CCCCXXIV.—*The Photolysis of Potassium Ferrioxalate Solutions. Part III.*

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THE experiments described below supplement earlier work already published (Allmand and Webb, J., 1929, 1518, 1531), and fall under three heads, *viz.*, (i) an investigation of the effect of temperature on the quantum efficiency in monochromatic light; (ii) a further study of the unexpected results obtained previously with polychromatic light; (iii) a few experiments on the closely related photo-reaction between ferric chloride and oxalic acid, which, according to Kornfeld (*Z. Elektrochem.*, 1928, **34**, 598), proceeds in a manner entirely different from the potassium ferrioxalate photolysis.

EXPERIMENTAL.

Apparatus and Methods.—Whereas Allmand and Webb used an arrangement in which both reaction vessel and thermopile were at room temperature, we have employed the apparatus and methods already fully described in connexion with the photo-reaction between potassium oxalate and iodine (Allmand and Young, *Trans. Faraday Soc.*, 1931, **27**, 515), the most important gain being that of steady and reproducible thermopile readings, with well-defined temperature conditions as an additional advantage.

Potassium ferrioxalate was prepared as described by Allmand and Webb. Ferric chloride was made by passing chlorine over iron wire and resubliming the product. Oxalic acid and potassium oxalate were of A.R. quality, once recrystallised. All solutions were made up separately in oxygen-free water before each experiment. A stream of oxygen-free carbon dioxide was passed through the photolyte by means of a capillary jet for 30 minutes prior to, and during the whole duration of, the insolation. Whilst primarily used to exclude oxygen, it also effected a certain degree of stirring. In experiments at 52°, this gas stream passed through a water-bubbler immersed in the thermostat before entering the reaction vessel. As before, the degree of decomposition was estimated by titration with standard titanous chloride solution.

Temperature Coefficients.—In these experiments, as in those described in the next section, the solutions used for photolysis were all of the composition $0{\cdot}02M$-$K_3Fe(C_2O_4)_3$ + $0{\cdot}1M$-$K_2C_2O_4$. Owing to the internal light filter effect of the ferro-oxalate produced during the reaction, it was insufficient merely to measure the total absorbed light and the total decomposition at the two working temperatures (22° and 52°); a knowledge of the variation with temperature of the extinction coefficients of reactant and resultant was necessary.

For 22°, we used the molecular extinction coefficients obtained by Allmand and Webb employing the spectrometer–thermopile–galvanometer method, by which our measurements were also made. The changes in extinction caused by raising the temperature to 52° (a solution of potassium ferrioxalate darkens perceptibly when thus heated) were determined by immersing the cell in a small thermostat, similar to that used by Allmand and Style (J., 1930, 603) in work on the temperature coefficient of hydrogen peroxide photolysis, and fitted in front of the spectrometer. A 5-cm. cell was used throughout, and the concentration of the solution varied from wave-length to wave-length in order to ensure a suitable degree of transmission. By adjusting a resistance in series with the electric heater, the temperature could be kept constant well within 1° whilst transmission measurements were being made. Four readings were taken at intervals between room temperature and about 58°, and the value for 52° was obtained by interpolation.

The transmissions of solutions of both salts for 436 $\mu\mu$ and 405 $\mu\mu$ were found to fall off linearly as the temperature was raised, the percentage change being greater for potassium ferri- than for ferro-oxalate. There was no perceptible alteration with 365 μμ. Owing to the negligible value of the internal light filter correction with 313 μμ (α for ferri- and for ferro-oxalate respectively 1600 and 105 at room temperature), no measurements were made with that line. From these relative transmissions and the data for 22°, the decadic molecular extinction coefficients for 52° were calculated. Table I contains the data for both temperatures, as used in the subsequent γ determinations.

TABLE I.

