} \times 10^4$.	$k_{\text{calc.}} \times 10^4$.
733°	512 509	510·5	522	$13{\cdot}8_8$	$13{\cdot}7_4$
755	230 226 222	226	224·5	30·9	29·6
777	120 116 121 118 114 123 116	118·5	114·2	60·6	61·0
785	93 87 96 95	$92{\cdot}_7$	$88{\cdot}_5$	78·3	78·5
799	57·3 61·8 60·0 57·7 61·3	59·6	55·9	124	121
820	35·2 34·0 33·5	34·2	31·3	222	224

The corrected heat of activation is 37,500 cals. ("Kinetics of Chemical Change," Oxford, 1929, p. 104). The number of collisions, Z, per c.c. between ether molecules at 1 atm. pressure and iodine molecules at the standard concentration of $\frac{20}{3}$ mm. at 750° Abs. is equal to $2{\cdot}89 \times 10^{26}$ at 773° Abs. (see Clusius and Hinshelwood, *loc. cit.*). Then the number of ether molecules per second undergoing the reaction according to the simple theory should be $2{\cdot}89 \times 10^{26} \times e^{-\frac{37{,}500}{R.773}} = 7{\cdot}44 \times 10^{15}$. The real value of k at 773° Abs. is $5{\cdot}36 \times 10^{-3}$; whence we get for the number of decomposed ether molecules $kN = 5{\cdot}36 \times 10^{-3} \times 9{\cdot}56 \times 10^{18} = 51{\cdot}2 \times 10^{15}$, $N = 9{\cdot}56 \times 10^{18}$ being the number of ether molecules per c.c. according to the assumption previously stated. Thus the number of molecules reacting is about seven times greater than expected.

Methyl iso*Propyl Ether.*—The ether was prepared in an analogous way by refluxing methyl iodide with an excess of sodium *iso*propoxide. *iso*Propyl alcohol was removed from the crude product by shaking with water, and traces of the iodide were destroyed by heating with wet silver oxide. The ether was then carefully dried with calcium chloride and sodium and fractionated in an all-glass apparatus; b. p. 32·5—32·8°. The decomposition of this ether took place between 450° and 520°, and appeared to be more complicated, as stated above. If the hydrogen atoms in the methyl group were unable to move at all under the influence of the catalyst, the ether would give only methane and acetone. The appearance, however, of an appreciable amount of carbon monoxide in the gaseous products, and the results of the combustion of the saturated hydrocarbons showed immediately that another simultaneous reaction had taken place. The results can be satisfactorily explained by assuming, not only that the hydrogen atom of the *iso*propyl group migrates, but that the methyl group also splits off hydrogen atoms: $CH_3{\cdot}O{\cdot}CHMe_2 \longrightarrow CH_2O + C_3H_8 \longrightarrow H_2 + CO + C_3H_8$ simultaneously with $CH_3{\cdot}O{\cdot}CHMe_2 \longrightarrow CH_4 + COMe_2$.

If this assumption is correct, the amount of carbon monoxide should be equivalent to the amount of propane and hydrogen. It is possible thus to account for the results of the combustion of the saturated hydrocarbons, as is shown in the following table. The amount of acetone was found by a quantitative iodoform test. A change in the reaction temperature had only little influence on the composition of the products.

Temp., 504°.

Unsat. hydrocarbons.	$CH_3{\cdot}CO{\cdot}CH_3$.	CH_4.	CO.	H_2.	C_3H_8.	CO_2.
3·8%	30·1%	25·0%	13·4%	13·4%	13·4%	0·9%

Combustion.

	Gas used	:	Oxygen used	:	CO_2 formed
Found	1	:	2·17	:	1·24
Calc.	1	:	2·25	:	1·26

Temp., 455°.

Unsat. hydrocarbons.	$CH_3{\cdot}CO{\cdot}CH_3$.	CH_4.	CO.	H_2.	C_3H_8.	CO_2.
3·2%	34·0%	28·5%	11·3%	11·3%	11·3%	0·4%

Combustion.

	Gas used	:	Oxygen used	:	CO_2 formed
Found	1	:	2·34	:	1·30
Calc.	1	:	2·33	:	1·22

The pressure increase was always 103—105% ; a certain amount of the ether disappeared by side reactions, and a slight tarry deposit was gradually formed on the wall of the silica vessel. The surface reaction was found to be not more than a few units per cent. of the homogeneous one.

The catalytic efficiency of the iodine was proportional to its own concentration, as expected from the results with the other ethers :

Temp., $488{\cdot}_5$°; ether pressure, about 200 mm.

$3I_2$ (mm.)	10	20	40
t_{50} (secs.)	206	102	52

The initial pressure of the ether had no appreciable influence on the reaction velocity :

Temp., $488{\cdot}_5$°; iodine pressure, 20/3 mm.

Ether pressure (mm.)	306·5	215	121
t_{50} (secs.)	105	102	108

The heat of activation was deduced from a series of experiments carried out at different temperatures ; the same corrections as before are made on the results.

