CCXXXVIII.—*Homogeneous Catalysis of a Gaseous Reaction. Kinetics of the Catalytic Decomposition of* iso*Propyl Ether.*

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The decomposition of gaseous *iso*propyl ether according to the equation $C_3H_7{\cdot}O{\cdot}C_3H_7 = CH_3{\cdot}CO{\cdot}CH_3 + C_3H_8$ is very markedly catalysed by small amounts of *iso*propyl iodide, as explained in the preceding paper, and since this reaction offers a good example of homogeneous catalysis, the kinetics have been investigated in more detail. It appears that the real catalyst is iodine produced by the decomposition of the iodide, and that the rate of reaction is proportional to the concentration of the ether and to that of the catalyst.

An interesting problem arises in connexion with the molecular statistics of the reaction. The uncatalysed decomposition of the ether is "unimolecular," and the heat of activation is contributed by a great many degrees of freedom. In ordinary bimolecular reactions the energy of activation is probably provided by the simple translational energy of the colliding molecules. The question arises whether the reaction depending upon collisions between the complex ether and the catalyst will belong to the first or the second of these types. The results show that only about two "square terms" are involved in the energy of activation. This, of course, corresponds closely to a simple collision mechanism, and differs entirely from the uncatalysed decomposition. Thus we have a change of mechanism, which throws light upon one mode of operation of a homogeneous catalyst.

EXPERIMENTAL.

The ether was prepared by Erlenmeyer's method (see preceding paper) and was refluxed with moist silver oxide to ensure absence of traces of *iso*propyl iodide; it was dried over sodium and fractionated, b. p. 67·8—68·4°.

The *iso*propyl iodide, prepared in the usual way, was dried and carefully fractionated, b. p. 88·9—89·1°.

The apparatus used was the same as before, except that an additional bulb was sealed to it from which iodide vapour could be admitted to the reaction bulb.

The ether bulb and the iodide bulb were first evacuated whilst immersed in a freezing mixture. An experiment performed with the ether alone showed that the reaction rate was concordant with the previously determined rate of the " uncatalysed decomposition."

In any experiment a small pressure of iodide vapour was admitted to the reaction vessel, followed by the ether vapour. The iodide alone appeared to decompose, for the pressure increased by approximately 50% when the vapour was left for a time. The nature of this decomposition will be dealt with later. Time was always allowed for the iodide to decompose before the ether was admitted. Thus the decomposed iodide is the catalyst, but the pressure is recorded as the pressure before decomposition.

Experiments on the catalysed decomposition of the di*iso*propyl ether were made between 300° and 400°. The pressure increase with respect to the ether was roughly 100% at 301°, 90% at 351°, and 80% at 401°, as shown in the following table.

T = 301°.		T = 351°.		T = 401°.	
Initial press. of ether (mm.).	Pressure increase (mm.).	Initial press. of ether (mm.).	Pressure increase (mm.).	Initial press. of ether (mm.).	Pressure increase (mm.).
118	120	127	115	250·5	211
112	112·5	217	193	125	90

The analysis of the gaseous products (after freezing out acetone, detected by the iodoform test) gave, as before, propane as the main constituent. Much of the unsaturated hydrocarbon present resulted from the decomposition of the iodide. The gas in the first analysis recorded below contained roughly 15% of decomposed iodide, and in the second about 1%.

	T = 301°.	T = 401°.
Unsaturated hydrocarbon	24·8%	12·2%
Carbon monoxide	3·8	4·3
Propane	71·4	83·5

With a constant pressure of iodide, the reaction rate, as measured by t_{50}, the time for a 50% pressure increase, was nearly independent of the pressure of ether vapour, thus :

	Pressure of iodide (mm.).	Pressure of ether (mm.).	t_{50} (secs.).
T = 351°.	23	217	392
	22	91	350
	20	51	312

The reaction rate, however, varied linearly with the pressure of iodide vapour added, *e.g.*,

	Pressure of iodide (mm.).	Pressure of ether (mm.).	t_{50} (secs.).
T = 351°.	7	87	1670
	22	91	350
	44	127	178
T = 301°.	26	112	2490
	25	104	2482
	47	128	1414

The reaction follows roughly a unimolecular course, but the velocity coefficient falls as time goes on. Details of a typical experiment are given below, a being the total pressure increase, x the increase after time t (secs.), and $k_{10} = 1/t \,.\, \log_{10} a/(a - x)$.

$T = 351°$; $a = 94$ mm.; iodide pressure $= 18$ mm.

t	107	177	222	276	340	415	505	610	727	3360
x	27	37	42	47	52	57	63	68	73	94
$100\,k_{10}$	1·37	1·23	1·16	1·09	1·03	0·98	0·96	0·92	0·90	—

The reaction rate in a packed silica bulb, having a surface/volume ratio some 16 times greater, was not appreciably different (the experiments were performed at 301° where wall reaction might be more prominent):

	Pressure of iodide (mm.).	Pressure of ether (mm.).	t_{50} (secs.).
Packed bulb	25	159	3668
,, ,, ...	53	118	1440
Unpacked bulb	47	128	1414

The experiments in the packed bulb are if anything slightly slower. Surface reaction in the unpacked bulb is thus negligible.

The temperature coefficient was determined for the range 360—419°, with pressures of ether of about 120 mm. and a constant pressure of 25 mm. of decomposed iodide. The results are given in the following table. τ (corr.) gives the time of half change of the ether referred to a constant *concentration* of iodide equal to that which gives a *pressure* of 25 mm. at 350°; τ (calc.) is found from the Arrhenius equation on the assumption that the heat of activation is 29,000 cals.

