THE PHOTO-REACTIONS OF OXALATES WITH BROMINE AND WITH IODINE. PART II—THEORETICAL.

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In the preceding paper (page 369) it has been shown that the photo-reactions of oxalates with bromine and iodine in aqueous solution conform to the equations:

(*a*) for the Br_2 — $HC_2O_4^-$ reaction :—

$$\gamma\sqrt{E} = constant\,.\,\frac{[HC_2O_4^-]}{\sqrt{[Br^-]\left\{[Br^-] + K_2\frac{\alpha_1}{\alpha_2}\right\}}}\,;$$

(*b*) for the Br_2 — $C_2O_4^{--}$ reaction :—

$$\gamma\sqrt{E} = constant\,.\,\frac{[C_2O_4^{--}]\{1 + K[Br^-]\}}{\sqrt{[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}}\,;$$

(*c*) for the I_2 — $C_2O_4^{--}$ reaction :—

$$\gamma\sqrt{E} = constant\,.\,\frac{[C_2O_4^{--}]}{\sqrt{[I^-]\left\{[I^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}}.$$

In these equations, γ represents quantum yield, E is the rate of absorption of energy in quanta per c.c. of beam per minute, K_3 is the equilibrium constant of trihalide formation, α_1 and α_2 are the molecular extinction coefficients of free halogen and trihalide ion respectively, and K is an (empirical) constant.

To interpret these expressions, it seems clear that, in agreement with previous investigators, we must postulate chain mechanisms in each case with halogen atoms as carriers of the chain. After examination of a number of possibilities, it has been found possible to derive the above kinetic equations only on the basis of the two following mechanisms, both of which are modifications of the original mechanism of Berthoud and Bellenot.[1]

Mechanism 1.

$$\begin{aligned}
&X_2 + h\nu \rightarrow 2X \quad . \quad . \quad . \quad (k_1)\\
&X_3^- + h\nu = \text{internal filter}\\
&X^- + X_2 \rightleftharpoons X_3^- \quad . \quad . \quad . \quad (K_3)\\
&X^- + X \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} X_2^- \quad . \quad . \quad . \quad (K_4)\\
&\left\{\begin{array}{ll} X + HC_2O_4^- \rightarrow C_2O_4^- + H^+ + X^- & (k_5)\\ X + C_2O_4^{--} \rightarrow C_2O_4^- + X^- & (k_6)\\ X_2^- + C_2O_4^{--} \rightarrow C_2O_4^- + 2X^- & (k_7)\end{array}\right.\\
&\left\{\begin{array}{ll} X_2 + C_2O_4^- \rightarrow 2CO_2 + X^- + X & (k_8)\\ X_3^- + C_2O_4^- \rightarrow 2CO_2 + 2X^- + X & (k_9)\end{array}\right.\\
&X_2^- + X \rightarrow X_3^- \quad . \quad . \quad . \quad (k_{10})
\end{aligned}$$

Mechanism 2.

$$\begin{aligned}
&X_2 + h\nu = \text{internal filter}\\
&X_3^- + h\nu \rightarrow X_2^- + X \quad . \quad . \quad (k_2)\\
&X^- + X_2 \rightleftharpoons X_3^-. \quad . \quad . \quad (K_3)\\
&X^- + X \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} X_2^-. \quad . \quad . \quad (K_4)\\
&\left\{\begin{array}{ll} X + HC_2O_4^- \rightarrow C_2O_4^- + H^+ + X^- & (k_5)\\ X + C_2O_4^{--} \rightarrow C_2O_4^- + X^- & (k_6)\\ X_2^- + C_2O_4^{--} \rightarrow C_2O_4^- + 2X^- & (k_7)\end{array}\right.\\
&\left\{\begin{array}{ll} X_2 + C_2O_4^- \rightarrow 2CO_2 + X^- + X & (k_8)\\ X_3^- + C_2O_4^- \rightarrow 2CO_2 + 2X^- + X & (k_9)\end{array}\right.\\
&X_2^- + X_2^- \rightarrow X_3^- + X^- \quad . \quad (k_{11})
\end{aligned}$$

