THE KINETICS OF THE IODINE-OXALATE REACTION.

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In recent papers we have shown that the thermal oxidation of oxalates by bromine[1] and by chlorine[2] follows the kinetic law :

$$\text{rate} \propto \frac{1}{[\mathrm{X}^-]\{K_3 + [\mathrm{X}^-]\}} \cdot \frac{[\mathrm{HC_2O_4}^-]}{[\mathrm{H}^+]} \cdot [\Sigma\mathrm{X}_2],$$

where X is the halogen, $[\Sigma X_2]$ is the concentration of titratable halogen, and $K_3 = [X_2][X^-]/[X_3^-]$. From this it was inferred that the rate-determining process is a reaction between the hypohalous acid HOX formed by hydrolysis of the halogen and the $HC_2O_4^-$ ion. It seemed to be of interest to investigate whether the thermal reaction between iodine and oxalates has the same mechanism. Since the published data on this reaction are somewhat scanty, we have therefore carried out a series of fresh measurements, the results of which are now communicated.

The oxidation of oxalates by iodine has previously been studied by Dhar[3] and by Berthoud and Bellenot.[4] The latter workers found the rate to be proportional to the concentration of titratable iodine and to the concentration of oxalate, but inversely proportional to the concentration of potassium iodide. Further, the reaction has a very high temperature coefficient : Berthoud and Bellenot give $k_{t+10}/k_t = 4{\cdot}36$ between 66° and 78°, in agreement with Dhar's values of 5·4 between

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[1] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **28**, 107, 1932.

[2] Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518, 616, 1932.

[3] Dhar, *J.C.S.*, **111**, 690, 1917.

[4] Berthoud and Bellenot, *J. Chim. phys.*, **21**, 308, 1924.

50° and 60°, 6·1 between 40° and 50°, and 7·2 between 25° and 40°. However, more recent observations of Berthoud[5] do not appear to have confirmed the original conclusions of Berthoud and Bellenot; the velocity is now stated to be approximately proportional to the concentration of oxalate and to the *square root* of the concentration of iodine. From this it is inferred that this thermal reaction has the same mechanism as the corresponding photochemical reaction, that is, a mechanism involving iodine atoms. Berthoud's experimental data, from which this conclusion is drawn, have not yet been published, so that it is not possible to judge how far his results are in accord with ours.

The data which we ourselves have obtained lead us to the view that the thermal oxidation is one in which *two* quite independent reactions are simultaneously operative. These two processes are:—

(*a*) a reaction between iodine atoms and oxalate ions, as already found by Berthoud;

(*b*) a reaction between HOI and $HC_2O_4^-$ ions, analogous to the chlorine and bromine-oxalate cases already studied. These follow from the kinetic equation which is found to fit the experimental results:—

$$\frac{dx}{dt} = k_{1/2} \cdot [C_2O_4^{--}] \sqrt{\frac{\Sigma I_2}{K_3 + [I^-]}} + k_1[C_2O_4^{--}] \cdot \frac{\Sigma I_2}{[I^-]\{K_3 + [I^-]\}}$$

$$= [C_2O_4^{--}]\left\{k_{1/2}\frac{\sqrt{\Sigma I_2}}{\sqrt{K_3 + [I^-]}} + k_1 \frac{\Sigma I_2}{[I^-]\{K_3 + [I^-]\}}\right\},$$

where $k_{1/2}$ is a semi-molecular constant, k_1 a unimolecular constant, ΣI_2 is the concentration of titratable iodine, and K_3 is the equilibrium constant of tri-iodide formation. Though it has not been possible to integrate this equation for the chosen experimental conditions, a satisfactory demonstration that the reaction does obey a kinetic law of this complex character has, we consider, been effected.

Experimental.

The oxalates, iodine and potassium iodide used were A.R. preparations. Conveniently measured rates of reaction are obtained in the temperature range 40° to 60° C., and since oxalate solutions slowly attack glass at these temperatures, the experiments were carried out in stoppered quartz flasks of about 300 c.c. capacity. Special precautions were taken to exclude all light from the reacting system. The change with time of titratable iodine was followed by running samples of the reaction mixture into excess of a standard sodium arsenite solution and back titrating with standard iodine. In all experiments the concentration of the oxalate ($M/12 - M/6$) was so much greater than that of the iodine ($M/100 - M/1500$) that it could be regarded as constant throughout the course of reaction. The initial concentration of potassium iodide was varied between $M/5$ and $M/1000$. All concentrations are given in gram-molecules per litre at 15° C.

