

CLXXII.—*The Decomposition of Ethylene Iodide under the Influence of the Iodide Ion.*

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WHEN crystals of iodine are exposed to an atmosphere of ethylene, ethylene iodide is slowly formed, whilst when the pure iodide is kept for some time it turns brown and crystals of iodine make their appearance. This formation and decomposition of ethylene iodide at the same temperature shows that in the gaseous phase the equilibrium point of the change represented by  $\text{C}_2\text{H}_4\text{I}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{I}_2$  is appreciably removed from both ends of the reaction. In solutions of these substances another such equilibrium is probably established. If one of the products of reaction is removed from the system, it is clear that a complete decomposition could be observed. In the present communication, the catalytic decomposition of the iodide is investigated under conditions such that the reaction is practically completed.

In the study of the reactions between this iodide and sodium thiosulphate described in a previous paper (this vol., p. 1286), it was observed that when the experiments were carried out with excess of the iodide the solutions, after all the thiosulphate had reacted, soon became brown. This liberation of iodine from the excess of

iodide was found to be due to the sodium iodide formed in the primary reaction, and further investigation showed that solutions of ethylene iodide easily decompose in the presence of certain metallic iodides. Qualitative experiments indicated that the decomposition is accelerated, not only by iodides, but also, although to a much less extent, by bromides, whilst the influence of chlorides is very slight. Nitric acid and the following salts: copper sulphate, potassium chlorate, stannous chloride, and ferrous sulphate have practically no effect on this decomposition. Bright sunlight increases the velocity of the reaction.

The influence of the iodides was so marked that quantitative experiments were made to investigate the amount of iodine liberated in the reaction. An alcoholic solution of ethylene iodide of known strength was decomposed by the addition of a strong solution of potassium iodide, and after the completion of the reaction the amount of free iodine was titrated by standard thiosulphate solution. The following table shows that practically the whole of the iodine is liberated from small quantities of ethylene iodide if the concentration of potassium iodide is greater than  $N/15$ .

TABLE I.

$C_2H_4I_2$ .	I liberated in c.c. $N/100$ solution.		Ratio. $C_2H_4I_2 : I_2$ .
	Found. c.c.	Calculated. c.c.	
Gram.			
0.0329	22.6	23.3	1 : 0.97
0.0500	34.9	35.5	1 : 0.98
0.0464	32.4	33.0	1 : 0.98
0.0343	23.9	24.3	1 : 0.98
0.0455	32.9	32.3	1 : 1.01
0.0419	29.4	29.7	1 : 0.99
0.0419	29.7	29.7	1 : 1.00
0.0440	31.4	31.2	1 : 1.01
Mean .....			1 : 0.99

With smaller concentrations of potassium iodide, the total amount of iodine is not liberated; this difference is probably due either to the potassium iodide forming tri-iodide and being removed from the system or to some secondary reaction. Other experiments were carried out to show qualitatively that ethylene is liberated in the reaction. A test-tube containing a mixture of potassium iodide and ethylene iodide was immersed in mercury to displace the air and then inverted over the liquid. About 2 c.c. of a mixture of alcohol and water were introduced into the tube, and after shaking some time a gas collected over the solution which was proved to be ethylene by its action on bromine water.

We may therefore conclude that the reaction under consideration is

the decomposition of ethylene iodide according to the equation  $C_2H_4I_2 = C_2H_4 + I_2$ . The action of the metallic iodide still remained to be investigated. From these preliminary experiments it is uncertain whether the iodide merely removes the free iodine as it is formed and hence helps the decomposition, or whether the influence is of a more profound character. Measurement of the velocity of the reaction seemed to be the simplest method of testing these possibilities, and the chief part of this paper is devoted to a description of such measurements. Titration of the free iodine, which is formed in the reaction, affords a ready means of following the change. The experiments are carried out in flasks placed in a thermostat, which is regulated at a suitable temperature. The solvent used in all these experiments is a mixture of alcohol and water (5 c.c. alcohol to 2 c.c. water). An alcoholic solution of ethylene iodide is prepared, the requisite quantity of water added, and after allowing the solution to acquire the temperature of the thermostat a weighed quantity of potassium iodide is introduced and the flask rapidly shaken so as to dissolve the solid. At suitable intervals of time, 5 c.c. of the mixture are taken out by means of a pipette and titrated with  $N/100$  sodium thiosulphate.

