with in weighable quantities, the interference from these elements is of no importance. The interference from sodium is more serious and prevents the use of the reagent for detecting potassium in the presence of sodium unless dealing with small residues of alkali chlorides. It should be mentioned, however, that the crystalline precipitates formed by potassium and sodium are quite different in appearance. The former yields short prisms and needles which, particularly when the amount of potassium is small, present an iridescent appearance in strong light while the latter forms long hair-like crystals which never present an iridescent appearance.

Conclusions

The interference of sodium in the above reaction restricts its use to a greater extent than has been generally supposed. Regardless of this limitation, however, it may be employed as a confirmatory test for potassium after the approximate separation of the two elements or for the examination of small residues of alkali chlorides. For these purposes it has certain advantages over the usual reagents for potassium. It is more sensitive than perchloric acid, chloroplatinic acid or tartaric acid and, while not as sensitive as sodium cobaltinitrite, it has the advantage of possessing much greater stability since solutions of picric acid in alcohol appear to keep indefinitely.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE KINETICS, STATICS AND ENERGETICS OF THE THERMAL REACTION $CH_2I-CH_2I = CH_2{=}CH_2 + I_2$ IN CARBON TETRACHLORIDE SOLUTIONS

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Introduction

The object of this research was to determine the kinetics of the decomposition of ethylene iodide in carbon tetrachloride solutions. Since the number of reactions that proceed in a direct and simple manner is limited, it was of great interest to find that this one follows a fairly simple law through a large range of concentrations and temperatures.

The results are of further interest since it was possible, by assuming a simple mechanism of reaction, to give a complete interpretation not only of the so-called "energy of activation" but of the actual magnitude of the rate as well. The plausibility of the interpretation is enhanced by the fact that it can be applied successfully to two similar reactions previously studied by other investigators. One of the reactions referred to is the decomposition of ethylene iodide in alcoholic solutions, in the presence of iodide ions. The other is the decomposition of phosgene in the gaseous phase.

Experimental Methods

Materials Used.—Commercial carbon tetrachloride was purified in the following way. Chlorine was bubbled through a large volume of the liquid until the concentration of the former reached about 0.1 *N*. Enough iodine was added to make its concentration about 0.015 *N*. The resulting mixture was allowed to stand for forty-eight hours and then it was refluxed near its boiling point for three hours. The halogens were extracted with 0.5 *N* sodium hydroxide and the organic phase was washed with 0.5 *N* hydrochloric acid and finally with water.

The carbon tetrachloride was dried by refluxing for sixteen hours over granulated calcium chloride, followed by five hours of refluxing over phosphorus pentoxide, both carried out near the boiling point. Finally, it was distilled over a fresh portion of phosphorus pentoxide into a carefully dried all-glass wash bottle.

Kahlbaum ethylene iodide was used. Although the solid contained some iodine because of partial decomposition, no attempt was made to purify it. Whenever an iodine-free solution was wanted the iodine was removed by shaking the solution with mercury.

In some of the experiments the initial iodine content was increased by adding a solution of iodine in carbon tetrachloride. The latter was prepared by dissolving "P. W. R." iodine crystals in the purified carbon tetrachloride.

Preparation of the Solutions.—The stock solutions were prepared by dissolving a weighed amount of the partially decomposed iodide in a weighed amount of carbon tetrachloride. The solution was titrated for free iodine. The ethylene iodide content was then readily calculated. More dilute solutions were obtained by the addition of carbon tetrachloride to the stock solutions.

Rate Measurements.—The rate of decomposition of the iodide is very small at ordinary temperatures. For this reason most of the measurements were carried out in the range 120 to 150°. In an ordinary experiment several (5 to 12) 8-cc. samples were sealed in glass bombs prepared from 18-mm. pyrex test-tubes. For rate measurements at the highest temperatures, at which the total duration of the experiment was short, the bombs were wrapped in tin foil. For measurements at lower temperatures ordinary toweling was used.

Suspended from copper wires, the samples were immersed in the thermostat and withdrawn at convenient intervals. Each bomb was opened and emptied into a weight buret. A weighed amount was introduced into a slightly acidified solution of potassium iodide and titrated with 0.05 or 0.005 *N* sodium thiosulfate solution, depending upon the iodine concentration. In the later experiments a known amount of the solution was withdrawn by means of a calibrated pipet.