T (Abs.).	τ (obs.), with 25 mm. decomposed iodide.	τ (corr.).	τ (calc.).
692°	32″	29″	29″
673	55·5	51·5	52·5
663	77	72·5	73
643	148	143·5	145
633	228	224	212

To find the nature of the real catalyst, the decomposition of *iso*propyl iodide had to be investigated, since previous work warrants only the conclusion that propane occurs in the products. *iso*Propyl iodide was admitted to the reaction vessel and allowed to decompose. At 351°, 168 mm. of iodide increased by 91 mm., or 54%, on decomposition; the time of half decomposition was 55 secs. At 301°, 134 mm. of iodide increased by 60 mm., or 45%, the time of half decomposition being 13 minutes. The products in each case were withdrawn and analysed:

	$T = 351°$.	$T = 301°$.
Propylene	54·5%	52·0%
Propane	42·6	47·5

The unsaturated constituent was in each case shown to be propylene by combustion of a whole sample of gas. In the second analysis, for example, the following results were obtained :—

	Satd. hydrocarbon.	Whole gas sample.	Calc. for $C_3H_8 + C_3H_6$.
CO_2 : gas burnt	3·02	3·02	3·00
Contraction : gas burnt	3·10	2·76	2·75
Oxygen used : gas burnt	5·12	4·78	4·75

Experiments in which small weighed quantities of *iso*propyl iodide were heated at 304° in a glass bulb, which was afterwards opened under potassium iodide solution, showed that the iodine was liberated in the free state. By titration with $N/100$-sodium thiosulphate, it was found that after 3 minutes about 4%, and after 30 minutes about 70%, of the total iodine had been liberated. Thus the decomposition takes place in accordance with the equation $2C_3H_7I = C_3H_6 + C_3H_8 + I_2$.

Now propane and, to some extent, propylene are formed from the ether decomposition alone. If, then, propane or propylene is the catalyst, the reaction products of the ether decomposition should themselves have a catalytic effect. An experiment at 387° with 25 mm. of *iso*propyl iodide and 172 mm. of ether gave a value for t_{50} of 125 secs. One-quarter of the products was left in the reaction vessel, and 121 mm. more ether added. The value of t_{50} was now 488 secs. (*i.e.*, four times as great), proving that the catalyst (i) comes specifically from the *iso*propyl iodide and (ii) is unaltered after the reaction. The conclusion is that the iodine is the actual catalyst.

We may now consider the molecular statistics of the reaction.

At 400°, half the ether decomposes in 51·5 secs. when the concentration of the decomposed iodide is such as to correspond to 25 mm. at 350°. Thus $k = \frac{1}{51\cdot5}\log_e 2 = 1\cdot35 \times 10^{-2}$. The number ($N_1$) of molecules of ether per c.c. at 400° and 760 mm. is $1\cdot10 \times 10^{19}$; thus the number decomposing per sec. is $1\cdot10 \times 10^{19} \times 1\cdot35 \times 10^{-2} = 1\cdot49 \times 10^{17}$.

The number of collisions between molecules of ether and iodine is given by

$$Z = N_1 N_2 \sigma_{12}^2 \{8\pi RT(1/M_1 + 1/M_2)\}^{\frac{1}{2}}.$$

In this equation, M_1 and M_2 are the respective molecular weights; σ_{12}, the mean molecular diameter of ether and iodine, is taken as $4\cdot38 \times 10^{-8}$ cm.; and N_2, the number of molecules of iodine per c.c. at 400°, is one-third of the number of molecules produced by decomposition of the iodide with pressure of 25 mm. measured at 350°, and therefore

$$N_2 = \frac{6{\cdot}06 \times 10^{23} \times 8{\cdot}33 \times 273}{22{\cdot}4 \times 10^3 \times 760 \times 623} = 1{\cdot}30 \times 10^{17}.$$

Hence $Z = 3{\cdot}8 \times 10^{26}$.

The heat of activation is 29,000 cals.; corrected for variation in the collision number with temperature, this becomes 28,500 to the nearest 500 cals.

Using the following expression (*Proc. Roy. Soc.*, 1926, *A*, **113**, 230) for the number of molecules reacting, *viz.*,

$$\frac{Z\,.\,e^{-\{28,500+(\frac{1}{2}n-1)RT\}/RT}\left\{\dfrac{28,500+(\frac{1}{2}n-1)RT}{RT}\right\}^{\frac{1}{2}n-1}}{\underline{|\tfrac{1}{2}n-1}}$$

we now calculate the smallest number, n, of energy terms among which the energy of activation must be distributed to give a rate of activation equal to the rate of reaction; the values of Z and of the number of molecules reacting have already been found, and by trial n is then found to be nearer to 2 than any other integer. For this value the special form $Z\,.\,e^{-28,500/RT}$ must be used ; it equals $1{\cdot}9 \times 10^{17}$, which agrees with the number of molecules reacting.

Summary.

The decomposition of di*iso*propyl ether is catalysed by *iso*propyl iodide : the iodine resulting from the decomposition of the iodide is shown to be the effective catalyst.

The reaction is completely homogeneous, and its rate is proportional to the concentration of the ether and to that of the catalyst.

It is shown that the energy of activation is drawn from two " square terms." This number is much less than that required in the uncatalysed decomposition of the ether, and corresponds to that usually found for a bimolecular reaction in which the energy of activation is probably supplied by the translational energy of the colliding molecules.

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