THE PHOTO-REACTIONS OF OXALATES WITH BROMINE AND WITH IODINE. PART I.---EXPERIMENTAL.

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In their well-known work, Berthoud and Bellenot¹ have elucidated the main features of the photo-oxidations of neutral oxalates by bromine and by iodine. The most significant result accruing from their work is that the rates of these reactions are proportional to the square root of the absorbed energy, and later work by others 2 has amply confirmed this fact. They infer that the reaction mechanism in both cases involves bromine (or iodine) atoms formed as a result of primary photodissociation.

The original intention of the present investigation was to study the photo-oxidation of oxalic acid by bromine, a reaction which has hitherto only been dealt with qualitatively (cf. Roloff 3). It soon became evident. however, that here we are dealing with two simultaneous and independent processes, the one involving the $HC_2O_4^-$ ion and the other the $C_2O_4^{--}$ ion. It was therefore found necessary to extend the investigation over the whole range of oxalate mixtures from neutral oxalate to oxalic acid. In the photo-reaction between bromine and neutral oxalate, Berthoud and Bellenot's measurements have been confirmed, but we have also extended the data by studying the effect of light of different wavelengths and particularly by studying the retardation by bromide at different wavelengths. These additional results are of particular significance for the interpretation of the reaction. Finally, it has been sought to apply the reaction mechanism which we suggest for the bromine-oxalate reaction to the corresponding reaction with iodine. For this purpose it has been necessary to extend the existing data for the latter reaction to regions of very low concentrations of the retarding iodide ion. In the present paper are presented the experimental results which we have obtained for the three photo-processes: (a) bromine and $HC_2O_4^{-1}$ ion; (b) bromine and $C_2O_4^{--}$ ion; and (c) iodine and $C_2O_4^{--}$ ion. Their theoretical interpretation is discussed in the paper which follows (p. 386).

Experimental.

A plan of the apparatus is given in Fig. 1. The light source was a quartz mercury lamp (burning at 150 volts and 3.8 amps.) of straight

369

¹ Berthoud and Bellenot, J. Chim. physique, 21, 308, 1924; Helv. Chem. Acta,

^{7, 307, 1924.} ² Briers, Chapman, and Walters, J.C.S., 562, 1926. Allmand and Young, Trans. Faraday Soc., 27, 515, 1931. ³ Roloff, Z. physikal. Chem., 13, 346, 1894.

tube pattern with a plane window at the anode end. The remainder of the apparatus (with the exception of the two large screens S_3 and S_4) was mounted on an optical bench. The screens were water-cooled and fitted with water-cooled shutters. The lenses in C, and the lenses L_1 , L_2 , L_3 were of quartz, the object of the last of these (L_3) being to bring the light transmitted by the reaction cell to a sharp focus on the thermopile P. Filter vessels containing liquid filters, coloured glass filters and neutral filters were mounted in front of the diaphragm D_1 . The reaction cells were permanently clamped into cylindrical jackets (for controlling the temperature) which sat accurately in a cradle. The cradle was fitted with various controls, which made it possible to adjust the position of the cell so that its axis coincided with the axis of the beam, and also ensured that once the position had been fixed it was always





possible after removing the cell to replace it in exactly the same position. Temperature control of the reaction mixture was obtained by pumping water from a thermostat into the cell jacket, whence it flowed back to the thermostat. Two cylindrical reaction cells made of quartz with plane parallel end-plates were used, the one 2 cm. in length, the other 10 cm. The former with its temperature jacket is depicted in Fig. 2; the other was essentially similar in construction. The object of the sidearm with bulb was to permit withdrawal of samples for analysis from the cell itself both before and after illumination. This procedure involves the application of small but definite corrections for the loss of bromine into the dead-space which results from the withdrawal of the initial sample. Since, for the experiments with bromine, the working temperature was usually below that of the room, precautions had to be taken to prevent the formation of dew on the end-plates of the reaction cells. This was done by blowing dry air against them.

The energies of (a) the incident and (b) the transmitted beams were measured with a Moll large-surface thermopile in conjunction with a

Moll galvanometer; (a) with the reaction cell containing water, and (b) with the cell containing reaction mixture. The thermopile was fitted with a blackened " stop " as recommended by Allmand and Beesley 4 and with a quartz window, and the whole was placed in a box heavily lined with felt. The thermopile - galvanometer combination was calibrated a carbonby means of filament lamp standardised by the National Physical Laboratory, and also with a standard Hefner lamp.



Re-calibration at the end of the whole series of measurements showed good agreement with the former calibration. For experiments with high intensities it was necessary to reduce the sensitivity of the thermopile-galvanometer combination; this was done by inserting a resistance in series with the galvanometer. Using the method suggested by Forbes,⁵ a linear relation between incident intensity and galvanometer deflection was shown to be applicable up to an intensity of at least 25 H.K. Corrections were applied in the calculations of quantum yields for losses due to reflection at quartz-air surfaces. For experiments in which the light absorption was less than 30 per cent., the energy absorbed was calculated from the incident intensity together with the appropriate extinction data (cf. footnote, p. 378).

Experiments have been carried out using light of wavelengths 579, 546, 436, 405, 365 and 313 $\mu\mu$. The following filters were used :-

- For 579 $\mu\mu$: 2 cm. 2¹/₂ per cent. CuCl₂ solution + Schott glass filter O.G. 2 (2 mm.). Transmission at 579 $\mu\mu = 45$ per cent.
- For 546 $\mu\mu$: 2 cm. 2¹/₂ per cent. CuCl₂ solution + Kodak green line monochromat No. 77 A. Transmission at 546 $\mu\mu = 53$ per cent.
- For 436 $\mu\mu$: 2 cm. $2\frac{1}{2}$ per cent. CuCl₂ solution + Schott glass filter B.G. 12 (I mm.) or Schott B.G. I (2 mm.) + I cm. 2 per cent. quinine sulphate solution. Transmission at 436 $\mu\mu =$ 51 per cent.
- For 405 $\mu\mu$: 2 cm. 2¹/₂ per cent. CuCl₂ solution + 1 cm. 0.1 per cent. quinine sulphate solution +5 mm. 0.02 per cent. diamant fuchsin. Transmission at 405 $\mu\mu = 16$ per cent.⁶
- For 365 $\mu\mu$: Schott glass filter U.G. I (2 mm.) + Schott B.G. 12
- (1 mm.). Transmission at 365 $\mu\mu$ = 50 per cent. For 313 $\mu\mu$: 2 cm. 2½ per cent. CuSO₄ solution + 5 mm. 0.02 per cent. K_2CrO_4 solution + Schott U.G. 2 (1 mm.). Transmission at 313 $\mu\mu = 13$ per cent.