Equilibrium Measurements.—The same general procedure was used as in the rate measurements, with the only difference that the bombs were kept in the thermostat for longer periods, depending on the concentration of the solution and on the temperature. In the experiments at 122 and 132° the reversibility of the reaction was tested. The samples were divided into two groups. One group of samples was first kept at a temperature 10° higher than the temperature under investigation for a time long enough to establish equilibrium. After that the thermostat was cooled and the second group of bombs added.

Temperature Control.—The temperature of the thermostat was kept constant to 0.1°. The temperature regulator, designed by the author to allow a rapid change of the temperature setting was described elsewhere.[1]

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[1] Polissar, This Journal, **52**, 636 (1930).

The Kinetics of the Decomposition

Preliminary experiments have shown that the decomposition is autocatalytic and that iodine is the accelerating agent. From an analysis of eight experiments performed at the same temperature, it appeared that the rate is proportional to the first power of the ethylene iodide and to the square root of the iodine concentrations. This kinetic relationship was next tested experimentally through a large range of temperatures and of concentrations and was found to hold true to within a very few per cent.

Let S be the total iodine content of the solution, free and in combination, and let x be the free iodine content. The kinetic equations and the rectified integrated equations can be represented as follows

$$\mathrm{d}(\mathrm{I}_2)/\mathrm{d}t = \mathrm{d}x/\mathrm{d}t = k_1(E\mathrm{I}_2)(\mathrm{I}_2)^{1/2} = k_1(S - x)x^{1/2} \tag{1}$$

$$y - y_0 = k_1(t - t_0), \text{ where } y = \frac{1}{\sqrt{S}} \ln \frac{1 + \sqrt{\frac{x}{S}}}{1 - \sqrt{\frac{x}{S}}} \tag{2}$$

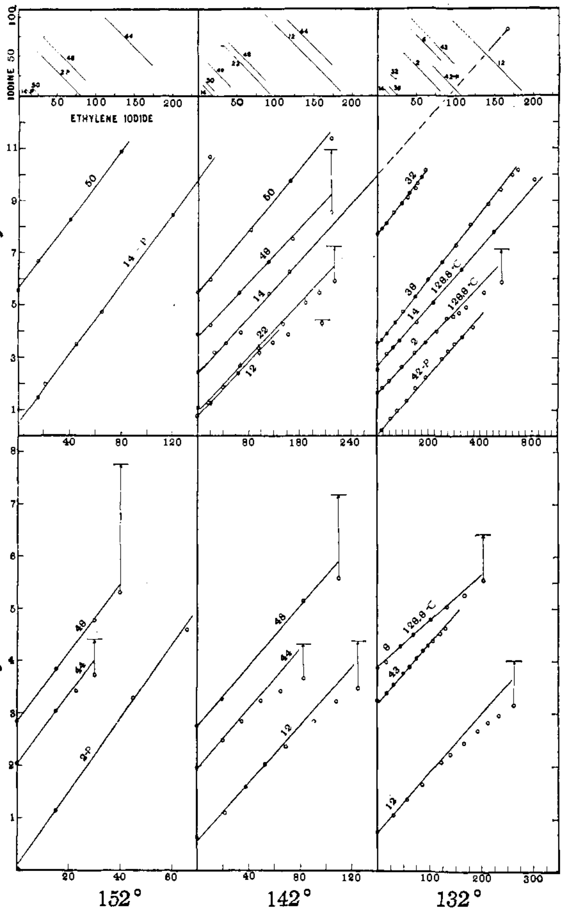
It will be seen from Equation 2 that the assumed kinetic law can be tested by plotting the experimental results on a y–t diagram. If the law is correct, then points corresponding to a single experiment must fall on a straight line; the slopes of all the lines corresponding to measurements at a single temperature must be the same, and equal to k_1.

In Figs. 1 and 2 are given the results of measurements made at six different temperatures, ranging from 40 to 152°. The iodine concentrations worked with ranged from 1.5×10^{-5} to 0.1 equivalent per kilogram; the ethylene iodide concentrations ranged from 0.011 to 0.19 equivalent per kilogram.