T Abs.	t_{50}.	$\bar{t}_{50}$.	$t_{\text{corr.}}$.	$k_{\text{obs.}} \times 10^3$.	$k_{\text{graph.}} \times 10^3$.
$725{\cdot}_7$°	277 235	256	264	2·62	2·50
$741{\cdot}_7$	172 185 187 171	$178{\cdot}_8$	$180{\cdot}_5$	3·84	3·91
$761{\cdot}_7$	101·6 101·5 102·0	$101{\cdot}_7$	$100{\cdot}_0$	6·93	6·73
$775{\cdot}_7$	75·0 75·6 79·5	$76{\cdot}_7$	$74{\cdot}_1$	9·35	9·61
$791{\cdot}_2$	49·7 52·8 52·3	$51{\cdot}_6$	48·8	14·2	14·2

The results in the last column show that the observed values for log k lie satisfactorily on a straight line when plotted against the reciprocal of the absolute temperature. From the slope of this line the heat of activation is found to be 30,200 cals., or corrected, 29,450 cals.

The statistical calculation of the reaction velocity upon the same assumptions as before leads to a value of 13×10^{17} for the number of molecules decomposed per sec. The observed value is $0{\cdot}85 \times 10^{17}$. The discrepancy is rather great and just the opposite of that usually observed. It may be noted that the existence of two simultaneous reactions makes it difficult to give a definite interpretation to the heat of activation, but the values for both reactions must be nearly the same, otherwise the composition of the gaseous products could not be practically independent of the temperature.

Methyl tert.-*Butyl Ether.*—The preparation of a pure sample of this ether was more difficult than that of the other ethers. Sodium *tert.*-butoxide was formed by boiling trimethylcarbinol in a round-bottomed flask so that the hot alcohol refluxed back over a known amount of metallic sodium in an extractor, the metal being slowly dissolved and washed into the flask. Then the thoroughly dry butoxide was heated in a Carius tube with the necessary amount of methyl iodide for 6 days at 60° (Henry, *Chem. Zentr.*, 1904, i, 1065). The ether formed was freed from the last traces of iodine compounds by heating with diethylamine (see also Bennett and Philip, J., 1928, 1930), washed with water and dilute acid, dried, and fractionated; b. p. 54—55°.

The ether was quite stable at 420°, but immediately decomposed in the presence of the catalyst. The pressure increase was always nearly 100%, and a black tarry deposit was rapidly formed on the walls.

There was no sign of a ketone or an aldehyde in the reaction products, and a gas analysis showed that principally unsaturated hydrocarbons were formed :

CO_2.	Unsaturated hydrocarbons.	CO.	Saturated hydrocarbons.
2·5%	60·6%	12·0%	24·9%

It is not possible to give any simple explanation of the reactions which may have occurred. Nevertheless, the result is interesting in so far as a catalytic effect exists at all, and it seemed unnecessary to investigate the decomposition of this ether in greater detail.

In the following table the heats of activation of certain compounds are given in calories. It appears that the heat of activation for the catalytic decomposition of the ethers is smaller the more complicated the molecule; for the uncatalysed decomposition the converse obtains. It is obvious that the catalyst attacks the complex molecule at a specific point.

Ether, etc.	Catalysed.	Uncatalysed.
Dimethyl ether	—	65,000
Methyl ethyl ether	38,000	47,000
Diethyl ether	34,000	53,000
Methyl *iso*propyl ether	29,500	—
Di*iso*propyl ether	28,500	60,500
Acetaldehyde	32,500	45,500

The question arises whether the reaction goes by way of iodine atoms or not. The fact that not only iodine but also alkyl halides and hydrogen bromide have analogous effects shows, however, that the reaction does not necessarily depend on the presence of free iodine. Furthermore, the fact that the reaction velocity is proportional to the iodine pressure and not to its square root demonstrates that the iodine molecules and not the atoms are the real catalyst.

It seems, moreover, to be unnecessary to make specific assumptions about possible intermediate products. It is known that hydrogen bromide, for instance, and diethyl ether form an addition product at low temperatures. This fact might suggest the idea that molecules of the catalyst as they approach the ether are directed, even at higher temperatures, to a certain point in the molecule by the same forces which operate in the formation of the addition product at low temperatures.

Summary.

The catalytic effect of iodine on the decomposition of the following ethers in the gaseous state has been investigated: Dimethyl, methyl ethyl, methyl *iso*propyl, and methyl *tert.*-butyl.

Iodine has no catalytic effect on the decomposition of dimethyl ether.

Methyl ethyl ether is catalytically decomposed between 460° and 550° according to the following consecutive reactions:

$$CH_3{\cdot}O{\cdot}C_2H_5 \longrightarrow CH_4 + CH_3{\cdot}CHO$$

and

$$CH_3{\cdot}CHO \longrightarrow CH_4 + CO.$$

The heat of activation of the first reaction is 38,000 cals.

Methyl *iso*propyl ether is decomposed simultaneously between 450° and 520° in two different ways:

$$CH_3{\cdot}O{\cdot}CH(CH_3)_2 \longrightarrow CH_4 + CO(CH_3)_2$$

and

$$CH_3{\cdot}O{\cdot}CH(CH_3)_2 \longrightarrow CH_2O + C_3H_8 \longrightarrow CO + H_2 + C_3H_8,$$

the heat of activation being 29,500 cals. for the net reaction.

Methyl *tert.*-butyl ether shows a very pronounced reaction in the presence of iodine but is not decomposed in a simple manner.

The results illustrate clearly the fact that the activation of a reactant molecule is dependent upon the structure of the whole molecule and not upon the presence of a certain group.

The catalyst attacks the molecule at a specific point, and the observed reactions can in every case be interpreted as the migration of a hydrogen atom from a carbon atom, which is also connected with an oxygen atom, to a second carbon atom.

I should like to take the opportunity of expressing my sincere thanks to Mr. C. N. Hinshelwood, F.R.S., for constant guidance and supervision.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.

[*Received, August 6th,* 1930.]