- ⁵ Forbes, J. Physical Chem., **32**, 482, 1928. ⁶ The light transmitted by this filter contains about 12 per cent. of 436 $\mu\mu$.

⁴ Allmand and Beesley, J.C.S., 2693, 1930.

The liquid filters in the above list were contained in glass cells, except for the isolation of the 313 $\mu\mu$ line when quartz cells were used. Variation of the light intensity was effected by inserting one or more of a series of neutral filters.

The chemicals used were A.R. preparations, supplied by Merck, Kahlbaum, and Hopkin and Williams. The extent of reaction was determined by estimating the initial and final concentrations of bromine (or iodine) by running the sample into sodium arsenite solution (containing excess $NaHCO_3$) and back-titrating with iodine using starch as indicator. With suitable precautions the method is accurate for the estimation of very low concentrations of the halogen (below M/1000). In the calculation of the quantum yields for the photo-reaction between bromine and oxalic acid or oxalates, it is necessary to subtract from the observed extents of reaction the contributions made by the simultaneously occurring thermal reaction. These latter were computed from the data of Griffith, McKeown, and Winn.⁷ It is to be noted that correction in this manner assumes additivity of the thermal and photo-processes, *i.e.* that neither reaction affects the other. This assumption can hardly be in serious error, since (a) in practically all our experiments the thermal correction is only a few per cent. (usually less than 5 per cent.) of the total change, and (b) the mechanisms of the thermal and photo-processes are entirely different. For the iodine reaction, the thermal correction was in all cases small enough to be neglected.

For each reaction mixture two or more experiments with different times of illumination were carried out. For the bromine reactions most of the experiments were carried out at 11.5° ; for the iodine reaction at 25° .

Experimental Data.

In what follows the following symbols are used :---

- $\Sigma[Br_2]_0 = initial concentration of total titratable bromine (moles/litre).$
 - x = extent of photochemical reaction (after correction for the thermal reaction) (moles/litre).
 - t =time of illumination (minutes).
 - c = percentage thermal correction = 100 x (thermal)/x (total).
 - $\theta = \text{temperature.}$
 - l =length of reaction cell (cm.).
 - A_m = mean percentage light absorption during the experiment.
 - E = rate of absorption of radiant energy in quanta per c.c. of beam per min.
 - $\gamma =$ quantum yield.

I. THE PHOTO-REACTIONS OF BROMINE WITH OXALIC ACID AND WITH NEUTRAL OXALATE.

(A) Variation of the Incident Intensity.

The results summarised in Tables I. and II. show that under otherwise identical conditions the quantum yield (γ) of both reactions is inversely proportional to the square root of the rate of quantum absorption (E). Thus, γ is inversely proportional to the square root of the incident

⁷ Griffith, McKeown, and Winn, Trans. Faraday Soc., 28, 107, 1932.

TABLE I.

Reaction Mixture = M/8 H₂C₂O₄ + M/32 KBr + M/600 Br₂.

			$\theta = 11.5^{\circ}.$			
t.	x. 104.	с.	A m.	E. 10 ⁻¹⁶ .	γ.	$\gamma \sqrt{E}$. 10 ⁻⁷ .
		$\lambda =$	546 μμ; l =	10 cm.		
45 40 90	2°42 2°08 1°98	12.0 12.2 21.2	17·3 16·3 14·9	0*644 0*572 0*114	0*80 0*86 1*84	6•4 6•5 6•2
		$\lambda =$	436 µµ; l =	10 cm.		
20 20 35 60 90	5'04 4'11 4'81 5'09 4'85	3°5 4'9 5°7 8°0 11°3	100 100 100 100	3*51 2*41 1*08 0*418 0*153	0.68 0.81 1.21 1.93 3.34	12.7 12.6 12.6 12.5 13.0
		$\lambda =$	365 µµ; l =	2 cm.		
12 20 35	5.11 4.95 4.79	2•3 3•4 4•6	85·5 88·3 87·2	12°4 4°28 1°36	0*57 0*96 1*67	20°0 19°8 19°5

~ 0

TABLE II.

 $\theta = 6.5^\circ; l = 2 \text{ cm.}$

t.	x.10 ⁴ .	с.	A _m .	E. 10 ⁻¹⁶ .	γ.	$\frac{\gamma\sqrt{E}\cdot10^{-10}}{[C_2O_4]_m}.$
	<i>M</i> /20 K	$C_2 C_2 O_4 + M/2$	2 KBr + M/	600 Br ₂ . λ =	= 546 μμ.	
20	4'50	3.8	1.60	0'204	10.3	1.13
35	5.00	4.4	1.24	0.002	10.3	1*21
59	5.13	6.0	1.47	0'034	33.1	1.22
	<i>M</i> /100	$K_2C_2O_4 + M$	/4 KBr + M	/600 Br ₂ . λ	= 436 μ μ.	
10	4'00	2.7	60.8	7.36	0.21	1.90
24	5.58	3.0	58.4	2.01	1.10	1.04
40	5.00	4.0	57.6	0*95	2'02	2*04
	M/100 K	$K_2C_2O_4 + M/$	4 KBr + $M/$	1200 Br ₂ . λ	= 365 μμ.	
8	3.80	1.3	75.2	7.73	0.82	2*34
16	4'31	I'4	75.4	2.38	1.48	2.34
28	4 49	1·8	72.8	0.94	2.23	2.22
					l	

energy, and the relation holds at the three wavelengths studied. This result is in agreement with Berthoud and Bellenot, who observed the same dependence of the rate on incident intensity for the case of the neutral oxalate reaction in white light.

* Since the concentration of the oxalate falls slightly during an experiment, $\gamma \sqrt{E}$ is divided by the mean value of $[C_2O_4^{-7}]$. This applies to all experiments with neutral oxalate.

(B) Variation of the Concentration of Bromine.

The effect of bromine concentration on the rate of the oxalic acid reaction has been studied at the five wavelengths 546, 436, 405, 365 and 313 $\mu\mu$, with the reaction mixture M/8 H₂C₂O₄ + M/32 KBr and varying the bromine concentration between M/300 and M/5000. The results obtained show that the product $\gamma\sqrt{E}$ is dependent on the absorption of the reaction mixture, but that it is constant over a considerable range of absorption extending to about 85 per cent. Within this range $\gamma\sqrt{E}$ is independent of (i) the initial concentration of bromine, (ii) the extent of reaction, and (iii) the dimensions of the reaction cell. Table III. gives the results obtained for the reaction mixture M/8 H₂C₂O₄ + M/32KBr + bromine at 11.5° with light of 436 $\mu\mu$. The results obtained with the other wavelengths (omitted to save space) were similar, except that at 313 $\mu\mu$ it was impossible to obtain incomplete absorption owing to the very high extinction of the solution.