Measurements obtained by such means show that the velocity of decomposition is proportional to the concentration of the ethylene iodide and approximately proportional to that of the potassium iodide. Free iodine in the solution has the effect of retarding the reaction, and therefore, in calculating the constants of the reaction, only initial velocities have been considered. When strong ( $N/10$ ) solutions of potassium iodide are used, the formation of free iodine causes no appreciable disturbance in the first third of the reaction. The final titre of iodine also agrees with that calculated from the initial concentration of ethylene iodide. With more dilute ( $N/40$ ) solutions of potassium iodide, the influence of the iodine is very soon noticeable; the calculated end point of the reaction is in these cases used to obtain the values of the velocity constants.

In the following tables:— $t$  = time in minutes, (I) = iodine titre obtained by titrating 5 c.c. of solution with approximately  $N/100$  thiosulphate solution,  $(C_2H_4I_2)$  = ethylene iodide titre = difference of final iodine titre and that after time  $t$ .

The constants  $K$  are obtained from the last column of figures by the formula for a unimolecular reaction  $K = \frac{1}{t} \log C_0/C_t$  where  $C_0$  = initial value of  $(C_2H_4I_2)$  and  $C_t$  = value of time  $t$ .

In Table II,  $n$  is the order of the reaction in relation to the ethylene iodide, and is calculated by the usual formula :

$$n = \frac{\log dc_1/dt - \log dc_2/dt}{\log C_1 - \log C_2},$$

where  $dc_1/dt$ ,  $dc_2/dt$  are the velocities at concentrations  $C_1$  and  $C_2$ .

These tables show that, within the experimental limits,  $n$  is equal to 1 and is independent of the concentration of potassium iodide. The values of  $K$  are approximately proportional to the concentration of this iodide and increase to about 2.5 times their former value for a temperature rise of  $10^\circ$ .

TABLE II.

*Influence of  $C_2H_4I_2$ -concentration.*

Temperature =  $25^\circ$ .

KI-concentration = 0.100 *N*.

<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .	<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .
0	1.3*	34.1	—	0	0.55*	17.15	—
10	5.1*	30.3	0.0051	15	3.4*	14.3	0.0053
20	8.4	27.0	0.0051	30	5.75	11.95	0.0052
30	11.25	24.15	0.0050	50	8.2	9.5	0.0051
$\infty$	35.4	0	—	$\infty$	17.7	0	—

$n$  (calculated from titrations\*) = 0.95.

From other experiments:

KI-concentration 0.0961 *N*,  $n = 1.05$   
 ,, 0.0462 *N*,  $n = 1.00$

KI-concentration 0.0276 *N*,  $n = 1.10$   
 ,, 0.0250 *N*,  $n = 1.05$

TABLE III.

*Influence of KI-concentration.*

Temperature =  $25^\circ$ .

KI-concentration = 0.1302 *N*.

<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .
0	0.8	30.3	—
10	4.7	25.4	0.0060
20	8.3	22.8	0.0062
30	11.3	19.8	0.0062
$\infty$	31.1	0	—

KI-concentration = 0.0718 *N*.

<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .
0	0.5	32.7	—
10	3.4	29.8	0.0040
20	5.7	27.5	0.0038
35	9.15	24.05	0.0038
$\infty$	33.2	0	—

KI-concentration = 0.0540 *N*.

<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .
0	0.9	30.2	—
10	2.8	28.3	0.0028
25	5.7	25.4	0.0030
45	8.6	22.5	0.0028
$\infty$	31.1	0	—

KI-concentration = 0.0250 *N*.

<i>t</i> .	(I).	( $C_2H_4I_2$ ).	<i>K</i> .
0	0.4	35.0	—
20	2.7	32.7	0.00148
50	5.55	29.85	0.00138
120	10.3	25.1	0.00120
$\infty$	35.4	0	—

TABLE III (*continued*).

KI-concentration.	$K$ .	1000K/KI-concentration.
0.1302 <i>N</i>	0.0061	47
0.1043	0.0052	50
0.1000	0.0051	51
0.0961	0.0049	51
0.0718	0.0039	54
0.0540	0.0029	54
0.0276	0.00167	61
0.0250	0.00148	59

TABLE IV.