For the sake of compactness the results of measurements made at three different temperatures were plotted on the same diagram. The heavy vertical lines separate the three regions. In Fig. 1 the experiments at each temperature were divided into two groups. Those of short duration were shown in the lower part of the plot; those of long duration, in the upper part. Since both the vertical and the horizontal scales have been doubled, the slope remained unchanged. In Fig. 2, which contains the summary of experiments with widely different rate constants, it was necessary to use different scales for the ordinates in the three regions. Furthermore, with the large scales used in the 75 and 40° regions, it was necessary to shift some of the lines in the vertical direction in order to bring them into the figure.

At the top of each temperature region is given the composition diagram for all the solutions used at the temperature in question. The 45° lines drawn on an ethylene iodide–iodine field show not only the initial composition of each solution but the concentrations of the two substances during the whole course of the experiment as well.

In some of the experiments the possible experimental error in y due to titration alone was of the same order of magnitude as the change in y due to the reaction. In such cases the size of the circle was made to indicate the experimental error.



Time in minutes.

Fig. 1.

It will be seen that of the thirty-five experiments shown in the two figures all but two satisfy a linear relationship. While in some of the experiments a certain amount of curvature can be observed, the vertical arrows showing the distance of the last point from the equilibrium value of y emphasize the fact that the deflection is due to the reverse reaction. The curvature appearing in the case of R–75°–14-P and –2-P will be taken up later in connection with the discussion on the superimposed slow reaction.

Table I gives a summary of the results of all the rate measurements. The concentrations are in equivalents ($EI_2/2$, $I_2/2$) per kilogram of solution. The values of k_1 given in this table were used in Fig. 3 to test the applicability of the Arrhenius equation for a second-order rate constant. It is seen that, with the exception of the 40° value, a satisfactory linear relationship is obtained. Thus the magnitude of k_1 is given by the following two forms of the Arrhenius equation

$$\text{Log}_{10}\, k_1 = 12.642 + {}^1/_2 \log_{10} T - \frac{6425.2}{T} \tag{3}$$

$$k_1 = 4.4 \times 10^{12} \sqrt{T}\, e^{-29{,}500/RT} \tag{4}$$

where the unit of concentration is one equivalent per kg. of solution and the unit of time is one minute.

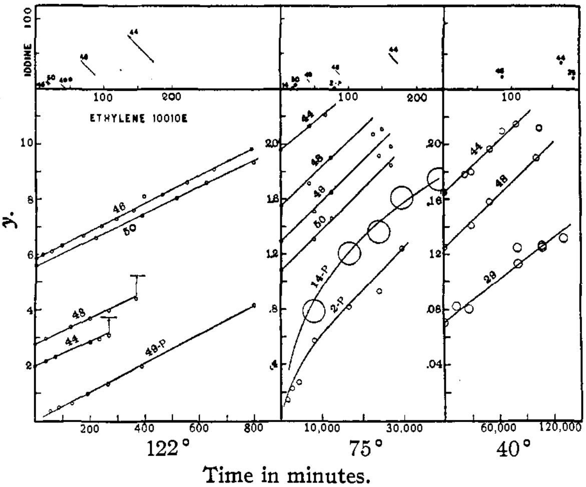


Fig. 2.

The significance of the quantity 29,500, usually called "the heat of activation," will be taken up in the theoretical part of the paper. In the discussion on the superimposed slow reaction a possible explanation is offered for the high value of the "constant" at 40°.[2]

The Decomposition in the Absence of Iodine.—In the preceding section it was shown that the main reaction is catalyzed by free iodine present in solution. The present section deals with a number of experiments

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[2] At the time this paper was completed for publication, our attention was called to a very recent research by R. B. Mooney and E. B. Ludlam, *Proc. Roy. Soc. Edinburgh*, **49**, 160 (1929), on the thermal equilibrium between ethylene, iodine and ethylene iodide. While these investigators studied chiefly the reaction in the gaseous phase, they have also carried out a few measurements on the rate of decomposition of the iodide in carbon tetrachloride at 100°. They have found that, with the same initial ethylene iodide concentration, the initial rate was approximately proportional to the square root of the iodine content.