TABLE III.

VARIATION OF CONCENTRATION OF BROMINE.

 $M/8 H_2 C_2 O_4 + M/32 \text{ KBr} + \text{Br}_2. \quad \theta = 11.5^\circ.$

$\Sigma[Br_2]_0 \times 10^4.$	l.	t.	x. 10 ⁴ .	с.	A _m .	E.10 - 16.	γ.	Y√E. 10-7
31.0	10	30 60	5'3	9.0 6.3	100	3°16 3°28	0.23	9'4 TO:0
29.9	10	90	18.7	4.4	100	3.36	0.20	10.8
17.38	10 10	10 20	1.91 4.11	7*7 4*9	100	2.45 2.41	0.74	11.0
16 · 49 14 · 61	10 10	30 50	6·25 11·75	3.8 3.0	97 83	2.38 2.91	0*83 0*77	12.8
9.87	10	8	2.07	3.7	93	3.11	0.29	13.9
9°05 9°35	10 10	10 24	4°02 5°75	2°2 1°7	87°5 79°4	2.99 2.70	0°80 0°84	13.8
16.82 16.08	2 2	12 тб	3.12	3*9 3*6	59°4 60°6	9.69 7.45	0'43 0'50	13'4 13'7
16·42	2	24	6.05	3.0	56.7	9·46	0.44	13.6
8.52	2 2	35 12	9°07 2°27	2.8 3.0	48°0 30°1	5°70 5°20	0.59	14.1
8.42	2	24	4'34	2.0	29.3	4.85	0.65	13.0

Mean of last nine = 13.7

 $\lambda = 436 \ \mu\mu$.

If we define the "extinction" of the reaction mixture as the quantity $\alpha \, . \, \Sigma[Br_2]_m \, . \, l$, where α is the extinction coefficient $\left(\alpha = \frac{\log_e I_0/I}{\Sigma[Br_2] \, . \, l}\right)$, it is possible to show that the observed variation of $\gamma \sqrt{E}$ with the extinction is a systematic one. Thus in Fig. 3, the ratio of $\gamma \sqrt{E}$ for a given extinction to the limiting value of $\gamma \sqrt{E}$ for weak absorption is plotted against the function $\alpha \, . \, \Sigma[Br_2] \, . \, l$. It is seen that the points obtained from results at three different wavelengths (436, 405, and 365 $\mu\mu$) lie on a single curve, showing that the ratio $\frac{\gamma \sqrt{E}}{\gamma \sqrt{E}}$ (limiting) is a function only of the extinction, and not of the wavelength used.

This result can be readily explained on the basis of a generalised mechanism of the simplest type for a photo-reaction with rate propor-

tional to I_0^{\dagger} . Thus for a halogen X_2 and an acceptor A^- , we postulate a mechanism of the type (I) $X_2 + h\nu \rightarrow 2X$, (2) $X + A^- \rightarrow X^- + A$, (3) $X_2 + A \rightarrow$ resultants, (4) $X + X \rightarrow X_2$. From this may easily be deduced the equation:

$$\gamma \sqrt{E} = 2k_2 \sqrt{\frac{k_1}{k_4}} [A^-] \frac{I - e^{-c\alpha l/2}}{\sqrt{I - e^{-c\alpha l}} \sqrt{c\alpha}},$$

in which c is the concentration of X_2 (*i.e.* $\Sigma[X_2]$). Putting $c\alpha l = y$, we have:

$$\sqrt{E} = 2k_2 \sqrt{\frac{k_1}{k_4}} [A^-] \frac{1 - e^{-y/2}}{\sqrt{1 - e^{-y}} \sqrt{y}}$$
 . (1)

It is to be noted that E is defined as the rate of absorption in quanta *per c.c. of beam* per minute, for in this way the product $\gamma \sqrt{E}$ is made independent of the cross-section of the beam and of the length of the

reaction cell. Table IV. gives the value of the function $\frac{1 - e^{-y/2}}{\sqrt{1 - e^{-y}}\sqrt{y}}$

for various values of y; the second column gives the percentage absorptions corresponding to these same values of y, and the last column gives the value of $\gamma \sqrt{E}$ obfrom tained equation (I)relative to $\gamma\sqrt{E}$ correspond ing to y = 0, i.e., the limit of very weak absorption.

It is seen that $\gamma\sqrt{E}$ is practically constant from y=0 to y=1.8, the slight fall which occurs over this range being within



the experimental error of measurement of $\gamma\sqrt{E}$, namely about 3 per cent. For values of y above 1.8, however, the value of $\gamma\sqrt{E}$ falls rapidly. The latter figure y = 1.8 corresponds to an absorption of 83.5 per cent., so that up to about 85 per cent. absorption $\gamma\sqrt{E}$ should be practically constant, which is in complete agreement with the experimental findings. Further, equation (1) shows $\gamma\sqrt{E}$ to be independent of the dimensions of the reaction cell except in so far as *l* determines the extent of absorption, so that $\gamma\sqrt{E}$ is completely independent of *l* for absorptions below

у.	(Per Cent.).	$\frac{1-e^{-y/2}}{\sqrt{1-e^{-y}}\sqrt{y}}.$	$\gamma \sqrt{E}$. (Relative).	y.	(Per Cent.).	$\frac{1-e^{-y/2}}{\sqrt{1-e^{-y}}\sqrt{y}}.$	$\gamma \sqrt{E}$. (Relative).
0.0 0.2 0.4 0.6 0.8 1.4 1.8	0 18·1 33·0 45·1 55·1 75·3 83·5	0°500 0°500 0°499 0°498 0°497 0°497 0°484	1.000 1.000 0.308 0.309 0.304 0.304 0.380 0.368	2.4 3.0 5.0 10.0 14.0 20.0	90.9 95.0 99.3 100 100 100	0°473 0°460 0°412 0°314 0°267 0°224	0.946 0.920 0.824 0.628 0.534 0.448

TABLE IV.

about 85 per cent. The calculated figures in Table IV. have been plotted in Fig. 3 for quantitative comparison with the experimental data. The agreement is good, considering that the reaction mixtures were not stirred; the fact that all the experimental points lie somewhat above the theoretical curve may be attributed to the fact that the concentration of bromine in the light beam was always below the mean concentration from which the extinction was calculated. The predictions of the generalised chain mechanism are thus in complete accord with the experimental facts.