Reaction Kinetics and Experimental Results.

The experimental data may conveniently be divided into two categories: (*a*) experiments in which the semimolecular reaction predominates; (*b*) experiments in which the semimolecular and the

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[5] Berthoud, *Trans. Faraday Soc.*, **27**, 527, 1931 (General Discussion on "Photochemical Processes"; Liverpool, April, 1931).

unimolecular reactions contribute comparable amounts to the whole. Examination of the complete kinetic equation given above shows that the favourable condition for predominance of the semimolecular process is a high concentration of the iodide ion. Actually we find that in a solution of $\frac{M}{10}\text{KI} + \frac{M}{100}\text{I}_2$ or $\frac{M}{20}\text{KI} + \frac{M}{250}\text{I}_2$ the unimolecular process is almost completely suppressed. The so isolated semimolecular component may now be examined from the standpoint of its dependence upon the concentrations of oxalate, iodine, and potassium iodide. First, the order of reaction with respect to iodine has been tested by comparing two experiments with the same (high) concentrations of oxalate and of potassium iodide but different initial concentrations of iodine. The results of several comparisons of this character are summarised under expts. 1, 1*a* to 5, 5*a* in Table I. The k_{semi}'s of the fifth column are calculated from the integrated form of the simple semimolecular equation

$$-\frac{d(a-x)}{dt} = k_{\text{semi}}(a-x)^{1/2},$$

viz.

$$k_{\text{semi}} = \frac{2}{t}\{a^{1/2} - (a-x)^{1/2}\}.$$

The k_{uni}'s of the sixth column are derived from

$$k_{\text{uni}} = \frac{1}{t}\log_e\frac{a}{a-x},$$

where a and $a - x$ represent the concentrations of titratable iodine initially and at time t (min.).

TABLE I.

Expt. No.	Temp.	[Oxalate].	[KI].	$[\Sigma I_2]_{\text{init.}}$	$k_{\text{semi}} \times 10^6$.	$k_{\text{uni}} \times 10^6$.	$k_{1/2} \times 10^6$.
1	60°	$M/6$ $K_2C_2O_4$	$M/10$	$M/200$	165	254	312
1*a*				$M/1000$	162	658	311
2	55°	$M/6$ $K_2C_2O_4$	$M/10$	$M/200$	70·8	104	133
2*a*				$M/1000$	73·2	243	140
3	55°	$M/6$ $Na_2C_2O_4$	$M/10$	$M/100$	65·7	69·6	121
3*a*				$M/400$	64·7	141	123
4	45°	$M/6$ $Na_2C_2O_4$	$M/10$	$M/100$	11·1	12·2	20·7
4*a*				$M/400$	10·6	23·4	20·1
5	45°	$M/6$ $Na_2C_2O_4$	$M/20$	$M/250$	15·7	26·9	21·0
5*a*				$M/1000$	14·8	55·0	20·1
6	45°	$M/12$ $Na_2C_2O_4$	$M/10$	$M/400$	5·74	—	21·8
7	45°	$M/6$ $Na_2C_2O_4$	$M/5$	$M/400$	7·64	—	20·6
8	50°	$M/6$ $Na_2C_2O_4$	$M/10$	$M/400$	26·8	—	50·8
9	40°	$M/6$ $Na_2C_2O_4$	$M/10$	$M/400$	4·25	—	8·1

In each pair of experiments the time interval from the start was the same, so that obedience to the unimolecular law would have entailed the same fractional loss of iodine for the two different initial concentrations of iodine. This, however, was very far from being the case, as is shown by the very decided differences in the k_{uni}'s for each pair. On the other hand, the k_{semi}'s for four and five-fold changes in $[\Sigma I_2]_{\text{init.}}$ are in very fair accord with one another, leaving no room for doubt as to the semimolecular nature of the process involved.