Table I

Values of k_1 at Temperatures 40 to 152°

t, °C.	Soln.	$(EI_2)_0 \times 10^3$	$(I_2) \times 10^3$ Initial	$(I_2) \times 10^3$ Final	$k_1 \times 10^4$	Av.
152	44	174	40.2	101.5	760	710
	48	87.7	19.9	52.1	650	
	50	22.1	4.85	13.6	780	
	2-P	80.6	0.01	49.8	700	
	14-P	17.4	0.01	6.46	660	
142	44	174	37.5	100	263	278
	48	87.8	18.9	62.7	285	
	49	43.8	9.45	33.5	267	
	50	22.1	4.75	17.0	297	
141.1	12	186	5.0	106	268	270
	14	18.7	0.47	14.7	272	
140.6	22	93.5	2.53	50.4	256	240
	12	186.0	5.0	84.9	224	
132	32	23.9	18.5	25.8	127	119
	36	24.3	2.07	12.1	125	
	42-P	107	0.01	37.4	118	
	43	98.5	40.3	71.4	105	
129.8	6	81.3	44.5	71.6	95	105
	2	81.7	4.92	42.1	105	
	14	18.7	0.58	6.76	117	
	12	186	5.0	68.8	105	
122	46	19.6	4.22	9.7	49.2	47.2
	44	174	37.5	76.9	46.0	
	48	87.8	18.9	40.1	46.8	
	50	22.1	4.75	11.0	49.2	
	49-P	43.8	0.01	7.2	50.0	
75	44	174	37.5	52.7	0.26	0.28
	48	87.8	18.9	25.9	.28	
	49	43.8	9.45	12.6	.28	
	50	22.1	4.75	5.9	.29	
40	44	174	37.5	39.1	0.0053	0.0059
	48	87.8	18.85	19.7	.0062	
	29	191.5	16.0	17.7	.0063	

which seem to indicate that ethylene iodide decomposes, at a very slow rate, even in the absence of iodine.

To detect the presence of the uncatalyzed reaction, rate measurements were carried out with "P" solutions. The latter were prepared by vigorously shaking the ordinary solutions for a few seconds with a small amount of mercury, decanting the carbon tetrachloride phase and forcing it through a cotton plug. The resulting solutions were clear and colorless, showing that the mercury had removed practically all of the iodine.

Fixing our attention on experiments 2-P and 14-P (at 75°, Fig. 2), we find an abnormally high initial slope which gradually decreases to the value yielded by ordinary solutions.[3] The physical interpretation of these results is not far to seek, if we assume the existence of a slow uncatalyzed reaction. The rate of this reaction is independent of the free iodine content of the solutions; during the early stages of the experiment, when the total iodine output is small, the effect of the superimposed reaction is appreciable. Toward the end of the experiment, when the iodine concentration is large, the catalyzed reaction completely obscures the presence of the uncatalyzed one.

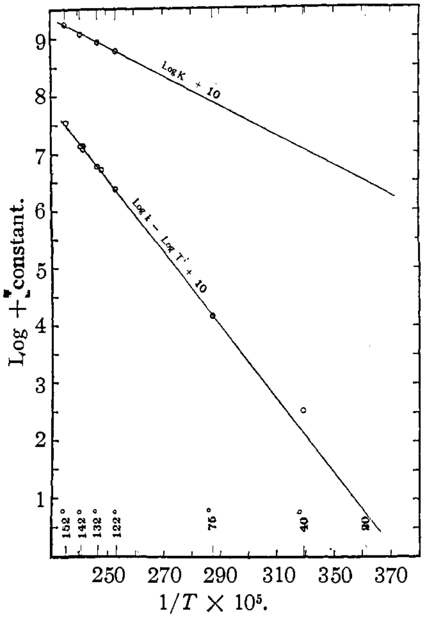

Fig. 3.—Upper line, equilibrium constant (log K + 10); lower line, rate constant (log K_1 − log $T^{1/2}$ + 10).

Experiments with "P" solutions were also performed at higher temperatures (122, 132, 152°, Figs. 1 and 2). In all of these experiments the curves obtained were indistinguishable from straight lines. This is due to the fact that at the higher temperatures the amount of iodine formed during the first several minutes was sufficient to obscure the presence of the side reaction. The existence of the uncatalyzed reaction at the higher temperatures was established in the following manner.

Assuming that iodine was formed through the operation of the iodine-catalyzed reaction only, and using the rate equation obtained from measurements with ordinary solutions, it was possible to calculate the amount of iodine that should be present at the time the first sample was taken. In every case it was found that the amount of iodine actually formed was larger than the calculated amount, in spite of the fact that it took from ten to twenty minutes for the temperature inside the bomb to reach the temperature of the thermostat. The difference observed was much larger than the maximum possible experimental error, proving without doubt the existence of a side reaction. However, the accuracy with which this type of measurement could be carried out was not sufficient to throw any light on the nature of the side reaction.