It will be appreciated that any attempt to investigate the dependence of the quantum yield (γ) on the other variables must be carried out within the region of constancy of $\gamma\sqrt{E}$. Thus, owing to the possibility of a change of α with the concentration of bromide in the system, any attempt to determine the effect of bromide concentration on γ under conditions such that the absorption is greater than 85 per cent. may lead to entirely erroneous results, due to a change with [Br-] of the variable α . $\Sigma[Br_2]_m$. l. It is for this reason that practically all the experimental data which follow refer to very low concentrations of bromine, so that all comparisons are made between values of $\gamma\sqrt{E}$ within its range of non-dependence on extinction. The necessity for the general recognition of some constant characteristic of an $I_0^{\frac{1}{2}}$ reaction, in the same way as the quantum yield is characteristic of a reaction proportional to the first power of the incident intensity, has been recognised by Allmand.⁸ It would appear that the function $\gamma \sqrt{E}$ corresponding to an absorption below about 85 per cent. adequately fulfils this requirement. For the interpretation of the remaining kinetic data, therefore, this quantity has been used as a function dependent solely on the variables (a) wavelength of light, (b) concentration of oxalate, (c) concentration of bromide, and (d) temperature.

For the reaction of bromine with neutral oxalate, the dependence of $\gamma\sqrt{E}$ on the concentration of bromine has only been tested for conditions such that the absorption is less than 85 per cent. In this range, in agreement with the behaviour of the oxalic acid reaction, $\gamma\sqrt{E}$ is found to be independent of $\Sigma[Br_2]$.

(C) Variation of the Wavelength (λ) of the Incident Light.

In the case of the oxalic acid reaction, the reaction mixture M/8 $H_2C_2O_4 + M/32$ KBr + Br₂ has been studied at 11.5° at five wavelengths. The results are summarised in Table V.

⁸ Allmand, J.C.S., 1557, 1929.

		1	1	······································	
λ (μμ)	546	436	405	365	313
$\gamma \sqrt{E} \cdot 10^{-7}$.	6.0	13.2	16.2	20*3	24.1
$\gamma\sqrt{E}$ relative to value at 546 $\mu\mu$	1.0	2.3	2'75	3*4	4.0

TABLE V.

For the neutral oxalate reaction, it was not found possible to study any single reaction mixture at all these five wavelengths, but two overlapping series at $6\cdot 5^{\circ}$ with different bromide concentrations give the desired data, as shown in Table VI.

TABLE VI.

(Bromide).		$\gamma \sqrt{E} \cdot 10^{-10} / [C_2 O_4 -]_m$							
	579.	546.	436.	405.	365 µµ.				
M/2	0*94	1.11	1.62	—	1.83				
M/4		1.10	1.98	1.99	2•33				

It would appear that the increase of $\gamma\sqrt{E}$ on decreasing the wavelength is much less rapid for the neutral oxalate reaction than for the oxalic acid reaction. That this is not an essential difference between the two reactions, however, but is due to the fact that the two variations of $\gamma\sqrt{E}$ with λ refer to different bromide concentrations is shown by the data in Table VII. In this Table the values of $\gamma\sqrt{E}$ given are not absolute values, and are comparable only for a given reaction mixture at the three different wavelengths. It will be seen that the increase of $\gamma\sqrt{E}$ with decreasing λ is dependent on the bromide concentration. It is greatest at low bromide concentrations, but for a given value of [Br⁻] the increase is the same for both the oxalic acid and neutral oxalate reactions.

TABLE VII.

Oxalate.	[KBr].	ү√ <i>Е</i> at 365 µµ.	у√Ē at 436 µµ.	ү√Ē at 546 µµ.	$\frac{(\gamma \sqrt{E})_{365}}{(\gamma \sqrt{E})_{436}}$	$\frac{(\gamma \sqrt{E})_{436}}{(\gamma \sqrt{E})_{546}}$	<u>K365</u> K436	K436 K546
$K_{2}C_{2}O_{4}$ $K_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$	M/2 M/4 M/4 M/8 M/8 M/16 M/32 M/64	1.83 2.33 2.27 3.02 3.93 7.15 13.3 24.2	1.67 1.98 1.94 2.43 3.26 5.42 9.27 15.3	1.11 1.10 4.00	1'10 1'18 1'17 1'24 1'21 1'32 1'44 1'58	1·50 1·80 — — 2·28 —	1.07 1.12 1.11 1.12 1.09 1.10 1.08 1.05	1.34 1.47 1.32

It is possible to account quantitatively for this variation of $\frac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$ with [Br-] by assuming that the kinetic equation for both reactions contains the term $\frac{I}{\sqrt{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$ where α_1 is the extinction coefficient

of Br₂ molecules, α_2 the extinction coefficient of Br₃⁻ ions, and K_3 the equilibrium constant of tribromide formation $\left(K_3 = \frac{[\text{Br}_2][\text{Br}^-]}{[\text{Br}_3^-]}\right)$. Thus, let

$$(\gamma\sqrt{E})_{\lambda} = \frac{K_{\lambda}}{\sqrt{[\mathrm{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$$
 . . (2)

where K_{λ} includes those quantities which vary with λ but are independent of [Br-]. Table VIII. gives the values of α_1 , α_2 and $K_3 \frac{\alpha_1}{\alpha_2}$ at various wavelengths.⁹ Application of equation (2) to the values of $\gamma \sqrt{E}$ given

(λμμ)	579	546	436	405	365	313	289
$\alpha_1 = \alpha_{Br_2}$	2.07	7*33	128	164	150	50	120
$\alpha_2 = \alpha_{\mathrm{Br}_3}$	ი•ვნ	2.08	167	454	860	7900	
K_3 . α_1/α_2	0.30	0.183	0*040	0.010	0.000	0.0003	

TABLE VIII.

in Table VII. yields the values of the ratio $K_{\lambda_1}/K_{\lambda_2}$ given in the last two columns of this Table. It will be seen that over the whole range of bromide studied (M/2 - M/64), $K_{\lambda_1}/K_{\lambda_2}$ is a reasonably good constant, showing that the effect under consideration is adequately interpreted by a term $\frac{I}{\sqrt{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$ in the kinetic equation for both reactions.

(D) Variation of the Concentration of Neutral Oxalate and of Oxalic Acid.

(a) Neutral Oxalate Solutions.—The results of 10 insolations at $6\cdot 5^{\circ}$ using solutions containing M/4 KBr + M/600 Br₂ with $\lambda = 546 \ \mu\mu$ and using solutions containing M/2 KBr + M/600 Br₂ with $\lambda = 436 \ \mu\mu$ show that $\gamma\sqrt{E}$ is directly proportional to the concentration of neutral oxalate (K₂C₂O₄) over the range M/25 to M/200. Since this is in agreement with Berthoud and Bellenot, who studied the effect of this variable over the concentration range M/2 - M/8 with white light, we may here refrain from publishing our data in detail.

