131. *The Kinetics of the Decomposition of Diphenyliodonium Iodide.*

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Diphenyliodonium iodide is known to decompose on heating into iodobenzene according to the equation $(C_6H_5)_2I{\cdot}I = 2C_6H_5I$. The study of the kinetics of this reaction is somewhat difficult on account of the small solubility of the iodide in nearly all solvents. It has been found possible, however, to study the decomposition both in the solid state and in solution in iodobenzene, by starting with a weighed amount of the solid, and estimating the amount of diphenyliodonium iodide which remains unchanged at different times. Under these conditions the decomposition is autocatalytic, which indicates that there is a much more rapid decomposition of the iodide that dissolves in the iodobenzene formed. As the reaction proceeds, the amount of iodobenzene increases and, therefore, more diphenyliodonium iodide goes into solution. Since the solubility is of the order of 1 mol. per 1000 mols. of iodobenzene, excess of the solid is present until the decomposition is nearly complete.

The curve obtained by plotting percentage decomposition against time can be interpreted as follows. If a be the weight in grams of diphenyliodonium iodide originally present, and x the weight decomposed after time t, the amount of iodide in solution is sx, where s is the solubility, expressed as g. of solute per g. of solvent.

Then
$$dx/dt = -d(a-x)/dt = k_1(a-x) + k_2sx.$$

Hence
$$t = \frac{1}{(k_2s - k_1)} \log_e \frac{k_1a + x(k_2s - k_1)}{k_1a}$$

On the assumption, subsequently justified, that k_2s is much greater than k_1, we have
$$t = (1/k_2s) \log_e \{(k_1a + k_2sx)/k_1a\}.$$

After the initial stage of the reaction, k_2s/k_1 will be great compared with a/x, so that

$$t = (1/k_2s)(\log_e x/a + \log_e k_2s/k_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the logarithm of the proportion changed, x/a, is plotted against time, a linear relationship should hold after the very first stages irrespective of the initial weight. The slope of the line is k_2s : from the value, t', of the time at which $x/a = 1$, and $\log_e x/a = 0$, k_1 may be found from the equation

$$t' = (1/k_2s) \log_e k_2s/k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

EXPERIMENTAL.

Diphenyliodonium iodide was prepared in the usual manner from iodobenzene. Estimation as iodide, by dissolving it in aqueous alcohol and titrating by Volhard's method, gave results exceeding 99% of the calculated.

A number of tubes containing a weighed quantity of the substance were sealed and placed in a thermostat. After a suitable time a tube was removed, and the contents dissolved in aqueous alcohol and analysed for unchanged iodide. A small quantity of free iodine was formed, but it amounted at the end of the reaction to less than 0·5% of the original diphenyliodonium iodide.

Electrically controlled thermostats were used below 100°, and vapour baths for the higher temperatures. The variations in temperature did not in general exceed 0·1°.

The solubility of diphenyliodonium iodide in iodobenzene was too small to be determined by the usual methods. A conductivity method was therefore adopted. A saturated solution was prepared at a given temperature, and rapidly forced through a Jena-glass filter into a weighed flask containing a known volume of conductivity water. The flask was shaken long enough to ensure complete partition of the diphenyliodonium iodide between the two solvents. The greater part passed into the aqueous layer, the partition coefficient at room temperature being approximately 10. The conductivity of the aqueous solution was determined by means of a Leeds and Northrup S.P. 929 bridge and A.C. galvanometer, type 2470(c). The limiting equivalent conductivity * of diphenyliodonium iodide was taken as 103, the sum of the ionic mobilities. Blank experiments in which water was shaken with iodobenzene were carried out, and corrections made accordingly. The iodobenzene used was dried with calcium chloride and distilled at 3 mm. pressure. From the measured conductivity the quantity of iodide originally present in the iodobenzene solution could be calculated. Allowance was made for the change in the equivalent conductivity with the concentration of the aqueous solution. Since diphenyliodonium iodide undergoes a photochemical decomposition, the solutions were protected from light.

Results.—The reaction was studied at five temperatures such that the time for complete reaction varied by a factor of 100 from just over 1 hour to nearly 5 days. Table I shows the course of the decomposition at 111·3°. Col. 3 shows that, from 10% decomposition onwards, a linear relation holds between $\log x/a$ and t, in agreement with equation (1).