An inspection of Fig. 3 will show that the rate "constant" at 40° as

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[3] In the case of 14-P the objection may be raised that a straight line could be drawn through the points indicated on the plot. However, the curve must pass through the point (not shown on the plot) corresponding to the initial, unknown but very low, iodine concentration.

obtained graphically from Fig. 2 is too high. This is probably due to the fact that, because of the operation of a smaller temperature coefficient, the rate of the side reaction acquires the same order of magnitude as that of the "main" reaction. Experiments with colorless solutions seemed to substantiate this explanation. While the results were not quite decisive, lack of time prevented any further study of these extremely slow reactions.

The Decomposition of the Solid

The decomposition of the solid is catalyzed by iodine. Thus when the unpurified sample was heated it decomposed rapidly at about 45°. The purified iodide gave a sharp melting point at 81.5°. No decomposition took place. The purified substance ground together with some iodine decomposed at 45°. Finally, the purified substance ground together with a neutral powder ($BaSO_4$) gave a sharp melting point at 81.1°, without decomposition.

The Equilibrium Constant

The second product of the decomposition is ethylene. This was manifest from the effect of the reaction mixture on bromine. While quantitative experiments were undertaken, no satisfactory agreement could be obtained between the ethylene content as found from bromination experiments and that calculated from the increase in iodine concentration. However, blank experiments with ethylene solutions in carbon tetrachloride have indicated that the bromine determination is extremely unreliable.

The equilibrium measurements were complicated by the fact that certain slow side reactions were taking place in the equilibrium mixture containing carbon tetrachloride, ethylene iodide, ethylene and iodine. In most of the experiments the "iodine content" increased to a maximum and then decreased very slowly. Blank experiments with pure carbon tetrachloride and with solutions of iodine in carbon tetrachloride have thrown only little light on this phenomenon. However, it was definitely established that the slow decrease in oxidizing agent content was not due to a slow splitting of hydrogen iodide from the ethylene iodide, followed by a recombination of ethylene and iodine to reëstablish equilibrium. The amount of hydrogen iodide formed was much too small to account for the total change in iodine content.

With the observed general trend in mind, it was possible to get a satisfactory estimate of the value of the equilibrium constant for four different temperatures. After all the values had been determined they were tested on a log K–$1/T$ plot (Fig. 3) and were found to be fairly well represented by the following empirical equation

$$\text{Log } K_{10} = 4.964 - \frac{2450}{T} = 4.964 - \frac{11,300}{2.3RT} \qquad (5)$$

Equation 5 yields a provisional value, 11,300 cal., for the heat of dissociation of EI_2 in carbon tetrachloride solution.

Kinetics of the Reverse Reaction

While the kinetics of the reverse reaction was not studied experimentally, the equation for the rate of formation of ethylene iodide may be derived from theoretical considerations. Thus, if we make the usual assumption that at equilibrium the direct and reverse reactions are taking place simultaneously, we get the following equation for the kinetics of the reverse reaction

$$dEI_2/dt = k_2(E)(I_2)^{3/2},$$

where $k_2 = k_1/K$.

Since the values of k_1 and of K have been obtained experimentally, it is possible to calculate the value of k_2 for any temperature. The equation is given in Table II.

Mechanism of the Reaction.—The order of the reaction with respect to iodine suggests the interpretation that the decomposition of EI_2 is catalyzed by free iodine atoms present in solution. Before we consider this possibility in detail, we may pause to offer another mechanism, of an altogether different nature, yet leading to the same kinetic equation

$$2EI_2 + I_2 = 2EI_3 \text{ (rapid and reversible)} \quad (6)$$
$$EI_3 = E + I_2 + I \text{ (rate determining step)} \quad (7)$$

This possibility is of interest in that it does not involve free iodine atoms. It was considered in the preliminary stages of the investigation, when it was thought that the solutions did not contain a sufficient number of free halogen atoms to account for the rate observed. However, since catalysis by free halogen atoms had been observed in several other reactions, and since such an assumption yields itself to a quantitative test, we shall proceed to examine it in the light of the modern theory of bimolecular reactions.