Mechanism 2 is identical, except for the introduction of the internal filter action, with the mechanism of Dickinson and Ravitz[2] for the $I_2 - C_2O_4^{--}$ reaction. It will be seen that the two mechanisms here suggested have different primary processes and different chain-breaking reactions, but have the same chain reactions (5)—(9), which are essentially those of Berthoud and Bellenot. Further, in both mechanisms the existence of the complex ion X_2^- is postulated. The necessity for this hypothesis is discussed later; for the present it suffices to state that reactions (4) and (4′) are assumed to be rapid, so that throughout an experiment, the equilibrium defined by $K_4 = \dfrac{k_4'}{k_4} = \dfrac{[X][X^-]}{[X_2^-]}$ is continuously maintained.

We first consider Mechanism 1, in which the photochemically effective absorption is ascribed only to the halogen molecule while the trihalide ion is presumed to act as an internal filter. We shall deal only with the case of weak absorption from a beam whose cross section is equal to that of the cell. Under these conditions, let E = total rate of absorption of radiant energy in quanta per c.c. per minute, E_1 = rate of absorption by the halogen and E_2 = that by the trihalide ion. Then the rate of formation of X atoms by (1) = $2\,k_1E_1$, where k_1 is an efficiency factor for process (1). Postulating, for conditions of constant illumination, the attainment of "stationary" concentrations of X and X_2^-, we obtain (with all concentrations expressed in the units molecules/c.c.):

$$2k_1E_1 + k_4'\,[X_2^-] - k_4[X][X^-] - k_{10}[X_2^-][X] = 0 \quad . \quad (13)$$

$$k_4[X][X^-] - k_4'\,[X_2^-] - k_{10}[X_2^-][X] = 0 \quad . \quad . \quad (14)$$

and, adding

$$k_1E_1 = k_{10}[X_2^-][X] \quad . \quad . \quad . \quad (15)$$

If now, we write[3]

$$[X_2^-] = \frac{[X][X^-]}{K_4}$$

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[1] Berthoud and Bellenot, *J. Chim. physique*, **21**, 308, 1924; *Helv. Chem. Acta* **7**, 307, 1924.

[2] Dickinson and Ravitz, *J. Amer. Chem. Soc.*, **52**, 4770, 1930.

[3] It is seen from equation (14) that this cannot be exactly true. The additional assumption is therefore necessary that the reciprocal processes (4) and (4′) are rapid, compared with reactions (5)—(11).

we obtain from (15)

$$[X] = \sqrt{\frac{k_1K_4E_1}{k_{10}[X^-]}} \quad . \quad . \quad . \quad . \quad (16)$$

For the absorption of a solution containing the two absorbing species X_2 and X_3^-, we have

$$E_1 = E\frac{\alpha_1[X_2]}{\alpha_1[X_2] + \alpha_2[X_3^-]},$$

where α_1 and α_2 are the molecular extinction coefficients of X_2 and X_3^- respectively.

Further

$$[X_2] = \frac{K_3}{K_3 + [X^-]}\Sigma[X_2] \quad \text{and} \quad [X_3^-] = \frac{[X^-]}{K_3 + [X^-]}\Sigma[X_2]$$

where $\Sigma[X_2]$ is the concentration of titratable halogen and $K_3 = \frac{[X^-][X_2]}{[X_3^-]}$.

Thus,

$$E_1 = \frac{K_3\frac{\alpha_1}{\alpha_2}}{[X^-] + K_3\frac{\alpha_1}{\alpha_2}}.E \quad . \quad . \quad . \quad (17)$$

Substitution in (16) gives

$$[X] = \sqrt{\frac{k_1K_4K_3\alpha_1E}{k_{10}\alpha_2[X^-]\left\{[X^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}}. \quad . \quad . \quad (18)$$

From (18) the experimentally observed kinetic expressions are easily obtained.