Table II summarises the results at different temperatures : k_2s and $\log_{10} k_1$ are calculated from equations (1) and (2). Both k_1 and k_2 are in reciprocal hours. When plotted against the reciprocal of the absolute temperature, $\log_{10} k_2s$ and $\log_{10} k_1$ conform to the Arrhenius equation, except in the case of $\log k_1$ at the highest temperature. It may be noted that, at the temperatures used, k_2s is always more than 10 times, and at 120° more than 100 times, greater than k_1. Two sources of error should be considered. (*a*) In estimating the time no allowance was made for that taken by the tube to reach the temperature of the thermostat. The error thus introduced does not affect the value of k_2s, which depends only upon the slope of the $\log x/a$–t line. It will, however, influence the value of t', and will be most serious at the highest temperature where t' is smallest. This may account for the low value of t' at 120·2°, for, if at this temperature t' is 1·00 and not 1·15 hrs., the value of k_1 agrees with that calculated from lower temperatures. (*b*) It has been assumed that all the iodobenzene present remains saturated with diphenyliodonium iodide as long as any solid is present. Any departure from this condition will make the observed values of k_2s and k_1 lower than the true values. Saturation is more likely to be maintained during the slower reactions. Thus the observed activation

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* The conductivity of iodonium salts has been investigated by Sullivan, *Z. physikal. Chem.*, 1899, **28**, 523.

energy would be too low. Since the results are reproducible even at high temperatures, it seems that saturation is, in fact, maintained.

The values for the solubility are given in Table III. At least two experiments were made at each temperature, and a mean taken. The results are considered accurate to within 10% except at 0°.

TABLE I.

Course of the reaction at **111·3°**.

Time (mins.).	x/a.	$\frac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.	Time (mins.).	x/a.	$\frac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.	Time (mins.).	x/a.	$\frac{2\cdot303 \log_{10} x/a}{t - 3\cdot00}$.
61	0·055	1·47	131	0·312	1·42	163	0·680	1·37
81	0·100	1·40	145	0·416	1·51	175	0·886	1·47
111	0·172	1·54	154	0·564	1·33	176	0·910	1·41

TABLE II.

Temp.	t' (hrs.).	k_2s.	$\log_{10} k_2s$.	$\log_{10} k_1$.	Temp.	t' (hrs.).	k_2s.	$\log_{10} k_2s$.	$\log_{10} k_1$.
120·2°	1·15	4·57	0·660	$\bar{2}\cdot38$	90·9°	31·0	0·118	$\bar{1}\cdot072$	$\bar{3}\cdot48$
111·3	3·00	1·44	0·158	$\bar{2}\cdot28$	80·6	116	0·0291	$\bar{2}\cdot464$	$\bar{3}\cdot00$
100·6	10·00	0·384	$\bar{1}\cdot584$	$\bar{3}\cdot92$					

TABLE III.

Temp.	95°	75°	55°	25°	0°
Solubility(s), g./g. × 10^4	3·34	1·65	0·925	0·290	0·106

When log s is plotted against $1/T$, the results lie on a straight line, from which the negative heat of solution (Q) is found to be 7380 ± 300 cals. From the plot of log k_2s against $1/T$, $E_2 + Q = 34{,}400$ cals., where E_2 is the activation energy of the reaction in solution; therefore $E_2 = 34{,}400 - 7380 = 27{,}020$ cals. The activation energy for the solid reaction is 26,300 cals.

DISCUSSION.

The decomposition of iodonium salts may be compared with that of ammonium, phosphonium, and sulphonium salts: the chemical nature of these changes has been discussed by Hughes, Ingold, and Patel (J., 1933, 526). Kinetic measurements of the decomposition of a quaternary ammonium iodide in aqueous solution indicate that the reaction is unimolecular (Hughes and Ingold, *ibid.*, p. 523). An extensive investigation of the decomposition of phenylbenzylallylammonium bromide in various solvents has been made by von Halban (*Ber.*, 1908, **41**, 2417). In each solvent the reaction is unimolecular. The observed rate has been compared (Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, p. 158 *et seq.*) with that calculated from the formula

$$k = (3\pi\eta\sigma/2m) \, . \, e^{-E'/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

based upon a rough value for the number of collisions between solvent and solute with activation energy E' in two square terms; E' is the observed activation energy corrected for the temperature variation of the solute–solvent collision number. In chloroform solution the observed rate is about 10^5 times greater than that given by (3). Similarly, the observed rate of decomposition of triethylsulphonium bromide (von Halban, *Z. physikal. Chem.*, 1909, **67**, 129) in various solvents is about 10^5 times as great as that given by the equation. These observed rates can naturally be explained if the energy of activation is distributed in a number of degrees of freedom, the minimum number required being about 7 in some examples.