Experiments 4*a* and 6 show the effect of doubling the concentration of oxalate upon the rate of this semimolecular process. The first k_{semi} is practically twice the other, so that we may assume the order of reaction with respect to oxalate to be unity. Actually, the ionic strengths of these solutions are rather high, and the value of the " constant " when allowance is made for the change in the concentration of oxalate may still be a function of the ionic strength of the reaction mixture. That specific ionic strength effects are present is suggested by a comparison of experiments 2, 2*a* and 3, 3*a*. The k_{semi} with potassium oxalate is distinctly higher than that with sodium oxalate at the same concentration. To avoid difficulties due to such effects, we have used sodium oxalate alone at a constant initial concentration of $M/6$ in all subsequent experiments.

Finally, experiments 4, 4*a*, 5, 5*a* and 7 are designed to illustrate the dependence of k_{semi} upon the iodide content. It will be seen that a four-fold increase in the concentration of potassium iodide (from $M/20$ to $M/5$) has practically halved the rate of reaction. This naturally suggests a kinetic equation with the rate of the semimolecular process inversely proportional to the square root of iodide concentration, or perhaps to the square root of iodide concentration plus a constant, the latter small compared with the concentrations of iodide used in these test experiments. For reasons which will appear later, the kinetic equation which we favour is :

$$\frac{dx}{dt} = k_{1/2} \cdot [\mathrm{C_2O_4}^{--}] \cdot \frac{\sqrt{\Sigma \mathrm{I_2}}}{\sqrt{K_3 + [\mathrm{I}^-]}}$$

and the $k_{1/2}$'s of the last column of Table I are computed on this basis. The values of K_3 used in the calculations are 1·75, 1·88, 2·02, 2·16 and $2{\cdot}30 \times 10^{-3}$ at 40°, 45°, 50°, 55° and 60°, these being based on the mean value $K_3 = 1{\cdot}39 \times 10^{-3}$ at 25° of a large number of workers and Fedotieff's value[6] of $1{\cdot}75 \times 10^{-3}$ at 40° C.

Turning now to experiments with low concentrations of potassium iodide ($M/160$ and less), examination of the data at once showed that the kinetic law which holds for high concentrations now breaks down. This showed itself in various ways. For example, the initial $k_{1/2}$ is considerably greater than the values given above ; in a reaction mixture with $M/6$ $\mathrm{Na_2C_2O_4}$ + $M/160$ KI + $M/1000$ $\mathrm{I_2}$ at 45° C. the initial $k_{1/2}$ is practically double the value of $20{\cdot}7 \times 10^{-6}$ which should obtain according to Table I. This disparity increases with diminishing concentration of potassium iodide, so that with $M/1000$ KI and other conditions as before, the initial $k_{1/2}$ is between three and four times the true value. Furthermore, in each experiment with a low concentration of potassium iodide $k_{1/2}$ falls with time, that is, with decreasing concentration of iodine and increasing concentration of iodide ion. These facts suggest that another simultaneous mode of reaction between iodine and oxalate, which is more strongly retarded by I^- ion and is therefore practically completely inhibited at high concentrations of iodide, is now contributing an appreciable amount to the measured rate of reaction. The process which naturally suggested itself to us in this connection is an oxidation of oxalate by iodine following a mechanism analogous to that already demonstrated in the cases of chlorine and bromine, *viz.* reaction between HOI and the $\mathrm{HC_2O_4}^-$ ion. The rate of this reaction is proportional

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[6] Fedotieff, *Z. anorg. Chem.*, **69**, 91, 1911.

to $[C_2O_4^{--}]$ and to ΣI_2, but the retardation by I^- ion is proportional to the product $[I^-]\{K_3 + [I^-]\}$. The whole reaction as measured should then follow the kinetic law :

$$\frac{dx}{dt} = [C_2O_4^{--}]\left\{k_{1/2}\frac{\sqrt{\Sigma I_2}}{\sqrt{K_3 + [I^-]}} + k_1\frac{\Sigma I_2}{[I^-]\{K_3 + [I^-]\}}\right\}.$$

We have tested this equation by means of our experimental data, and, as already stated, find that it is in satisfactory agreement.