*Influence of Temperature.*

Temperature = 35°.

KI-concentration = 0.100 <i>N</i> .				KI-concentration = 0.075 <i>N</i> .			
<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	$K$ .	<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	$K$ .
0	1.3	27.0	—	0	2.9	30.9	—
5	5.05	23.25	0.0130	5	6.4	27.4	0.0104
15	10.9	17.4	0.0127	15	11.85	21.95	0.0099
25	15.2	13.1	0.0126	25	15.9	17.9	0.0095
∞	28.3	0	—	∞	33.8	0	—
$\frac{K_{35}}{K_{25}} = 0.0127.$				$K_{35} = 0.0104.$			
$K_{25} = 0.0051.$				$K_{25} = 0.0041.$			
Temperature quotient = 2.5.				Temperature quotient = 2.55.			

We may conclude from these measurements that the accelerative influence of potassium iodide is not merely due to the removal of free iodine from the solution, for if such were the case the initial velocities would (within certain limits) be independent of the concentration of this salt. The velocity constants are approximately proportional to the concentration of the potassium iodide, showing that the salt takes either a direct or a catalytic part in the reaction.

The value  $\frac{K}{\text{KI-concentration}}$  (Table III) shows a slight increase with increasing dilution, suggesting that the I<sup>-</sup> ion is the important factor in determining the velocity of reaction. This observation is confirmed by other measurements; it is found that sodium and ammonium iodides, which are dissociated to about the same extent as potassium iodide, have approximately the same accelerative influence in equivalent solutions, whereas salts such as cadmium iodide, which are known to be less dissociated, are much less active, and the addition of such substances as iodine and mercury iodide, which form complexes with the I<sup>-</sup> ion, greatly decreases the activity of potassium iodide.

TABLE V.—Temperature = 25°.

NaI-concentration = 0.100 <i>N</i> .				NH <sub>4</sub> I-concentration = 0.100 <i>N</i> .			
<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	<i>K</i> .	<i>t</i> .	(I).	(C <sub>2</sub> H <sub>4</sub> I <sub>2</sub> ).	<i>K</i> .
0	0.75	28.55	—	0	1.7	29.4	—
10	3.95	25.35	0.00515	10	4.9	26.2	0.0050
20	6.7	22.6	0.0051	20	7.8	23.3	0.0050
30	9.1	20.2	0.0050	35	11.2	19.9	0.0048
∞	29.3	0	—	∞	31.1	0	—

KI-concentration = 0.100 *N*. . . . . *K* = 0.0051 (Table II).

TABLE VI.

Catalyser.	$\Delta c/\Delta t$ .	Catalyser.	$\Delta c/\Delta t$ .
0.100 KI .....	0.32	0.072 KI + 0.071 I .....	0.14
0.100 NH <sub>4</sub> I .....	0.32	0.036 KI + 0.059 I .....	0.032
0.100 KI + 0.100 HCl .....	0.25	0.036 KI + 0.162 I .....	0.018
0.100 CdI <sub>2</sub> /2 .....	0.011	0.100 NaBr .....	0.006
0.100 K <sub>2</sub> HgI <sub>4</sub> /2 .....	0.012	Without catalyser .....	< 0.0001
0.072 KI .....	0.25		

The initial velocities of reaction ( $\Delta c/\Delta t$ , Table VI) show a great variation with different catalysers. Thus, cadmium iodide and mercuric potassium iodide have only about 1/30th of the activity of potassium or ammonium iodide. Hydrogen iodide has less influence than potassium iodide, for the addition of hydrochloric acid to potassium iodide lowers the velocity by about 20 per cent. Addition of iodine to potassium iodide in the proportion I : KI decreases the activity of the iodide by nearly one-half, a further addition has less effect, and a mixture in the proportion I<sub>2</sub> : KI still has an accelerative action. Bromides have about 1/50th of the activity of iodides.

The results obtained from the foregoing experiments may be summarised by the equation  $dI/dt = K \cdot C_{C_2H_4I_2} \cdot C_{I'}$ , that is, the rate of formation of free iodine is proportional to the concentration of the ethylene iodide and the I'-ion. More than one reaction can be constructed which agrees with this result; thus the change measured under these conditions may be a direct action of the I'-ion on the organic iodide according to the equation  $C_2H_4I_2 + I' = C_2H_4 + I'_3$ . The direct formation of the I'<sub>3</sub>-ion is, however, not very probable. The I'-ion may be considered to be a catalytic agent which accelerates the decomposition of the organic iodide, and, until further evidence is brought forward to explain the mechanism of the reaction, it is perhaps the most convenient view to adopt.