⁹ The values of K_3 are those obtained by Griffith, McKeown, and Winn (*Trans. Faraday Soc.*, 28, 101, 1932). Values of α_{Br_3} and α_{Br_3} -were obtained by measurement of the extinctions of aqueous bromine solutions and of solutions of bromine in aqueous KBr. The figures given are molecular extinction coefficients to the base 10. They were determined at room temperature using Scheibe cells, (a) for the visible wavelengths with the Nutting photometer, and (b) in the ultra-violet by the sector-photographic method. The extinction measurements are not claimed to be of special accuracy, but may be regarded as sufficiently accurate for the purpose in view, viz., the determination of the magnitude of the term

 $\sqrt{\frac{1}{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$ to within 2 or 3 per cent.

(β) Solutions containing Neutral Oxalate, Acid-Oxalate, and Oxalic Acid.—Table IX. gives the variation of $\gamma\sqrt{E}$ for a series of oxalate solutions of increasing [H⁺], ranging from neutral oxalate with a $p_{\rm H}$ about 7 to a solution containing oxalic acid + HBr with a $p_{\rm H}$ of less than I. The whole series was effected with M/4 bromide and $\lambda = 436 \ \mu\mu$ at 11.5°. The Table gives also the compositions of these solutions, *i.e.*, the concentrations of $C_2O_4^{--}$, $HC_2O_4^{-}$, and H⁺, calculated using the values of K_1 and K_2 (the two ionisation constants of oxalic acid) obtained by Griffith, McKeown, and Winn.?

Oxalate.	[c ₅ 0,].	[HC ₂ 0,].	[H ⁺].	Y√ <u>E</u> .10 ^{−7} .	$\frac{\gamma\sqrt{E} \cdot 10^{-8}}{[HC_2O_4^{-}] + 100[C_2O_4^{}]}.$	Percentage C ₂ O ₄ Reaction.
$\begin{array}{cccccccc} M/100 & K_2C_2O_4 & & & & \\ M/16 & KHC_2O_4 & & & & \\ M/25 & KHC_2O_4 + M/40 & H_2C_2O_4 \\ M/16 & H_2C_2O_4 & & & & \\ M/8 & H_2C_2O_4 + M/4 & HBr & & \\ \end{array}$	0*00978 0*00448 0*000813 0*00021 0*000021	0.0563 0.0549 0.0413 0.0280	$\begin{array}{c} circa \ 10^{-7} \\ 2 \cdot 64 \times 10^{-3} \\ 1 \cdot 42 \times 10^{-2} \\ 4 \cdot 13 \times 10^{-2} \\ 2 \cdot 78 \times 10^{-1} \end{array}$	28·3 14·0 3·86 1·94 0·76	2·9 2·8 2·8 3·1 2·5	100 89 60 34 7

These results are most easily interpreted by the assumption that in all solutions more acid than neutral oxalate solutions, two independent photo-processes are occurring, the one with $HC_2O_4^{--}$ ions, the other with $C_2O_4^{--}$ ions, the latter being intrinsically much the more rapid. It is unnecessary to assume that H⁺ has any specific effect other than that of altering the ratio $\frac{[HC_2O_4^{--}]}{[C_2O_4^{--}]}$ in the solution. Analysis of the above figures on this basis shows that the intrinsic rate of the $C_2O_4^{--}$ reaction is about 100 times that of the $HC_2O_4^{--}$ reaction in the presence of M/4 bromide. Column 6 of Table IX. gives the values of $\frac{\gamma\sqrt{E}}{[HC_2O_4^{--}] + 100[C_2O_4^{---}]}$, which on this basis should be constant, and the last column gives the extent of the " $C_2O_4^{--}$ reaction" as a percentage of the total reaction. It will be seen that it occurs to an appreciable extent even with the reaction mixture M/8 H₂C₂O₄ + M/4 HBr

preciable extent even with the reaction mixture $M/8 H_2 C_2 O_4 + M/4 HB$ in which the concentration of $C_2 O_4^{--}$ ions is as low as 2×10^{-5} .

(γ) **Oxalic Acid Solutions.**—The results of Table IX. refer to solutions M/4 with respect to bromide. In Table X. are summarised values of $\gamma\sqrt{E}$ for oxalic acid solutions of varying concentration in solutions M/32 with respect to bromide. The wavelength and the temperature are again 436 $\mu\mu$ and 11.5° respectively. The calculated concentrations of HC₂O₄— and C₂O₄— in these solutions are also given. Owing to the fact that the C₂O₄— reaction has a much smaller retardation by bromide than has the HC₂O₄— reaction (see page 381), the ratio of the intrinsic rates of the two reactions is a function of the bromide concentration. Combining the value of 100 obtained for this ratio at [Br⁻] = M/4 with the bromide retardations of the two reactions arrived at in section E, we calculate a value of 34 for the ratio of the rate of the

$\Sigma[\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4}].$	[HC ₂ O ₄].	[C ₂ O ₄].	$\gamma \sqrt{E} \cdot 10^{-7}$.	$\frac{\gamma \sqrt{E} \cdot 10^{-9}}{[\text{HC}_2\text{O}_4^-] + 34[\text{C}_2\text{O}_4^{}]}.$	Percentage [HC ₂ O ₄ ~] Reaction.
M/8	0°0656	0'00014	13.9	2'0	93
M/16	0°0399	0'00013	9.3	2'I	90
M/32	0°0234	0'000125	6.2	2'2	84:5
M/64	0°0131	0'000115	3.8	2'2	77

TABLE X.

 $C_2O_4^{--}$ reaction to that of the $HC_2O_4^{-}$ reaction at $[Br^-] = M/32$. The fifth column of Table X. gives the values of $\frac{\gamma\sqrt{E}}{[HC_2O_4^{--}] + 34[C_2O_4^{---}]}$ which on this basis should be constant. It will be seen that for the reaction mixture M/8 $H_2C_2O_4 + M/32$ KBr, with which the dependence of $\gamma\sqrt{E}$ on bromine concentration and on incident energy was studied (cf. Tables I. and III.), the $HC_2O_4^{--}$ reaction is contributing 93 per cent. to the total measured reaction. The conclusions there drawn may therefore be regarded without serious error as referring to the pure $HC_2O_4^{--}$ reaction.

(E) Variation of the Bromide Ion Concentration.

In the preceding section it has been shown that two reactions occur, the one a photo-oxidation of $C_2O_4^{--}$, the other of $HC_2O_4^{--}$. We now deal with the effects of bromide on the separate processes.