With low iodide concentrations, the value of $[I^-]$ increases considerably with time in each experiment, and, though $[I^-]$ is approximately a linear function of x, the above equation assumes a non-integrable form. We have therefore had to employ the method of finite differences, with the kinetic equation written in the form :

$$-\frac{\Delta(\Sigma I_2)}{\Delta t} = \frac{\Delta x}{\Delta t} = [C_2O_4^{--}]\,.\left\{k_{1/2}\frac{\sqrt{\Sigma I_2(m)}}{\sqrt{K_3 + [I^-](m)}} + k_1\frac{\Sigma I_2(m)}{[I^-](m)\{K_3 + [I^-](m)\}}\right\}.$$

Here, Δx = moles per litre of iodine transformed in the time interval Δt(min.), and $\Sigma I_2(m)$ and $[I^-](m)$ are the mean concentrations of titratable iodine and of free iodide ion in the time interval. The concentrations of free iodide ion at various stages of an experiment are obtained from the relation (*cf.* ref. (1), p. 111) :

$$[I^-]_t = \tfrac{1}{2}\{c - a - K_3 + 3x + \sqrt{(c - a - K_3 + 3x)^2 + 4K_3(c + 2x)}\},$$

in which c = initial concentration of total iodide, $a = \Sigma I_2$ (initial), and $a - x = \Sigma I_2$ at time t. The method of procedure then followed may be illustrated by considering two typical experiments (Tables II and III).

TABLE II.

$\frac{M}{6}\,Na_2C_2O_4 + \frac{M}{320}\,KI + \frac{M}{750}$ (approx.) I_2. Temp. = 50° C.

ΣI_2. × 10⁴.	$[I^-]$ × 10³.	Δt.	$\Sigma I_{2(m)}$ × 10⁴.	$[I^-](m)$ × 10³.	$\Delta(\Sigma I_2)$(tot.) × 10⁴.	$\Delta(\Sigma I_2)$(semi) × 10⁴.	$\Delta(\Sigma I_2)$(uni) × 10⁴.	k_1 × 10⁸.
12·19	2·585							
		19·95	11·22	2·812	1·940	0·810	1·130	41·3
10·25	3·040							
		26·25	9·294	3·274	1·911	0·927	0·984	42·2
8·339	3·508							
		36·95	7·389	3·748	1·900	1·115	0·785	37·6
6·439	3·989							
		46·35	5·531	4·224	1·815	1·164	0·651	40·5
4·624	4·460							
		67·53	3·709	4·703	1·830	1·338	0·492	37·5
2·794	4·946							

Mean value of $k_1 \times 10^8 = 39{\cdot}8$

The $\Delta(\Sigma I_2)_{(tot.)}$ of the sixth column of these tables corresponding to the time interval Δt requires to be apportioned between the semimolecular process and the simultaneous unimolecular process. In computing the semimolecular contribution $\Delta(\Sigma I_2)_{(semi)}$ for each time interval, the value of $k_{1/2}$ in the relation

$$\Delta(\Sigma I_2)_{(semi)} = k_{1/2}[C_2O_4^{--}]\,.\,\frac{\sqrt{\Sigma I_2(m)}}{\sqrt{K_3 + [I^-](m)}}\,.\,\Delta t$$

TABLE III.

$\frac{M}{6}$ $Na_2C_2O_4$ + $\frac{M}{1000}$ KI + $\frac{M}{1200}$ (approx.) I_2. Temp. = 40° C.

ΣI_2 × 10⁴.	$[I^-]$ × 10³.	Δt.	$\Sigma I_{2(m)}$ × 10⁴.	$[I^-]_{(m)}$ × 10³.	$\Delta(\Sigma I_2)_{(tot.)}$ × 10⁴.	$\Delta(\Sigma I_2)_{(semi)}$ × 10⁴.	$\Delta(\Sigma I_2)_{(uni)}$ × 10⁴.	k_1 × 10⁸.
8·119	0·811							
		51·97	7·400	0·954	1·437	0·3643	1·0727	4·32
6·682	1·098							
		66·88	6·092	1·227	1·179	0·4053	0·7737	4·18
5·503	1·357							
		92·20	4·934	1·483	1·138	0·4827	0·6553	4·15
4·365	1·610							
		141·25	3·751	1·756	1·227	0·6190	0·6080	4·24
3·138	1·902							