(*a*) For the $Br_2 - HC_2O_4^-$ reaction, by assuming (5) as the rate-determining step, we find

$$-\frac{d\Sigma[Br_2]}{dt} = k_5[Br][HC_2O_4^-]$$

$$= k_5[HC_2O_4^-]\sqrt{\frac{k_1K_4K_3\alpha_1E}{k_{10}\alpha_2[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}},$$

from which, by an easy transformation

$$\gamma\sqrt{E} = k_5\sqrt{\frac{k_1K_4K_3\alpha_1}{k_{10}\alpha_2}} \cdot \frac{[HC_2O_4^-]}{\sqrt{[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \quad . \quad (19)$$

(*b*) For the $Br_2 - C_2O_4^{--}$ reaction, by assuming that both Br and Br_2^- react with $C_2O_4^{--}$, *i.e.*, that both reactions (6) and (7) occur, we obtain

$$\gamma\sqrt{E} = k_6\sqrt{\frac{k_1K_4K_3\alpha_1}{k_{10}\alpha_2}} \cdot \frac{[C_2O_4^{--}]\left\{1 + \frac{k_7}{k_6K_4}.[Br^-]\right\}}{\sqrt{[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \quad . \quad (20)$$

(*c*) For the $I_2 - C_2O_4^{--}$ reaction, by assuming reaction (6) alone as the rate-determining step, it follows that

$$\gamma\sqrt{E} = k_6\sqrt{\frac{k_1K_4K_3\alpha_1}{k_{10}\alpha_2}} \cdot \frac{[C_2O_4^{--}]}{\sqrt{[I^-]\left\{[I^-]+K_3\frac{\alpha_1}{\alpha_2}\right\}}} \quad . \quad (21)$$

Equations (19), (20) and (21) based on Mechanism I are all in formal agreement with experiment. On further examination, however, Mechanism I is found to be untenable. This follows from an examination of Table VII. of the preceding paper (p. 377), in which are given relative values of K_λ for the $Br_2 - HC_2O_4^-$ and $Br_2 - C_2O_4^{--}$ reactions, K_λ being defined by the equation

$$\gamma\sqrt{E} \propto \frac{K_\lambda}{\sqrt{[Br^-]+K_3\frac{\alpha_1}{\alpha_2}}} \quad . \quad . \quad . \quad (22)$$

and including those parameters which are dependent on λ, but independent of the bromide concentration. Comparison of this equation with equations (19) and (20) shows that on the basis of Mechanism I :

$$K_\lambda = \sqrt{\frac{k_1\alpha_1}{\alpha_2}}.$$

In this comparison, it is assumed that no variation of k_5, k_6 or k_7 with λ occurs, although there is a possibility that at frequencies greater than the convergence limit the excess kinetic energy of the halogen atoms immediately after the optical dissociation of the molecule might promote reactions (5)—(7), and so increase the respective velocity constants. No such effect has, however, been observed for a photo-reaction of bromine in the gaseous phase (*cf.* Jost[4]), and its occurrence is certainly more improbable in the liquid state, where the chances of deactivation are so much greater. We thus obtain

$$k_1 = \frac{\alpha_2}{\alpha_1} . K_\lambda^2 \quad . \quad . \quad . \quad . \quad (23)$$

From the data of Tables V., VI., VII. and VIII. of the preceding paper, we have calculated values of K_λ^2 for the bromine reactions relative to K_λ^2 for $\lambda = 579$ $\mu\mu$. These together with values of k_1 calculated therefrom by applying equation (23) are given in Table I.

TABLE I.