(a) The $C_2O_4^{--}$ Reaction.—For the experiments carried out with neutral oxalate solutions it was shown in the last section that the measured reaction consists solely of the oxidation of $C_2O_4^{--}$ ions. In Table XI. are given the bromide retardations experimentally observed at 6.5° for progressive doubling of the bromide concentration, *i.e.*, the ratio of $\frac{\gamma\sqrt{E}}{[C_2O_4^{--}]_m}$ for a given bromide concentration to $\frac{\gamma\sqrt{E}}{[C_2O_4^{--}]_m}$ for double the bromide concentration. It is seen that these ratios range from

Bromide \rightarrow	$M/2 \rightarrow M/4.$	$M/4 \rightarrow M/8.$	$M/8 \rightarrow M/16.$
$\lambda = 546 \ \mu\mu$ $\lambda = 436 \ \mu\mu$ $\lambda = 365 \ \mu\mu$	1.00 (1.02) 1.13 (1.14) 1.27 (1.17)	1·23 (1·23) 1·30 (1·29)	 1·45 (1·42)

TABLE XI.—BROMIDE RETARDATIONS IN THE C_2O_3 — Reaction.

1.0 to 1.45, that for constant λ they increase with decreasing [Br-], and for constant bromide concentration they increase with decreasing λ . The bracketed figures are calculated values (see page 378). (β) The HC₂O₄- Reaction.—Tables IX. and X. show that, owing to

(β) The HC₂O₄⁻ Reaction.—Tables IX. and X. show that, owing to the higher intrinsic rate of the C₂O₄⁻⁻ reaction, the HC₂O₄⁻⁻ reaction has in no case been completely isolated. In the experiments with oxalic acid solutions (Table X.), however, the HC₂O₄⁻⁻ reaction contributes the greater part of the observed effect, and it is possible, by correcting for the simultaneously occurring C₂O₄⁻⁻ reaction, to arrive at the bromide retardation of the "pure HC₂O₄⁻⁻ reaction." The details of this correction need not here be reproduced; the final results are to be found in

Table XII., which gives the bromide retardations of the $HC_2O_4^-$ reaction at 11.5° .

 $M/16 \rightarrow M/32$. $M/4 \rightarrow M/8.$ $M/8 \rightarrow M/16.$ $M/_{32} \rightarrow M/_{64}$. Bromide \rightarrow 1·48 (1·51) 1·79 (1·70) 1·47 (1·47) 1·70 (1·60) $\lambda = 546 \ \mu\mu$ 2.06 (1.88) 1.81 (1.80) $\lambda = 436 \,\mu\mu$ 2.10 (1.96) 1 98 (1 94) 1.04 (1.80) 1.87 (1.81) $\lambda = 365 \ \mu\mu$

TABLE XII .- BROMIDE RETARDATIONS IN THE HC204- REACTION.

Comparing Table XII. with Table XI., it will be seen that the retardation of the $HC_2O_4^-$ reaction by bromide is considerably greater than that of the $C_2O_4^-$ reaction. Another difference between the two reactions is that for the $HC_2O_4^-$ reaction the bromide retardations increase with increasing [Br-], while Table XI. shows the reverse to be true for the $C_2O_4^-$ reaction. The two reactions, however, possess one feature in common in that in both there is a definite increase in the bromide retardation with decreasing λ .

(γ) Mathematical Representation of the Bromide Retardations of the Two Reactions.—Of the two, the HC₂O₄⁻ reaction is the simpler, since it is found that its retardation by bromide may be quantitatively expressed by the equation

$$\gamma \sqrt{E} \propto \frac{I}{\sqrt{[Br^-]}} \times \frac{I}{\sqrt{[Br^-]} + K_3 \frac{\alpha_1}{\alpha_2}}$$
 (3)

in which the second term on the right-hand side is the one already used (p. 377) to account for the dependence of $\frac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$ on the bromide concentration. In Table XII. the comparison is made between the experimental retardations and those predicted by this equation (figures in brackets). It will be seen that over the range of KBr from M/8 to M/64the agreement is satisfactory. The deviations which occur in the range $[Br^-] = M/4 - M/8$ are to be attributed to the relatively large corrections which have to be applied in this region for the simultaneously occurring $C_2O_4^{--}$ reaction, which make the experimental ratios considerably less accurate.

The effect of Br⁻ on the $C_2O_4^{--}$ reaction is more complex, as evidenced by the fact that in contrast with both the $HC_2O_4^-$ photo-reaction and the thermal reaction ⁷ the retardation now decreases with increasing [Br⁻]. Since, however, it has been shown that for the $C_2O_4^{--}$ reaction as for the $HC_2O_4^-$ reaction, the expression for the rate (*i.e.*, for $\gamma\sqrt{E}$) contains the term $\frac{I}{\sqrt{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$, and since also the retardation is

now considerably less, it follows that the observed retardation can best be reproduced by an equation in which we have an additional term containing [Br-] in the numerator. Actually an equation of the type

$$\gamma \sqrt{E} \propto \frac{I + K[\mathrm{Br}^-]}{\sqrt{[\mathrm{Br}^-]} \times \sqrt{[\mathrm{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2}}} \cdot \qquad (4)$$

is found to fit the results, K having a value 9.0 independent of the wavelength. In Table XI. the comparison is made between the observed bromide retardations and those calculated (bracketed values) on the basis of this equation.

(F) Temperature Coefficients.

The effect of temperature on the two reactions has been studied using light of wavelengths 365, 436 and 546 $\mu\mu$ at the four temperatures 6.5°, 11.5°, 16.5° and 21.5°. For the HC₂O₄⁻ reaction the following values of the ratio $(\gamma \sqrt{E})_{\theta+5}/(\gamma \sqrt{E})_{\theta}$ were obtained : 1.52, 1.50, 1.51, 1.49, 1.47, 1.43, 1.42, 1.40 and 1.43, the figure being independent of the wavelength and of the bromide concentration. Taking the mean as 1.47, this corresponds to a temperature coefficient of $(1.47)^2$ or 2.16. For the $C_2O_4^{--}$ reaction, the mean of nine determinations for a five degree rise was 1.44, and again the figure is independent of the wavelength and also of the Br⁻ concentration. This corresponds to a temperature coefficient of $(1.44)^2$ or 2.07, in good agreement with Berthoud and Bellenot's value of 2.04 in white light. The HC2O4- reaction thus appears to have a very slightly higher temperature coefficient than that of the $C_2O_4^{--}$ reaction.

(G) The Effect of Addition of Ammonium Salts.