The method by which the decomposition of diphenyliodonium iodide has been studied does not give the order of the reaction, as the concentration remains constant, but the change is probably unimolecular, as in the other examples. This being assumed, calculations similar to those described above may be carried out. The activation energy (E_2) must be increased by Q' of the equation $- d \log_e \eta/dT = Q'/RT^2$, where η is the viscosity of iodobenzene; $Q' = 2480$ cals. (Intl. Crit. Tables), so $E' = 27{,}020 + 2480 = 29{,}500$ cals. If $\sigma = 5 \times 10^{-8}$ cm., the value of the right-hand side of (3) at 90·9° is of the order 10^{-5} to 10^{-6} sec.$^{-1}$. The observed value of k_2s at 90·9° is 0·118 hr.$^{-1}$ or $3\cdot28 \times 10^{-5}$ sec.$^{-1}$. From the graph of log s against $1/T$, s at 90·9° is $2\cdot83 \times 10^{-4}$; therefore $k_2 = 0\cdot116$. The observed rate is thus 10^4—10^5 times as great as that calculated from equation (3), this ratio being comparable with that found with ammonium and sulphonium salts. The observed rate of reaction is many powers of ten greater than that calculated for a bimolecular reaction between two molecules of the solute, or between a diphenyliodonium ion and an iodide ion. It seems probable, therefore, that the assumption of a unimolecular reaction is justified.

The Reaction of the Solid.—Many solid reactions take place only at an interface between the reacting substance and one of the products. Widely differing types of behaviour are found, but in certain examples, such as the dehydration of copper sulphate pentahydrate (Topley, *Proc. Roy. Soc.*, 1932, *A*, **136**, 413), the rate of reaction and its variation with temperature have been accounted for satisfactorily.

From the nature of the experimental method, only the initial stage of the decomposition of solid diphenyliodonium iodide contributes towards the velocity constant, k_1. The course of reaction to be expected if decomposition occurs only at an interface will not therefore be apparent.

The velocity constant (k_1 in sec.$^{-1}$) is given by $k_1 = 6{\cdot}0 \times 10^9 . e^{-26{,}300/RT}$. It is of interest to see the result of assuming that the reaction may take place uniformly throughout the whole mass of solid. If the energy of activation is contained in two square terms, $6{\cdot}0 \times 10^9$ is the probability of decomposition of the activated molecules, and the reciprocal of this is the average life of an activated molecule. If the energy of activation is distributed throughout the molecule in a number of degrees of freedom, and the probability of decomposition represents the chance that sufficient energy becomes localised in a certain part of the molecule (*e.g.*, the C–I bond), then the expression $e^{-26{,}300/RT}$ must be replaced by a more complex one. If all the C–C and C–I bonds were involved, the number of square terms could be very great, and the average life might work out to be as great as 10^{-4} sec. This state of affairs would be comparable with that met with in the unimolecular decompositions of complex molecules in the gaseous state.

Further knowledge of the rate of reaction in other solvents seems necessary before more can be said about the mechanism of the change. Without definite knowledge of the number of degrees of freedom participating in the decomposition of the solid, and in the decomposition in solution, it is not permissible to compare the activation energies directly. If the number is the same in the two cases, the energy of activation in iodobenzene appears to be somewhat greater than that for the solid.

SUMMARY.

The rate of decomposition of diphenyliodonium iodide has been studied in the solid state and in solution in iodobenzene. The activation energy for the reaction in the solid is 26,300 cals., and that for the reaction in solution 27,000 cals. (uncorrected for change of viscosity). The solubility of diphenyliodonium iodide in iodobenzene has also been measured.

The rates of reaction are discussed in relation to different activation mechanisms.

One of the authors (C. J. M. F.) thanks the Commonwealth Fund for a Fellowship which has made part of this work possible.

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