Mean value of $k_1 \times 10^8 = 4·22$

is the value obtained in the experiments with high iodide concentrations and given in Table I, *viz.* $8·1 \times 10^{-6}$ and $50·8 \times 10^{-6}$ at 40° and 50° respectively. Subtracting the figures of column (7) from those of column (6) gives the values $\Delta(\Sigma I_2)_{(uni)}$ of column (8), from which the unimolecular constant k_1 is then calculated by means of the equation

$$k_1 = \frac{\Delta(\Sigma I_2)_{(uni)}}{\Delta t} \cdot \frac{1}{[C_2O_4^{--}]} \cdot \frac{[I^-](m)\,\{K_3 + [I^-](m)\}}{(\Sigma I_2)(m)}.$$

It will be seen that, having regard for the mode of calculation, k_1 is reasonably constant in each experiment. The postulated mechanism is, however, further substantiated by the results of Table IV, which summarises all our kinetic measurements with low concentrations of iodide. Calculated by the method described above, each value of k_1 in this Table is the mean of the four or five values resulting from each experiment. It will be observed that at each temperature the same value of k_1 is obtained from experiments with different initial concentrations of the retarding iodide ion, which involves considerable variations in the ratio $\Delta(\Sigma I_2)_{(semi)}/\Delta(\Sigma I_2)_{(uni)}$.

TABLE IV.

$Na_2C_2O_4 = \frac{M}{6}$; $(\Sigma I_2)_{init.} = \frac{M}{500} - \frac{M}{1500}$.

Temp. = 40°. $k_{1/2} = 8·1 \times 10^{-6}$.		Temp. = 45°. $k_{1/2} = 20·7 \times 10^{-6}$.		Temp. = 50°. $k_{1/2} = 50·8 \times 10^{-6}$.	
[KI]init.	$k_1 \times 10^8$	[KI]init.	$k_1 \times 10^8$	[KI]init.	$k_1 \times 10^8$
$M/1000$	4·22	$M/1000$	13·7	—	—
$M/640$	4·28	$M/640$	14·0	$M/640$	40·9
$M/320$	4·26	$M/320$	13·5	$M/320$	39·8
—	—	$M/160$	14·1	$M/160$	39·1

The constancy of k_1 at each temperature supports strongly not only the kinetic equation adopted for the unimolecular part of the reaction, but also that which we have used to represent the semimolecular fraction.

It will be recalled that at the high iodide concentrations necessary to isolate the semimolecular process, it is impossible to distinguish between an iodide retardation proportional to $\sqrt{[I^-]}$ and one proportional to $\sqrt{K_3 + [I^-]}$. Now, however, if the rate of the semimolecular process is assumed inversely proportional to $\sqrt{[I^-]}$, the resulting k_1 in the experiments of Table IV is constant neither within each experiment nor from experiment to experiment. Certainly, an additive constant of the order of magnitude of K_3 seems to be required under the square root in the denominator, and since, further, a semimolecular reaction with a velocity inversely proportional to $\sqrt{K_3 + [I^-]}$ is capable of a simple theoretical interpretation, we may regard this form of iodide retardation to be as satisfactorily established as circumstances permit.

Discussion.

Accepting our interpretation of the experimental data, the thermal reaction between $Na_2C_2O_4$ and I_2 at temperatures between 40° and 60° occurs simultaneously by two entirely different processes, one semimolecular and the other unimolecular with respect to iodine, both retarded by iodide ions, the unimolecular process, however, more strongly. In the above temperature interval, with concentrations of iodine of the order of $M/1000$, and with iodide concentrations in the range $M/160$ to $M/1000$, both reactions occur with speeds of the same order of magnitude.

Discussing first the unimolecular process, whose rate, as already stated, is determined by the reaction

$$HOI + HC_2O_4^- \rightarrow 2CO_2 + H_2O + I^-,$$

it has been shown (*cf.* Refs. (1) and (2)), that the observed unimolecular constant k_1 is equal to the function kKK_3/K_2, where k is the bimolecular velocity constant of the rate-determining reaction, K is the hydrolytic constant of iodine ($K = [HOI][H^+][I^-]/[I_2]$), K_3 is the equilibrium constant of tri-iodide formation ($K_3 = [I_2][I^-]/[I_3^-]$), and K_2 is the second ionisation constant of oxalic acid ($K_2 = [H^+][C_2O_4^{--}]/[HC_2O_4^-]$).