λ ($\mu\mu$) . .	579	546	436	405	365	313
K_λ^2 (relative) .	1·0	1·19	2·10	2·10	2·57	2·83
k_1 (relative) .	1·0	1·94	15·5	33·6	84·4	2570

Now k_1 is the efficiency of the primary process of the photo-reaction, and although in general quantum yields of photo-processes (and possibly also the efficiencies of primary processes) tend to increase with diminishing wavelength, an increase of the order of magnitude of that given in Table I. has never been observed. This result is certainly sufficient justifica-

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[4] Jost, *Z. physikal. Chem.*, **134**, 92, 1928.

tion for rejecting Mechanism 1; further, the large rise in k_1 between 365 $\mu\mu$ and 313 $\mu\mu$, together with the general similarity in the plots of log k_1 and of log α_2 against λ both emphasise that this large increase in k_1 with diminishing λ is a direct result of the passive rôle ascribed to Br_3^- ions in Mechanism 1. Of the terms on the right-hand side of equation (23), K_λ^2 alters little with decreasing λ, α_1 increases comparatively slowly, but α_2 increases very rapidly. The large (and improbable) increase in k_1 with decreasing λ naturally results.

We therefore revert to Mechanism 2, in which the rôles of X_3^- and X_2 are reversed, X_2 acting now as an internal filter, while X_3^- absorbs in a photochemically effective manner. The chain-breaking reaction is also changed and is now assumed to be

$$X_2^- + X_2^- \rightarrow X_3^- + X^- \qquad (11)$$

We need not deduce the kinetic equations which emerge, since the method of procedure has already been indicated. The resulting expressions are:

(*a*) For the $Br_2 - HC_2O_4^-$ reaction, assuming (5), (8) and (9) as chain reactions:

$$\gamma\sqrt{E} = k_5K_4\sqrt{\frac{k_2}{k_{11}}}\cdot\frac{[HC_2O_4^-]}{\sqrt{[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \qquad (24)$$

(*b*) For the $Br_2 - C_2O_4^{--}$ reaction, assuming (6), (7), (8) and (9) as chain reactions:

$$\gamma\sqrt{E} = k_6K_4\sqrt{\frac{k_2}{k_{11}}}\cdot\frac{[C_2O_4^{--}]\left\{1 + \frac{k_7}{K_4k_6}[Br^-]\right\}}{\sqrt{[Br^-]\left\{[Br^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \qquad (25)$$

(*c*) For the $I_2 - C_2O_4^{--}$ reaction, with (6), (8) and (9) as chain reactions:

$$\gamma\sqrt{E} = k_6K_4\sqrt{\frac{k_2}{k_{11}}}\cdot\frac{[C_2O_4^{--}]}{\sqrt{[I^-]\left\{[I^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \qquad (26)$$

As before, these kinetic expressions are in agreement with the experimental observations.

Comparison of equation (22) with equations (24)—(26) shows that, on the basis of Mechanism 2,

$$k_2 = K_\lambda^2.$$

Combining the data of the preceding paper (Tables V.-VIII. and XIII.) with this relation, we obtain the results given in Table II., showing the variation of the efficiency of the primary process (k_2) with λ for the bromine reactions and for the iodine reaction.

TABLE II.

	Bromine Reactions.						Iodine Reaction.		
λ	579	546	436	405	365	313	579	546	436
k_2	0·35	0·42	0·72	0·74	0·90	1·00	0·85	0·95	1·00

The figures given are in each case relative to the value of k_2 at the lowest wavelength studied. Increases of the efficiency of the primary process of this order of magnitude are of general occurrence in photochemical reactions, and in this respect Mechanism 2 is completely satisfactory. If these values of k_2 are plotted against frequency (ν), it is found that for both reactions k_2 is tending towards a maximum with increasing ν, and the maximum appears almost to be reached at the lowest wavelengths investigated. The maxima clearly correspond to efficiencies of unity, and hence the figures of Table II. may be taken as giving approximately the actual values of k_2 at various wavelengths, if Mechanism 2 be accepted.

It may be surmised that, since the dissociation of X_2 makes no detectable contribution to the observed quantum yield, k_1 cannot exceed about one-tenth the value of k_2 at wavelengths such that α_1 and α_2 are of the same order of magnitude. Thus it may be estimated that k_1 (546 $\mu\mu$) for I_2 is less than 0·09, and k_1 (546 $\mu\mu$) for Br_2 is less than 0·04. For the ultra-violet wavelengths, however, α_2 is much greater than α_1, with the result that practically the whole of the absorption is due to X_3^- ions. Under these circumstances k_1 could conceivably rise to a value comparable with k_2 (*i.e.*, X_2 molecules could absorb effectively) without the dissociation of X_2 contributing appreciably to the observed effect.