It is possible indeed to formulate several detailed mechanisms involving iodine atoms and leading to the observed kinetic law. However, they are all experimentally indistinguishable from one another and can be represented by the following scheme

$$I_2 = 2I \text{ (reversible)} \quad (8)$$
$$EI_2 + I = (X) = E + I_2 + I \text{ (rate determining)} \quad (9)$$

This is a condensed symbolic presentation of the physical process that is taking place and can be elaborated as follows. It is assumed that the decomposition of the ethylene iodide molecule must be preceded by its collision with an iodine atom. While the majority of collisions is elastic, a small fraction results either in the immediate disruption of the molecule or in a series of transformations that leads to the eventual separation of the ethylene group. It is evident that, while the collision between reactant and catalyst is a necessary condition, it is not always a sufficient one; the group, as a whole, must possess a minimum amount of energy before the reaction can take place.

The Energetics of the Reaction

Introduction.—In the discussion that follows, the magnitude of the heat of activation is estimated from the temperature coefficient and is found to be nearly equal to the heat of dissociation of ethylene iodide; the same result is obtained when the heat of activation is estimated from the ratio of the number of effective collisions to the total number of collisions; two analogous reactions, studied by other investigators, are next examined by the same method and are found to yield similar results.

The Heat of Activation.—If the kinetics of the decomposition were represented by the scheme

$$dI_2/dt = k'(EI_2)(I);\ \text{Log}\ k' = A' + {}^1/_2 \log T - Q'/2.3RT \qquad (10)$$

then the heat of activation, Q', could be obtained directly from the second equation. However, the equations actually used were of the form

$$dI_2/dt = k_1(EI_2)(I_2)^{1/2};\ \log k_1 = A_1 + {}^1/_2 \log T - Q/2.3RT \qquad (11)$$

From 10 and 11 it follows that

$$29{,}500 = Q' + Q'' \qquad (12)$$

where $2Q''$ is the heat of dissociation of iodine in carbon tetrachloride solution. Although the magnitude of this quantity is unknown, we can use, as a first approximation, the results of Starck and Bodenstein on the dissociation of the gas at high temperatures.[4]

Their equation for the equilibrium constant is reproduced here, since it will later be used again for the estimation of the concentration of iodine atoms

$$\text{Log}\ K_p = 35{,}480/2.3RT + 1.75 \log T = 0.000416T + 0.422 \qquad (13)$$

Since these workers investigated the reaction at an average temperature of 1273°K., it is estimated that the heat of dissociation of iodine at 132° is about 33,000 cal., and the heat of formation of a gram-atom of free iodine atoms is 16,500 cal. Substituting this value of Q'' in Equation 12, we find that the heat of activation is equal to 13,000 cal. We have previously found that the heat of dissociation of ethylene iodide is 11,300 cal. (Equation 5). We therefore arrive at the highly interesting result that, within the limits of experimental error, the heat of activation, obtained from kinetic measurements, is equal to the heat of dissociation of the molecule, obtained from equilibrium measurements.

The Heat of Activation from the Number of Effective Collisions.—In a gaseous bimolecular reaction in which the heat of activation, Q', is known, it is possible to predict the rate, provided it is assumed that every colli-

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[4] Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

sion in which the joint energy exceeds Q' is effective; for the number of effective collisions, defined as. above, is given by the equation[5]

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-Q'/RT} \qquad (14)$$

and the total number of collisions can be calculated from gas kinetic laws. On the other hand, with the same assumption it is possible to use Equation 13 to calculate Q', if the rate is known. We propose to use this second method to obtain the value of Q' and to compare this value with the one calculated from the temperature coefficient of the rate constant.

It would be surprising indeed to find a bimolecular reaction in which every collision satisfying the energy requirement led to decomposition. However, several cases are known[6] in which the probability factor lies between 1.0 and 10^{-2}. Furthermore, there is no *a priori* reason why the probability factor should be smaller in solution, since we are unable to foretell the effect of the participation of a solvent molecule in a triple collision on the issue of an encounter. We shall proceed, then, to evaluate Q', bearing in mind the approximations involved, as well as the fact that, at the temperature used, a ten-fold error on the left side of Equation 14 introduces an error of 1800 cal. in the magnitude of Q'.[7]

To carry out the computation, we shall assume a solution containing 1.0 equivalent/kg. of EI_2 and 1.0 equivalent/kg. of iodine. With the use of the experimentally observed rate constant we shall determine the speed of iodine formation in such a solution at 142°. We shall also estimate the number of collisions between EI_2 molecules and I atoms under those circumstances. The ratio of the two quantities will give us the value of $e^{-Q'/RT}$. In our calculations we shall make use of the following information.