In a previous communication (this vol., pp. 1297) it has been shown that sodium thiosulphate has a direct action on ethylene iodide, and that the action is bimolecular. The change which is here measured is probably  $C_2H_4I_2 + Na_2S_2O_3 \rightarrow C_2H_4I \cdot NaS_2O_3 + NaI$ , and is followed

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by a rapid reaction between the iodo-ester and another equivalent of sodium thiosulphate.\*

Experiments were carried out to investigate whether this reaction is in any way connected with the decomposition of ethylene iodide by the action of potassium iodide. If sodium thiosulphate, potassium iodide, and ethylene iodide are brought together in solution, we should expect the thiosulphate to be used up partly by acting directly on the organic iodide and partly by interaction with the liberated iodine. If the two reactions have no influence on each other, the rate of disappearance of thiosulphate would be determined by the sum of the velocities of the two single reactions. If, however, interference took place, this agreement would not be observed.

Experiments carried out to detect any such influence show that the observed rate and that calculated from the velocity of the single reactions agree approximately, and we may therefore assume that the reactions are distinct from one another and may be superimposed without appreciable interference.

A solution containing the three reagents was prepared, taking care to have excess of ethylene iodide. The time which elapsed from the mixing of the solutions to the appearance of free iodine was measured and compared with the value calculated from the known velocity of the single reactions.

Assuming no interference of the reactions, the rate at which thiosulphate disappears is given by the following equation :

$$-dx/dt = K_1 \cdot x(x+a) + K_2 \cdot (x+a) \quad \dots \quad (1)$$

where

$x$  and  $x+a$  represent the concentrations of thiosulphate and ethylene iodide respectively, and  $K_1$  and  $K_2$  = velocity constants of the two single reactions.

Integration of equation (1) gives

$$0.4343 K_1(a - K_2/K_1)t = \log \frac{x+a}{x + K_2/K_1} + \text{constant}.$$

If  $x = x_0$  when  $t = 0$

$$\text{the constant} = -\log \frac{x_0 + a}{x_0 + K_2/K_1}.$$

Substituting and calculating the time for  $x = 0$ , we get

$$t = \frac{\log \frac{aK_1(x_0 + K_2/K_1)}{K_2 \cdot (x_0 + a)}}{0.4343 K_1(a - K_2/K_1)} \quad \dots \quad (2)$$

\* Some ethylene is liberated in this reaction and also in the reaction between ethylene bromiodide and sodium thiosulphate. The product in these two reactions is, therefore, not wholly sodium ethylene thiosulphate.

If, therefore, ethylene iodide is in excess, the time when free iodine will appear is given by formula (2), where  $x_0$  and  $x_0 + a$  represent the initial concentrations of thiosulphate and ethylene iodide respectively, and where  $a$  = excess of ethylene iodide, expressed in gram-equivalents per litre.

The measurements were carried out by mixing 5 c.c. of an alcoholic ethylene iodide solution with 2 c.c. of an aqueous solution of sodium thiosulphate and potassium iodide. The temperature of the two solutions was so arranged that, on mixing, the aqueous alcoholic solution was about 25°. The tube containing the mixture was vigorously shaken in the water of the thermostat to bring the contents exactly to 25°.

The solution was allowed to remain in the thermostat and watched until the faint yellow colour of free iodine made its appearance. It may be noted that starch is useless as an indicator in these aqueous alcoholic solutions. The yellow coloration is, however, distinct enough to give consistent results, as is shown by the following table:

TABLE VII.