The temperature coefficient of k_1 is an extraordinarily high one. From Table IV it is seen to amount to 9·4 between 40° and 50°, which corresponds to a critical increment (E) of 45,100 calories. To obtain the critical increment of the rate-determining reaction, we must subtract from this value 2850 cal. for the variation of K_3, about 1000 cal. for the variation of K_2 (*cf.* Ref. (1), p. 122), and 22,700 cal. for the variation of the hydrolytic constant K with temperature. (The last of these values is derived from the figures $K = 3 \times 10^{-13}$ at 25° C.[7] and $K = 9 \times 10^{-15}$ at 0° C.[8]). We thus arrive at the value $E = 18{,}550$ cal. as the critical increment of the reaction between HOI and $HC_2O_4^-$, which corresponds to a temperature coefficient of 3·08 between 10° and 20°, and of 2·51 between 40° and 50°. The reaction has thus a somewhat higher critical increment than those of the corresponding reactions of HOCl and HOBr, for both of which $E = 15{,}000$ cal.

The absolute value of k is also easily calculated. We have, for example at 45°, $k_1 = 13·8 \times 10^{-8}$. This refers to a solution of $M/6$ $Na_2C_2O_4$, for which the ionic strength (μ) is 0·5. We estimate that under these conditions $K_2 = 1·75 \times 10^{-4}$ and $K_3 = 1·88 \times 10^{-3}$.* For

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[7] Bray, *J. Amer. Chem. Soc.*, **32**, 914, 1910.

[8] Jones, *J. Amer. Chem. Soc.*, **37**, 24, 1915.

* No allowance for the effect of ionic strength on K_3 has been made.

K at $\mu = 0$ and a temperature of 45° we obtain $3{\cdot}33 \times 10^{-12}$; by analogy with the variations of the hydrolytic constants of chlorine and bromine with ionic strength (*cf.* Refs. (1) and (2)), we estimate that the above value of K increases to about $5{\cdot}8 \times 10^{-12}$ when $\mu = 0{\cdot}5$. We then obtain

$$k = \frac{k_1K_2}{KK_3} = \frac{13{\cdot}8 \times 10^{-8} \times 1{\cdot}75 \times 10^{-4}}{5{\cdot}8 \times 10^{-12} \times 1{\cdot}88 \times 10^{-3}} = 2000 \text{ (approx.)}$$

at 45°, or about 250 at 20°. The latter figure may be compared with the corresponding k for the HOCl — $HC_2O_4^-$ reaction of about 600, and with that for the HOBr reaction of about 16500 at the same temperature.

Turning now to the semimolecular process, there appears to be little doubt that, as suggested by Berthoud,[5] this must involve reaction between iodine atoms and $C_2O_4^{--}$ ions. The simplest possible interpretation on this basis of the kinetic law which the semimolecular process obeys is the following reaction mechanism :—

$$I_2 \rightleftarrows 2I \quad \ldots \text{ thermal equilibrium,}$$

$$I_2 + I^- \rightleftarrows I_3^- \quad \ldots \text{ thermal equilibrium,}$$

$$\left.\begin{array}{l} I + C_2O_4^{--} \xrightarrow{k'} I^- + C_2O_4^- \\ C_2O_4^- + I_2 \longrightarrow 2CO_2 + I + I^- \end{array}\right\} \quad \ldots \text{ chain reactions.}$$

These chain reactions are identical with those originally suggested by Berthoud and Bellenot [4] for the *photo-oxidation* of $K_2C_2O_4$ by I_2. Writing $K_0 = [I]^2/[I_2]$, and $K_3 = [I_2][I^-]/[I_3^-]$, the stationary concentration of iodine atoms is given by

$$[I] = \sqrt{K_0[I_2]} = \sqrt{\frac{K_0K_3(\Sigma I_2)}{K_3 + [I^-]}},$$

and the rate of reaction by

$$-\frac{d[C_2O_4^{--}]}{dt} = k' \cdot [C_2O_4^{--}] \cdot \sqrt{\frac{K_0K_3(\Sigma I_2)}{K_3 + [I^-]}},$$

in formal agreement with the kinetic law to which our experiments conform.