The rate constant at 142° is 2.94×10^{-2} e./kg./min. (from Fig. 2). The density of carbon tetrachloride at 142° is 1.42. The number of collisions is given by

$$Z = 10^{28.4427}\,\sigma_{12}^2\sqrt{\frac{M_1 + M_2}{M_1M_2}\,T}\,(EI_2)(\mathrm{I}) \qquad (15)$$

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[5] Cf. C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1926, pp. 53 and 97.

[6] Hinshelwood, Ref. 6, p. 48.

[7] It may be worth while to list the errors involved in the two methods of evaluating Q'. In the temperature-coefficient calculation the quantity 29,500 was obtained from the slope of the Arrhenius line for the experimentally observed rate constants. The heat of formation of a gram-atom of iodine in carbon tetrachloride solution was estimated from equilibrium measurements on the gaseous phase at very high temperatures. The maximum possible error in Q' was, roughly, 4000 cal.

In the calculation involving the number of collisions, gas laws will be applied for a solution. The degree of dissociation of iodine in carbon tetrachloride will be estimated with the aid of Equation 13, which was obtained from measurements in the gaseous phase at about 1273°K. Finally, the assumption will be made that the probability factor is unity. Here, again, the possible error is about 4000 cal.

where Z is the number of moles/cc. suffering collision per second, σ_{12}, is the average diameter, M is the molecular weight, and the concentrations are in moles/cc.[8] The concentration of iodine atoms is calculated by the aid of Equation 13.

Assuming $\sigma_{12}^2 = 10^{-15}$, the results obtained are as follows

$$(EI_2) = (I_2) = 1.0 \text{ e./kg.} = 3.52 \times 10^{-4} \text{ mole/cc.}$$
$$(I) = 6.6 \times 10^{-12} \text{ mole/cc.}$$

Observed rate of iodine formation = 1.72×10^{-7} mole/cc./sec.

Number of collisions = 0.14 mole/cc./sec.

$$e^{-Q'/RT} = (1.72 \times 10^{-7})/0.14; \quad Q' = 11{,}250 \text{ cal.}$$

Collecting the values obtained, we find that the heat of activation as evaluated by the two methods is equal to 13,000 and 11,250, respectively. The heat of dissociation of EI_2 is equal to 11,300 cal. We may conclude that, within the limits of experimental error, the mechanism assumed leads to a satisfactory interpretation of the magnitude of the rate at a single temperature, as well as that of the temperature coefficient.

Similar Reactions

The Decomposition of Phosgene.—The plausibility of the interpretation given in the preceding section is strengthened by evidence from an entirely different source. The decomposition of phosgene, $COCl_2 = CO + Cl_2$, is analogous to that of ethylene iodide, in that in both cases a dihalide breaks up into unsaturated and halogen molecules. Moreover, the kinetics of the reaction was shown to be represented by the equation[9]

$$dCl_2/dt = k(COCl_2)(Cl_2)^{1/2} \text{ (moles/liter/min.), in which}$$
$$\text{Log } k = -11.420/T + 15.54$$

Christiansen suggested two mechanisms, both of which involve chlorine atoms as the catalyst. Bodenstein and Plaut,[10] in their paper on the kinetics of the direct and of the reverse reactions, have estimated that at 668°K. the fraction of collisions that results in decomposition is about 4×10^{-7}.

We can go a step further and, using the ideas developed in the previous section, offer an interpretation of the energetics of the process. The "apparent heat of activation" is $4.57 \times 11{,}420 = 52{,}200$. (At the high temperatures used the effect of omitting the $^1/_2 \log T$ term in the Arrhenius equation for a bimolecular constant is small.) This is equal to the sum of the heat of formation of a gram-atom of chlorine and of the true heat of activation. Taking the former as 28,000 we arrive at the result that the heat of activation is 24,200. On the other hand, the heat of dissociation of phosgene, as calculated from equilibrium measurements, is 26,000.