Temperature = 25°. KI-concentration = 0.100 *N*.

$$0.4343 K_1 = 0.99 \quad (\text{Table XII, p. 1298}).$$

$$0.4343 K_2 = 0.0051 \quad ( \quad , \quad \text{II, p. 1700}).$$

$x_0$ .	$x_0 + a$ .	$a$ .	$t$ .	
			Calculated.*	Observed.
0.0103	0.0419	0.0316	13.7 mins.	15.7, 15.7, 15.5 mins.
0.0106	0.0210	0.0104	34.5 "	40.9, 40.6 "
0.0105	0.0251	0.0146	26.4 "	31.3, 31.3, 31.1 "

KI-concentration = 0.050 *N*.

$$0.4343 K_1 = 0.99.$$

$$0.4343 K_2 = 0.00270.$$

$x_0$ .	$x_0 + a$ .	$a$ .	$t$ .	
			Calculated.*	Observed.
0.0100	0.0484	0.0384	16.1 mins.	17.2, 17.3 mins.
0.0100	0.0242	0.0142	38.6 "	40.7, 40.8 "

The above table shows that with a *N*/10 solution of potassium iodide the calculated values of the time are about 16 per cent. lower than the observed values, whilst with a *N*/20 solution the difference is about 6 per cent. The approximate agreement shows that the reactions have

\* In this calculation the accelerating influence of the sodium iodide which is formed in the reaction has not been considered. This correction would make the calculated values about 3 per cent. smaller.



no great influence on each other, and the difference may be explained if we assume that the ions ( $S_2O_3^{''}, I'$ ) interact and the ionic concentrations are decreased by the addition of other salts.\*

It is a well-known fact that solutions of alkyl iodides if kept some time become brown owing to the liberation of iodine. The rate of the reaction depends on the constitution of the compound and is specially marked among the lower members of the series (K. A. Burke and F. G. Donnan, this vol., p. 574). Experiments were made to test whether these reactions were accelerated by potassium iodide. Test-tubes containing aqueous alcoholic solutions of the organic iodides and potassium iodide were kept and the coloration compared with that observed when no potassium iodide is added. The results obtained from experiments with methyl iodide, *isopropyl* iodide, and ethyl iodoacetate show a very appreciable acceleration, due to the presence of potassium iodide. These reactions are probably oxidations, for on excluding air from the mixture only faint yellow colorations could be obtained. It is possible that these reactions are in some way analogous to that of the decomposition of ethylene iodide, for both are accelerated by the addition of potassium iodide.

Iodine compounds in which two iodine atoms are united to adjacent carbon atoms show a special tendency to decompose, forming the olefinic compound and liberating free iodine. This is noticeable, not only in the case of ethylene iodide, but is evident in certain other reactions. Organic iodides are often prepared by the action of metallic iodides on the corresponding organic bromide or chloride. In these preparations, some free iodine is invariably liberated, especially in the presence of moisture. With the dihalogen compounds, this secondary reaction takes place to such an extent that the product is often entirely an ethylene compound and free iodine, thus  $\alpha\beta$ -dibromopropionic acid on treatment with potassium iodide gives acrylic acid, and not the di-iodide. These reactions are evidently closely related to the decomposition of organic iodides under the influence of metallic iodides, and the question arises whether, in these preparations, the di-iodide is first formed and then decomposed by a further action of potassium iodide, or whether the decomposition takes place without the intermediate formation of the di-iodide.

Ethylene bromiodide decomposes in presence of potassium iodide according to the equation  $C_2H_4BrI + KI = C_2H_4 + KBr + I_2$ , and this reaction was investigated with the view of determining whether ethylene iodide is an intermediate product or not. Measurements of the velocity of the reaction were carried out in a similar manner to

\* The velocity of reaction between methyl iodide and sodium thiosulphate is lowered about 10 per cent. by the addition of potassium iodide to form a  $N/10$  solution (this vol., p. 1293).

that described in the case of ethylene iodide, and, as the following tables show, analogous results were obtained. The velocity is proportional to the bromiodide concentration and approximately to that of the potassium iodide. The temperature quotient is 2.45 for a rise of 10°. The rate of decomposition is about one-third of that of the ethylene iodide.

TABLE VIII.

I liberated in c.c. *N*/100 solution.

Grams $C_2H_4BrI$ .	I liberated in c.c. <i>N</i> /100 solution.		Ratio. $C_2H_4BrI : I_2$ .
	Found.	Calculated.	
0.0251	21.0	21.4	1 : 0.98
0.0651	55.7	55.4	1 : 1.01

TABLE IX.

*The Influence of the Bromiodide Concentration.*Temperature = 25°. KI-concentration = 0.1000 *N*.