As Mechanism 2 satisfactorily accounts for the kinetic equations to which these reactions conform and is also not unsatisfactory in its predictions regarding the dependence of quantum yield on wavelength, it will be tentatively adopted and subjected to further discussion. This mechanism postulates that for photo-reactions of bromine and iodine in aqueous solution, the absorption by free halogen molecules constitutes an internal filter action. This assumption is a novel one, and on *a priori* grounds would appear to have little to recommend it. Yet, the introduction of the term $\sqrt{\dfrac{1}{[Br^-] + K_3\dfrac{\alpha_1}{\alpha_2}}}$ in the kinetic expression for the bromine reactions accounts remarkably well for the variation of the function $\dfrac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$ with bromide concentration and for the variation of the bromide retardation with wavelength, and no formulation other than one involving an internal filter action can be found which will yield the same result. In the absence of other physical or chemical evidence definitely opposed to the view that absorption of visible light by I_2 and Br_2 molecules in aqueous solution does not lead to atom formation, the present work furnishes, we consider, reasonable grounds for advocating this view.

Further features of Mechanism 2 are the postulation of the existence of the ion X_2^- and the assumption that the chain-breaking reaction is $X_2^- + X_2^- \rightarrow X_3^- + X^-$. The first hypothesis has already been made by Wagner,[5] Dickinson and Ravitz,[2] and Allmand and Young.[6] In the present instance the further assumptions are necessary (i) that the equilibrium $X^- + X \rightleftharpoons X_2^-$ is rapidly attained and maintained even in the presence of the acceptor molecules ($HC_2O_4^-$ and $C_2O_4^{--}$) which are rapidly destroying and re-forming X atoms, and (ii) that $K_4 = \dfrac{[X][X^-]}{[X_2^-]}$

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[5] Wagner, *Z. physikal. Chem.*, **113**, 261, 1924.

[6] Allmand and Young, *Trans. Faraday Soc.*, **27**, 515, 1931.

is small (see later) so that over ordinary ranges of concentration of X^- the X_2^- ion is present in considerable excess over the X atom.

Considering the chain-breaking reaction, there are the three possibilities, *viz.*,

$$X_2^- + X_2^- \rightarrow X_3^- + X^- \quad . \quad . \quad . \quad (k_{11})$$
$$X_2^- + X \rightarrow X_3^- \quad . \quad . \quad . \quad . \quad . \quad (k_{10})$$
$$X + X \rightarrow X_2 \quad . \quad . \quad . \quad . \quad . \quad (k_{12})$$

If all three reactions occur simultaneously, then on the basis of Mechanism 2, we obtain on illumination a stationary concentration of X atoms given by the equation :

$$[X] = \sqrt{\frac{k_2E[X^-]}{\left\{k_{12} + \frac{k_{10}[X^-]}{K_4} + \frac{k_{11}[X^-]^2}{K_4{}^2}\right\}\left\{[X^-] + K_3\frac{\alpha_1}{\alpha_2}\right\}}} \quad . \quad (27)$$

The rate being proportional to [X] for the $I_2 - C_2O_4^{--}$ and $Br_2 - HC_2O_4^-$ reactions, it is clear that to obtain the experimentally observed halide retardation, it is necessary to assume that the term $\frac{k_{11}[X^-]^2}{K_4{}^2}$ is considerably greater than either k_{12} or $\frac{k_{10}[X^-]}{K_4}$, both of which are to be neglected in comparison. On *a priori* grounds, k_{11} would be expected to be smaller than k_{12}, since the latter will approximate to a collision number while reaction (11) will possess an energy of activation, even if this only corresponds to the energy which the ions must possess to overcome each other's electrostatic fields. It therefore becomes necessary, as already indicated, to introduce the further assumption that K_4 is small, so that it is the large excess of X_2^- over X which is responsible for the preponderance of reaction (11). Some justification of this assumption is given later.