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[8] Cf. R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, p. 71.

[9] J. A. Christiansen, *Z. physik. Chem.*, **103**, 99 (1922).

[10] Bodenstein and Plaut, *ibid.*, **110**, 399 (1924).

It follows that in the decomposition of phosgene, the heat of activation is also roughly equal to the heat of dissociation of the molecule, thus completing the analogy between this reaction and the one under investigation.

When we attempt to estimate Q' from the fraction of fruitful collisions, we have $4 \times 10^{-7} = e^{-Q'/RT}$, and $Q' = 19{,}600$. The agreement is not as good as in the previous calculation. Looked at from another angle, it may mean that the rate observed is about fifty times as large as the theoretical number of effective collisions, calculated with the use of the gas-kinetic formula for the number of collisions. This may be due to two causes. The mean velocity of the "hot" molecule is much larger than the average velocity assumed in the derivation of the formula. Secondly, the effective mean diameter in a "chemical" collision may be larger than that in a "physical" one.[11]

The Decomposition of Ethylene Iodide in the Presence of I^-.—The decomposition of EI_2 in aqueous alcoholic solution was found to be catalyzed by iodide ions.[12] The reaction was found to be of the first order with respect to both reactant and catalyst. The reaction constant at 25° was 0.05 (mole/liter/min.). The temperature quotient was about 2.5.

Here, again, we shall assume that the decomposition takes place after those collisions between EI_2 and I^- molecules in which the energy available is equal to or greater than the heat of activation. Here, too, the heat of activation can be obtained by two methods: from the temperature coefficient of the reaction constant and from the number of effective collisions. The values obtained are 16,800 and 16,200, respectively. While the excellent agreement is fortuitous, since the gas laws for the number of collisions were used for a solution, and the value of σ_{12}^2 was arbitrarily taken as 10^{-15}, still it is believed that the evidence obtained from this, as well as from the other two reactions, points to the fact that there are some elements of reality in the crude picture of the mechanism as proposed in the preceding pages.

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Summary

The statics and kinetics of the autocatalytic decomposition of ethylene iodide in carbon tetrachloride solutions have been investigated. A simple mechanism has been proposed, and with its aid the energetics of the

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[11] *Cf.* Hinshelwood, Ref. 6, p. 63.

[12] A. Slator, *J. Chem. Soc.*, 35, 1697 (1904).

reaction has been interpreted. (The relations are summarized in Table II.)

TABLE II

SUMMARY OF STATIC AND KINETIC RELATIONS

A. Equilibrium (experimental)

$$11{,}300 \text{ cal.} + CH_2I\text{—}CH_2I \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_2{=}CH_2 + I_2$$

$$(E)\ (I_2)/(EI_2) + K;\ \log K = -11{,}300/4.57T + \begin{cases} 4.964 \text{ equiv./kg.} \\ 4.663 \text{ moles/kg.} \end{cases}$$

B. Kinetics of the decomposition (experimental)

$$d(I_2)dt = k_1(EI_2)(I_2)^{1/2}$$

$$\text{Log } k_1 = -29{,}500/4.57T + {}^1/_2 \log T + \begin{cases} 12.642 \text{ equiv./kg./min.} \\ 12.793 \text{ moles/kg./min.} \end{cases}$$

C. Kinetics of the reverse reaction (deduced from A and B)

$$d(EI_2)/dt = k_2(E)(I_2)^{3/2}$$

$$\text{Log } k_2 = -18{,}200/4.57T + {}^1/_2 \log T + \begin{cases} 7.678 \text{ equiv./kg./min.} \\ 8.130 \text{ moles/kg./min.} \end{cases}$$

D. Values of the constants at 142°

$k_1 = 0.042$ (moles/kg./min.) $k_2 = 0.87$ $K = 0.05$

E. Proposed mechanism of reaction

The decomposition of a molecule must be preceded by its collision with a free iodine atom. Only those collisions are effective in which the energy available is equal to or greater than the heat of activation. The heat of activation cannot be smaller than, and turns out to be approximately equal to, the heat of dissociation of the molecule.

Attention has been called to two analogous reactions that can be interpreted with the aid of the same mechanism.

It has been found that, aside from the main reaction, there takes place a slow decomposition which is independent of the iodine concentration.

The decomposition of the solid iodide has been found to be catalyzed by iodine.

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