In their study of the photo-reaction between neutral oxalates and bromine, Berthoud and Bellenot found that addition of small quantities of ammonium salts caused induction periods. We have carried out a few experiments to test this observation, and have found that, while in the case of neutral oxalate NH₄ salts retard the reaction, they exert no appreciable effect on the $HC_2O_4^-$ reaction. Thus for a reaction mix-ture M/8 $H_2C_2O_4 + M/32$ KBr + M/600 Br₂ at 11.5° with $\lambda = 546 \mu\mu$, we found $\gamma \sqrt{E}$. 10⁻⁷ = 6.5, while with the same reaction mixture plus M/1000 NH₄NO₈ under the same conditions, $\gamma \sqrt{E} \cdot 10^{-7} = 6.6$. With $M/100 \text{ K}_2\text{C}_2\text{O}_4 + M/4 \text{ KBr} + M/600 \text{ Br}_2$, however, at 6.5° and $\lambda = 436 \ \mu\mu$, the figures in the absence and in the presence of M/5000 $\gamma \sqrt{E}$

 NH_4NO_3 were $\frac{\gamma \sqrt{E}}{[C_2O_4^{--}]_m}$. 10⁻¹⁰ = 1.96 and 1.44 respectively.

Blank experiments showed that in the case of the last of these experiments (neutral oxalate reaction in the presence of NH_4 salt) about 50 per cent. of the ammonium salt had been thermally oxidised before the initial sample of the reaction mixture had been removed. It is probable that the bulk of the remainder was oxidised during the period of exposure. In spite of this, however, a fall in net quantum yield (calculated with respect to disappearance of Br₂) occurred, suggesting a considerable fall in the quantum yield of the $C_2O_4^{--}$ photo-oxidation process. The thermal oxidation of ammonium salts by bromine is a reaction very strongly retarded by H +, and consequently the complication of a simultaneous thermal reaction does not arise in the experiments with oxalic acid + Br₂ + ammonium salt, that is, with a solution of sufficiently high $[H^+]$. It appears that the entity which causes the induction period is the NH₃ molecule formed by hydrolysis of the ammonium salt, and that the phenomenon only occurs at $p_{\rm H}$ values greater than about 5.

II. THE PHOTO-REACTION OF IODINE WITH NEUTRAL OXALATE.

As this photo-reaction has already been the object of much intensive work^{1,2} which has succeeded in resolving its main features, we have

confined ourselves to one point only, viz., the nature of the function expressing the retardation by iodide ions. It may be stated at once that the function which our experimental observations suggest in the case of the $I_2 - C_2O_4^{--}$ reaction is exactly analogous to that which we have shown to hold in the case of the photo-reaction between bromine and the *acid-oxalate* ion, where the retardation by bromide is expressed by

$$\gamma \sqrt{E} = \frac{const.}{\sqrt{[Br^-] \left\{ [Br^-] + K_3 \frac{\alpha_1}{\alpha_2} \right\}}} \quad . \qquad . \qquad (5)$$

In the latter case, since K_3 is about 0.05 and α_1 and α_2 are of the same order of magnitude for wavelengths in the visible, $\gamma\sqrt{E}$ becomes inversely proportional to [Br⁻] only for high values of [Br⁻], and considerable deviations from inverse proportionality to [Br⁻] can occur within the concentration range M/2 to M/50 of bromide.

For the iodine-oxalate reaction, although in the visible α_1 and α_2 are again of the same order of magnitude, K_3 is considerably less, viz., 0.00138 at 25°. Even if the iodine-oxalate reaction obeys an equation analogous to (5), no deviations from inverse proportionality to [I⁻] would be detected in the range of iodide concentration above M/50. In agreement with this, Berthoud and Bellenot have shown that the rate of reaction is inversely proportional to [I⁻] in the range M/20 - M/40, but did not extend their measurements to lower iodide concentrations. It is for this reason that we have reinvestigated the iodide retardation of this photo-reaction over a range of [I⁻] from M/100 to

M/1600 within which the term $K_3 \frac{\alpha_1}{\alpha_2}$ becomes comparable with [I-].

The results definitely show that at low iodide concentrations the rate is

not inversely proportional to [I⁻], but is proportional to $\frac{I}{\sqrt{[I^-]\{[I^-]+Z\}}}$,

where Z is of the order of magnitude of $K_3 \frac{\alpha_1}{\alpha_2}$. Experimental difficul-

ties have prevented as complete a study of the iodine reaction as has been made of the bromine reaction. Thus, the necessity of having to restrict the measurements to regions of partial absorption of the incident light has limited us to the three wavelengths 436, 546 and 579 $\mu\mu$. Further, for solutions weak in iodide, it was necessary to cut down as far as possible the increase in [I-] which occurs during insolation, in order that the mean value of [I-] should be of significance. It is only possible to do this by working with very low iodine concentrations, which naturally reduces the accuracy of measurement. Even so, considerable increases of [I-] occurred during the experiments, which were all carried out at 25° with solutions containing initially M/10 Na₂C₂O₄, with KI concentrations from M/100 to M/1600, and with iodine concentrations from M/1500 to M/3000.

Table XIII. contains a summary and analysis of the experimental data. From the initial concentrations of KI and iodine and the measured extent of the photo-reaction (Columns 1, 2 and 3), values of $[I^-]_{initial}$ and $[I^-]_{final}$ have been calculated. The $[I^-]_m$ of Column 4 is the mean of these figures. The fifth column gives the values of $\gamma\sqrt{E}$, while the last three columns give the values of $\gamma\sqrt{E}$ multiplied by three possible iodide functions, viz., $[I^-]_m$, $\sqrt{[I^-]_m \{[I^-]_m + K_3 \frac{\alpha_1}{\alpha_2}\}}$ and $\sqrt{[I^-]_m}$ re-

spectively. The extinction coefficients α_1 and α_2 of I_2 and I_3^- employed were $\alpha_1 = 580$, 131 and 63, and $\alpha_2 = 1300$, 134 and 70 at 436, 546 and 579 $\mu\mu$ respectively. The values at 546 $\mu\mu$ are those of Allmand and Young.² That of α_3 at 436 $\mu\mu$ is given by Winther,¹⁰ while the remaining values were obtained by us by the thermopile-galvanometer method.