Inspection of equations (24)—(26) shows that, in explaining the fact that the $Br_2 - C_2O_4^{--}$ photo-reaction has a different halide retardation from the other two photo-reactions, we assume that both Br and Br_2^- react with $C_2O_4^{--}$, whereas only Br (and not Br_2^-) reacts with $HC_2O_4^-$ and only I (and not I_2^-) reacts with $C_2O_4^{--}$. Comparison of equation (25) with equation (4) of the preceding paper (p.), shows that this leads to $\frac{k_7}{k_6K_4} = 9{\cdot}0$. Since, however, K_4 is very small, this means that $k_7 \ll k_6$ or the intrinsic rate of the reaction of Br_2^- with $C_2O_4^{--}$ must be considerably smaller than that of the reaction of Br with $C_2O_4^{--}$.

For the bromine reactions it is not possible to make any quantitative estimates of the magnitudes of the constants k_5, k_6, k_7, k_{11} and K_4 appearing in equations (24) and (25), but for the $I_2 - C_2O_4^{--}$ reaction this may be done by correlating the photochemical data with measurements of the *thermal* reaction between iodine and oxalates. The result of this correlation also lends additional support to the hypothesis of an equilibrium $I^- + I \rightleftharpoons I_2^-$. The *thermal* reaction has been studied by Griffith and McKeown,[7] who found that it occurs by two independent processes, of which one is semi-molecular with respect to iodine. This part of the reaction was found to conform to the kinetic law :

$$\frac{dx}{dt} = k_{\frac{1}{2}}[C_2O_4^{--}]\sqrt{\frac{\Sigma[I_2]}{K_3 + [I^-]}} \quad . \quad . \quad . \quad (28)$$

[7] Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 752, 1932.

in which $k_{\frac{1}{2}}$ is the semi-molecular velocity constant and $\Sigma[I_2]$ the concentration of titratable iodine. The result was interpreted in terms of the mechanism:

$$\begin{array}{lr} I_2 \rightleftharpoons 2I \text{ . . . thermal equilibrium} & \text{. . (12)} \\ I_2 + I^- \rightleftharpoons I_3^- \text{ . . . thermal equilibrium} & \text{. . (3)} \\ \left.\begin{array}{r} I + C_2O_4^{--} \rightarrow I^- + C_2O_4^- \\ I_2 + C_2O_4^- \rightarrow 2CO_2 + I^- + I \end{array}\right\}\text{chain reactions}\left\{\begin{array}{l} \text{. . (6)} \\ \text{. (8)} \end{array}\right. & \end{array}$$

This mechanism yields the expression

$$\frac{dx}{dt} = k_6[C_2O_4^{--}]\sqrt{\frac{K_{12}K_3\Sigma[I_2]}{K_3 + [I^-]}} \quad . \quad . \qquad (29)$$

in which $K_{12} = \frac{[I]^2}{[I_2]}$ is the equilibrium constant of the thermal dissociation of iodine into atoms.

Although the rate-determining reaction (6) is assumed to be the same for the thermal and photo-reactions,[8] there is a striking difference between the iodide retardations of the two processes. The photo-reaction is the more strongly retarded; thus equation (28) shows that at high iodide concentrations, the thermal rate is inversely proportional to $\sqrt{[I^-]}$, but from equation (26) it is seen that under the same conditions the photo-rate is inversely proportional to $[I^-]$. The explanation of this difference is as follows. In the interpretation of the photochemical reaction, the participation of the equilibrium $I^- + I \rightleftharpoons I_2^-$, together with the chain-breaking reaction:

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \quad . \quad . \quad . \quad . \quad (11)$$

has been postulated. It follows therefore that in a *non-illuminated* solution of iodine in KI, we have, in addition to the equilibria (12) and (3), the equilibria:

$$\begin{array}{lr} I^- + I \rightleftharpoons I_2^- & \text{. . . . . . (4)} \\ I + I_2^- \rightleftharpoons I_3^- & \text{. . . . . (10)} \\ I_2^- + I_2^- \rightleftharpoons I_3^- + I^- & \text{. . . . (11)} \end{array}$$