<i>t</i> .	(I).	( $C_2H_4BrI$ ).	<i>K</i> .	<i>t</i> .	(I).	( $C_2H_4BrI$ ).	<i>K</i> .
0	0.4*	20.3	—	0	0.2*	54.7	—
20	1.9	18.8	0.00167	15	3.2*	51.7	0.00163
49	3.8*	16.9	0.00162	40	7.3	47.6	0.00153
110	6.95	13.75	0.00154	60	10.1	44.8	0.00145
∞	20.7	0	—	∞	54.9	0.	—

*n* (calculated from titrations\*) = 1.00.

TABLE X.

*The Influence of Potassium Iodide Concentration.*

Temperature = 35°.

KI-concentration = 0.050 <i>N</i> .				KI-concentration = 0.100 <i>N</i> .			
<i>t</i> .	(I).	( $C_2H_4BrI$ ).	<i>K</i> .	<i>t</i> .	(I).	( $C_2H_4BrI$ ).	<i>K</i> .
0	0.15	20.55	—	0	0.4	20.3	—
30	3.0	17.7	0.00216	10	2.2	18.5	0.0041
60	5.0	15.7	0.00195	27	4.95	15.75	0.0041
125	8.65	12.05	0.00186	50	7.75	12.95	0.0039
∞	20.7	0	—	∞	20.7	0	—

KI-concentration = 0.150 *N*.

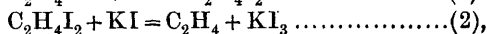
<i>t</i> .	(I).	( $C_2H_4BrI$ ).	<i>K</i> .
0	0.4	20.3	—
25	6.25	14.45	0.0059
40	8.65	12.05	0.0057
∞	20.7	0	—

KI-concentration.		<i>K</i> .	1000 <i>K</i> /KI-concentration.
0.050 <i>N</i>		0.00216	43
0.100		0.0041	41
0.150		0.0059	39

Temperature quotient = 2.45.

These results may be used for determining whether ethylene iodide

is an intermediate product of the reaction or not. If we assume that the reaction goes through the steps,



we have the following possibilities.

Reaction (1) may proceed much faster than (2) and the velocity measured would then be that of reaction (2). This is not the case, for reaction (2) proceeds with about three times the velocity measured in these experiments. Neither can we assume that the velocity of reaction (1) is incomparably smaller than that of (2), for then the measured velocity would be that of reaction (1) and the ratio of the two velocities would be 1 : 3. The only other possibility is that the two velocities are comparable and that the reactions are superimposed. If this were the case, the initial velocity of liberation of iodine would be zero. The rate would increase to a maximum and then decrease. Increase in the concentration of potassium iodide would probably increase the velocity of both reactions, and the rate of liberation of iodine would be proportional to the concentration of potassium iodide raised to a higher power than one.

Experimental evidence gives no indication of these results, and we may therefore assume that ethylene iodide is probably not an intermediate compound in the reaction. This result shows that it is possible for potassium iodide to have a direct action on organic chlorides and bromides, liberating iodine without the intermediate formation of the organic iodide.

### *Summary of Results.*

1. Ethylene iodide in aqueous alcoholic solution decomposes quantitatively in the presence of potassium iodide, yielding ethylene and iodine.

2. The velocity of reaction is proportional to the concentration of ethylene iodide and that of the I<sup>-</sup>-ion, showing that the potassium iodide takes some direct (or catalytic) part in the reaction. The temperature for 10° is 2.5.

3. This reaction is quite distinct from that between ethylene iodide and sodium thiosulphate, for on carrying out the two reactions in the same solution the rate of disappearance of the thiosulphate is approximately equal to that calculated from the velocity of the two single reactions.

4. The rate of liberation of iodine from solutions of methyl iodide, isopropyl iodide, and ethyl iodoacetate is accelerated by the addition of potassium iodide.

5. Ethylene bromiodide in presence of potassium iodide liberates iodine according to the equation:  $C_2H_4IBr + KI = C_2H_4 + I_2 + KBr$ .

6. The velocity of the preceding reaction is proportional to the concentration of the bromiodide and to that of the potassium iodide, and the temperature quotient for  $10^{\circ}$  is 2.45. Ethylene iodide is probably not an intermediate product in this reaction. The iodide decomposes about three times as fast as the bromiodide.

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