Initial Concentrations.					њ°	3 25 3 25 3 25	 		
[KI].	2[I2] × 10 ⁴ .	£.10 ⁴ .	[[¹] _m , 10 ³ .	$\gamma \cdot \sqrt{E} \cdot 10^{-8}$.	γ√ <u>E</u> .[I ^{-]} m.10 ⁻	$\times \sqrt{\frac{\gamma\sqrt{E} \cdot 10^{-5}}{[1^-]_m} \{ [1^-]_m + K}$	$\gamma\sqrt{E}\cdot\sqrt{[1^-]}_m$. 10		
$\lambda = 436\mu\mu; K_3 \cdot \alpha_1/\alpha_2 = 0.00061.$									
1/1600 1/800 1/400	3*57 3*92 3*97	2*04 2*18 2*29	0'742 1'33 2'55	1•18 0•72 0•41	0*87 0*96 1*06	1·18 1·16 1·17	3.21 2.63 2.08		
			Mean 1·17						
$\lambda = 546 \mu \mu$; $K_3 \cdot \alpha_1 / \alpha_2 = 0.0014$.									
1/1600 1/800 1/400 1/200 1/100	3*68 7*09 7*30 7*32 7*60	2°03 4°78 4°42 3°78 2°82	0*742 1*56 2*62 4*95 9*74	0*880 0*556 0*340 0*204 0*108	0.65 0.79 0.89 1.01 1.05	1·12 1·13 1·10 1·14 1·12	2°41 2°17 1°74 1°44 1°06		
					Μ	lean 1•12			
$\lambda = 579 \mu \mu$; $K_3 \cdot \alpha_1 / \alpha_2 = 0.00125$.									
1/1600 1/800 1/400	4°36 8°32 8°60	1·99 3'97 4'09	0•725 1•295 2•545	0*86 0*61 0*36	0*62 0*79 0*92	1.11 1.10 1.03	2·32 2·17 1·80		
					M	ean 1.08			

TABLE XIII.—IODINE-OXALATI	z R⊧	EACTION.
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Comparison of the last three columns shows that

$$\gamma\sqrt{E} \times \sqrt{[\mathbf{I}^-]_m \left\{ [\mathbf{I}^-]_m + K_3 \frac{\alpha_1}{\alpha_2} \right\}} = constant$$

There appears little doubt therefore best fits the experimental results. that for all iodide concentrations less than M/20 (the highest used by Berthoud and Bellenot) the halide retardation is of the same character for the $I_2 - C_2O_4^{--}$ reaction as we have found for the $Br_2 - HC_2O_4^{--}$ reaction.¹¹

¹⁰ Winther, Z. physikal. Chem., 108, 236, 1924. ¹¹ There remains the possibility that at higher iodide concentrations the functional dependence of rate upon [I-] might require to be expressed by an $\sqrt{[I^-]\left\{ [I^-] + K_3 \frac{\alpha_1}{\alpha_2} \right\}}$, the constant K s negligible corrections equation analogous to (4), viz. $\gamma \sqrt{E} \propto -$

in the numerator being such that K[I-] is negligible compared with unity for [I-] < M/20.

Two further points call for comment. The first is that there appears to be a real difference between the intrinsic rates of the photo-reactions of iodine with $K_2C_2O_4$ and with $Na_2C_2O_4$. With M/10 solutions of these oxalates, the value of $\gamma\sqrt{E}$ (or the rate of reaction) with $\lambda = 546 \ \mu\mu$ and $t = 25^{\circ}$ is 12 per cent. greater for the potassium salt than for the sodium salt. The second point is that in a reaction mixture containing M/10 NaHC₂O₄ + M/800 KI + M/1500 I₂, the observed rate is almost but not quite accounted for as a I₂ - C₂O₄⁻⁻ reaction, in spite of the fact that in the solution used the ratio $\frac{[C_2O_4^{--}]}{[HC_2O_4^{--}]}$ is only I/20. Attributing the *residual* reaction to photo oxidation of HC₂O₄⁻⁻ ions by iodine, it is inferred that the intrinsic rate of the latter reaction in the above mixture is only about 1/70 of that of the I₂ - C₂O₄⁻⁻ reaction.

Summary.

The photochemical reactions of bromine with neutral oxalate and with oxalic acid have been studied at $6\cdot 5^\circ$, $11\cdot 5^\circ$ and $16\cdot 5^\circ$ with light of wavelengths between 579 $\mu\mu$ and 313 $\mu\mu$. (a) A convenient measure of the reactivity of any mixture is given by

(a) A convenient measure of the reactivity of any mixture is given by the function $\gamma\sqrt{E}$, where γ is the quantum yield and E is the rate of absorption of radiant energy (quanta per c.c. of beam per minute). Within an absorption range up to 85 per cent., $\gamma\sqrt{E}$ is found to be independent of (i) the initial concentration of bromine, (ii) the extent of reaction, (iii) the incident energy, and (iv) the dimensions of the reaction cell. For absorptions greater than 85 per cent., $\gamma\sqrt{E}$ progressively falls; the variation of this function with percentage absorption can be quantitatively accounted for on the basis of a reaction mechanism involving a bromine atom chain.

(b) Two independent processes occur, the one involving $C_2O_4^-$ - ions, the other $HC_2O_4^-$ ions. These two processes are differently retarded by Br-ions; thus, with M/4 KBr the intrinsic rate of the $C_2O_4^-$ - reaction is 100 times that of the $HC_2O_4^-$ reaction, while in the presence of M/32 KBr the ratio of the intrinsic velocities is 34, *i.e.*, the $C_2O_4^-$ - reaction is less strongly retarded by bromide. For both reactions the retarding influence of the Br- ion increases with decreasing wavelength.

(c) The temperature coefficient of the C_2O_4 - reaction is 2.07, that of the HC_2O_4 - reaction 2.16.

(d) The results of all experiments are quantitatively reproduced by the equations:

for the HC₂O₄- reaction :
$$\gamma \sqrt{E} = constant \cdot \frac{[\text{HC}_{2}O_{4}^{-}]}{\sqrt{[\text{Br}^{-}]\left\{[\text{Br}^{-}] + K_{3}\frac{\alpha_{1}}{\alpha_{2}}\right\}}}$$

for the C₂O₄- - reaction : $\gamma \sqrt{E} = constant \cdot \frac{[\text{C}_{2}O_{4}^{--}]\{\mathbf{I} + K[\text{Br}^{-}]\}}{\sqrt{[\text{Br}^{-}]\{[\text{Br}^{-}] + K_{3}\frac{\alpha_{1}}{\alpha_{2}}\}}}$

where α_1 and α_2 are the extinction coefficients of Br_2 and Br_3 -respectively, $K_3 = \frac{[Br_2][Br^-]}{[Br_3^-]}$, K is a constant whose value is 9.0, and the *constants* are functions only of wavelength and temperature.

The photochemical reaction of iodine with neutral oxalate has been studied at 25° with light of the three wavelengths 579 $\mu\mu$, 546 $\mu\mu$ and 436 $\mu\mu$ in the presence of low concentrations of KI.

(a) The reaction conforms to the kinetic equation

$$\gamma \sqrt{E} = constant \cdot \frac{[C_2 O_4^{--}]}{\sqrt{[I^-] \left\{ [I^-] + K_3 \frac{\alpha_1}{\alpha_2} \right\}}}$$

(b) The rate of reaction is somewhat greater with $K_2C_3O_4$ than with $Na_2C_2O_4$.

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