These additional balanced reactions cannot, however, affect the stationary concentration of iodine atoms in the thermal system, and, independent of their occurrence, equation (29) must apply for the rate of the thermal reaction. In the photo-reaction, however, the stationary concentration of iodine atoms is given by equation (27), and here, depending on whether (12), (10) or (11) is assumed to be the effective chain-breaking process, we will obtain (for high values of $[I^-]$) a photo-rate independent of $[I^-]$, or inversely as $\sqrt{[I^-]}$, or inversely as $[I^-]$. The fact that the photo-rate is found to be inversely proportional to $[I^-]$ decides that (11) is the preponderating chain-breaking process. It therefore follows that under *thermal* conditions the processes $I_3^- + I^- \rightleftharpoons I_2^- + I_2^-$ and $I_2^- \rightleftharpoons I^- + I$ (and not $I_2 \rightleftharpoons 2I$) are predominant in the maintainance of the stationary iodine atom concentration in a solution of iodine in KI.

The assumption that (11) constitutes the chain-breaking reaction under photochemical conditions, made above to account for the kinetic

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[8] We may here refer to two points of similarity between the thermal and photo-processes. (*a*) In both cases the rate of reaction is about 12 per cent. higher for potassium oxalate than for sodium oxalate; and (*b*) from both the thermal and photochemical data it has been shown that the specific rate of reaction between iodine atoms and $HC_2O_4^-$ ions is more than fifty times slower than that between iodine atoms and $C_2O_4^{--}$ ions.

behaviour of the reaction, receives independent support from a comparison of the observed rates of the thermal and photo-processes. Identifying the thermal semi-molecular constant $k_{\frac{1}{2}}$ of equation (28) with $k_6\sqrt{K_{12}K_3}$ of equation (29), Griffith and McKeown have estimated k_6 to be about $4{\cdot}5 \times 10^6$ at 45°, the units being $\frac{\text{litres}}{\text{moles . min.}}$. They have also shown k_6 to have a critical increment of about 18,000 cals. It follows that k_6 at 25° in the units $\frac{\text{c.c.}}{\text{molecules . min.}} = 1{\cdot}27 \times 10^{-15}$. Substituting this value in the expression for $\gamma\sqrt{E}$ which naturally derives from equation (27), and applying the data of Table XIII. of the preceding paper referring to $\lambda = 436$ $\mu\mu$, it follows, independent of any assumption regarding the particular chain-breaking reaction, that

$$\sqrt{\frac{k_2[\mathrm{I}^-]^2}{k_{12} + \dfrac{k_{10}[\mathrm{I}^-]}{K_4} + \dfrac{k_{11}[\mathrm{I}^-]^2}{K_4{}^2}}} = 9 \times 10^{20} \quad . \quad . \quad (30)$$

Assuming that for this wavelength the efficiency (k_2) of the primary process is unity, and considering an iodide concentration of $M/100$, *i.e.*, $6 \, . \, 10^{18}$ ions per c.c., then

$$k_{12} + \frac{k_{10}[\mathrm{I}^-]}{K_4} + \frac{k_{11}[\mathrm{I}^-]^2}{K_4{}^2} = 4 \times 10^{-5} \quad . \quad . \quad (31)$$

An estimate of the value of k_{12} can be obtained by assuming that every collision between iodine atoms is effective in forming an iodine molecule; k_{12} is thus equal to the collision number, *viz.* 3×10^{-9}. Adopting this as a *maximum* value of k_{12} it follows that this term can be neglected in comparison with the other terms of the left-hand side of equation (31). Presumably the second term is intermediate in value between the first and third, and hence, in agreement with the assumption necessary to account for the nature of the iodide function, the first and second terms of equation (31) can be neglected in comparison with $\frac{k_{11}[\mathrm{I}^-]^2}{K_4{}^2}$, and it can be stated that, for the photochemical reaction, $\mathrm{I_2}^- + \mathrm{I_2}^- \rightarrow \mathrm{I_3}^- + \mathrm{I}^-$ is the dominant chain-breaking process.