While the above represents the simplest interpretation of the semimolecular process, it is capable of a variety of modifications. For example, there may enter the equilibrium

$$I + I^- \rightleftarrows I_2^-,$$

involving the ion I_2^-, whose existence has been postulated by a number of workers,[9] together with such processes as

$$I_2^- + I \rightleftarrows I_3^-$$

and

$$I_2^- + I_2^- \rightleftarrows I_3^- + I^-.$$

Provided, however, that thermodynamic equilibrium holds for each of the reversible reactions postulated, their existence cannot affect the final result so long as the rate-determining reaction is one between iodine atoms and oxalate ions. We have nevertheless mentioned the possible intervention of I_2^- in the present case, since in the *photochemical* re-

[9] Wagner, *Z. physikal. Chem.*, **113**, 261, 1924; Dickinson and Ravitz, *J. Amer. Chem. Soc.*, **52**, 4770, 1930; Allmand and Young, *Trans. Faraday Soc.*, **27**, 515, 1931.

actions between iodine (and bromine) and oxalates, which we are now reinvestigating, I_2^- (and Br_2^-) ions appear to play important rôles.

Identifying the semimolecular constant $k_{1/2}$ with $k'\sqrt{K_0K_3}$, it is possible to calculate—at least approximately—the temperature coefficient and critical increment E' of k'. From Table I it is seen that $k_{1/2}$ has the temperature coefficients (per 5°) 2·56, 2·45, and 2·40 between 40° and 45°, 45° and 50°, and 50° and 55° respectively. These yield critical increments of the measured reaction of 37,200, 36,700, and 37,000 calories, giving a mean of 37,000 calories. Assuming now that the heat of dissociation of molecular iodine into atoms has the same value in aqueous solution as in the gaseous state, namely 35,600 calories,[10] we have to subtract half this heat of dissociation plus half the heat of dissociation of KI_3 from the observed critical increment to obtain that of k'. We thus find $E' = 37{,}000 - (17{,}800 + 1400) = 17{,}800$ calories. This would correspond to a temperature coefficient between 40° and 50° of 2·42 for the reaction between iodine atoms and $C_2O_4^{--}$ ions.

Only a very rough estimate of the absolute value of k' is possible, owing to the fact that a very extended extrapolation of the equilibrium data for the thermal dissociation of iodine into atoms must be made, and even then the resulting value of K_0 refers to the gaseous state and not to dissociation in aqueous solution. Application of the formula of Braune and Ramstätter[11] for the variation of the gaseous equilibrium with temperature yields $K_0 = 3{\cdot}7 \times 10^{-21}$ at 45° C., while the formula of de Vries and Rodebush[12] gives $K_0 = 4{\cdot}9 \times 10^{-20}$ at the same temperature. On the one basis k' at 45° works out to 7×10^6, on the other to 2×10^6, the units being litres/moles-minutes.

Finally, it might be mentioned that we have attempted without success to obtain evidence of a reaction between iodine atoms and $HC_2O_4^-$ ions. In an experiment with a solution containing $NaHC_2O_4$, iodine, and potassium iodide, the observed small extent of reaction could be accounted for entirely in terms of the reaction between the $HC_2O_4^-$ ion and HOI and of that between iodine atoms and the small amount of $C_2O_4^{--}$ ions present as a result of the slight dissociation of the $HC_2O_4^-$ ions. If a reaction between $HC_2O_4^-$ and I does occur, we estimate that its specific rate is not greater than 2 per cent. of that of the reaction between $C_2O_4^{--}$ and I.

Summary.

The thermal reaction $Na_2C_2O_4 + I_2 \rightarrow 2NaI + 2CO_2$ in aqueous solution has been studied in the temperature range 40° to 60°, and over a range of iodide concentration from *M*/5 to *M*/1000. The measured reaction is composite of two simultaneous and independent processes, the one unimolecular, the other semimolecular with respect to iodine. The first of these is interpreted as a reaction between $HC_2O_4^-$ and HOI, the other as a reaction between $C_2O_4^{--}$ and iodine atoms. The velocity constants and the critical increments of these two reactions have been evaluated.

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