Continuing, we can obtain a *maximum* value for K_4 by assuming that the *maximum* value of k_{11} is equal to the collision number between two $\mathrm{I_2}^-$ ions. Thus, from equation (30) we have

$$K_4/\sqrt{k_{11}} = 9 \times 10^{20},$$

and taking $k_{11} = 5 \times 10^{-9}$, we obtain K_4 (*maximum*) to be of the order 6×10^{16} (molecules/c.c.) or 10^{-4} (moles/litre). It follows that with an iodide concentration of $M/100$, the concentration of $\mathrm{I_2}^-$ ions is *at least* 100 times that of iodine atoms, and, since k_{11} is probably several powers of ten less than the collision number, the concentration of $\mathrm{I_2}^-$ would appear, in agreement with the original premise, to be very much in excess of the iodine atom concentration throughout the range of iodide concentration investigated. The mean iodine atom concentration during a particular experiment follows from equations (27) and (30) together with the pertinent values of $[\mathrm{I}^-]_m$ and E. Thus for the solution $M/400$ KI + $M/1500$ $\mathrm{I_2}$ illuminated with $\lambda = 546$ $\mu\mu$ (see preceding paper, Table XIII., sixth experiment), we have $[\mathrm{I}^-]_m = 1{\cdot}57 \times 10^{18}$ ions per c.c., $E =$

$4{\cdot}49 \times 10^{16}$ quanta per c.c. per minute, and $[\mathrm{I}] = 10^{11}$ atoms per c.c. or 2×10^{-10} gm. atoms per litre.

Finally, it is possible to obtain an approximate estimate of the temperature coefficient of K_4. In equation (26) the temperature coefficient of $\gamma\sqrt{E}$ for the visible wavelengths is given by the data of Berthoud and Bellenot [1] and of Allmand and Young [6] as 3·1 between 25° and 35°. In the same range k_6 has according to Griffith and McKeown [7] a temperature coefficient of 2·42. Hence that of $K_4\sqrt{\dfrac{k_2}{k_{11}}}$ is equal to 1·28. The temperature coefficient of k_2 is doubtless unity and that of k_{11} cannot be very different. Hence this value of 1·28 refers almost entirely to K_4. This would correspond to a positive heat of formation of $\mathrm{I_2^-}$ ions from I atoms and $\mathrm{I^-}$ ions of 4500 cals.

Summary.

The experimental data of the preceding paper for the photo-reactions of bromine and iodine with oxalates have been interpreted in terms of reaction mechanisms which postulate that:

(*a*) The effective primary process is a photo-dissociation of the trihalide ion, the free halogen acting as an internal light filter.

(*b*) The bulk of the halogen atoms (X) formed by the primary process are transformed into $\mathrm{X_2^-}$ ions *via* the equilibrium $\mathrm{X + X^- \rightleftharpoons X_2^-}$.

(*c*) The rate-determining reactions are:

$$\mathrm{HC_2O_4^- + Br \rightarrow C_2O_4^- + H^+ + Br^-}$$

$$\left\{\begin{array}{l}\mathrm{C_2O_4^{--} + Br \rightarrow C_2O_4^- + Br^-}\\ \mathrm{C_2O_4^{--} + Br_2^- \rightarrow C_2O_4^- + 2Br^-}\end{array}\right.$$

and $$\mathrm{C_2O_4^{--} + I \rightarrow C_2O_4^- + I^-}$$

and these are followed by reactions of $\mathrm{C_2O_4^-}$ with $\mathrm{Br_2}$ (and $\mathrm{Br_3^-}$) or $\mathrm{I_2}$ (and $\mathrm{I_3^-}$) with regeneration of Br or I atoms.

(*d*) In all cases the effective chain-breaking reaction is that represented by:

$$\mathrm{X_2^- + X_2^- \rightarrow X_3^- + X^-}.$$

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