	$K_3Fe(C_2O_4)_3$.		$K_2Fe(C_2O_4)_2$.	
	22°.	52°.	22°.	52°.
365 μμ	720	(720)	145	(145)
405 μμ	121	145	98	102
436 μμ	20·5	26·6	50	61·5

Measurements of quantum efficiency were then carried out with the above three lines at both temperatures. The light filters employed were as described elsewhere (Allmand and Young, *loc. cit.*). The filter used for 313 μμ light (containing potassium chromate and *p*-nitrosodimethylaniline—see Allmand and Spinks, this vol., p. 1652) passed both green and yellow light in considerable amounts; further, the energy distribution in the lamp used had not been determined at the time of the experiments. Consequently, thermopile measurements were omitted, and we merely determined the relative rates of decomposition under conditions identical in the two cases except for temperature. It had been shown, during the experiments on the effect of temperature on extinction, that no perceptible absorption of the mercury green and yellow lines took place at 52°, and as absorption of the 313 μμ line was complete with the solution used, the ratio of the rates of decomposition will also be that of the quantum efficiencies. In all cases the solutions were taken to approximately the same degree of decomposition, *viz.*, 8—12%, the time required for this being 15—30 hours. It was shown that there was no perceptible dark decomposition at 52° in 48 hours. Table II contains the γ values at both temperatures for the three less refrangible mercury lines.

TABLE II.

	22°.	52°.
365 μμ	1·07, 1·03 (1·16)	1·18, 1·16
405 μμ	0·86 (0·91)	1·11, 1·01
436 μμ	0·83, 0·79 (0·89)	0·99, 0·99

The figures in parentheses are those obtained by Allmand and Webb at room temperature. The agreement is satisfactory, particularly when the differences in experimental technique are considered.

The velocities observed with the 313 $\mu\mu$ line, given in arbitrary units, were as follows :

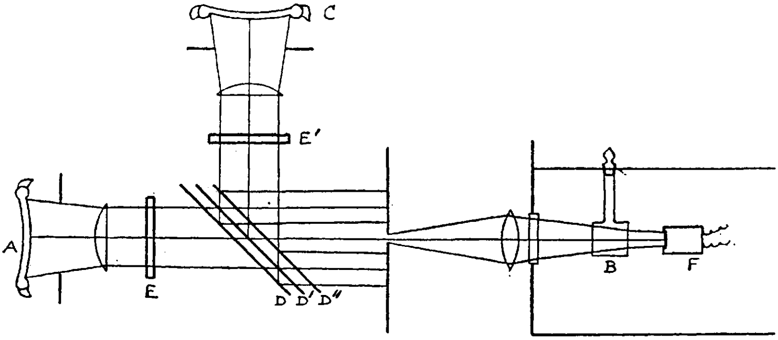
22°	52°
2·02, 2·03	2·16, 2·20, 2·24

One obviously erroneous (very high) figure at 52° has been omitted. The cube root of the ratios of the γ (or velocity) values at 52° and at 22° gives the temperature coefficients, the results being contained in Table III.

Table III.

λ	313 $\mu\mu$	365 $\mu\mu$	405 $\mu\mu$	436 $\mu\mu$
Temp. coeff.	1·029	1·039	1·057	1·060

Fig. 1.



Experiments with Dichromatic Light.—Whereas Allmand and Webb, in their experiments in this connexion, used glass filters of which the majority passed appreciable amounts of three of the mercury lines, in our work we have employed mixtures of two rays only. Moreover, in all except one of our experiments, we obtained the dichromatic light by the superposition of two monochromatic light beams (Fig. 1). Two lamps were used, the beam from the first (*A*) falling on the front face of the reaction-cell *B* in the usual manner. The second lamp *C* was placed to one side, at right angles to the first, and its beam was partially reflected into the cell by means of three parallel thin clear glass plates *D*, *D′*, *D″*, placed at an angle of 45° with either beam. These plates, of course, weakened in a similar way the intensity of the beam of the first lamp. A monochromatic light filter (*E*, *E′*) was interposed in front of either lamp, and the arrangement of diaphragms and lenses was such that the two beams were completely superposed before entering the reaction vessel. The intensities of the two beams incident on the cell were measured separately by the thermopile *F*, and their sum was shown to be equal to the total incident intensity when both lamps were simultaneously in use. One experiment (the last in the table) was carried out by the method of Allmand and Webb, using the same G. 586 A Corning filter employed by them in their Expt. 19. Our results are set out in Table IV. The calculated figures for the extent of reaction are based on the average γ values at 22° given in Table II.

TABLE IV.

Quanta absorbed by ferrioxalate per hour $\times 10^{-18}$.			Duration of run,	Decomposition,	Mols. reacted $\times 10^{5}$.		Ratio,
365 $\mu\mu$.	405 $\mu\mu$.	436 $\mu\mu$.	hours.	%.	Calc.	Found.	found/calc.
1·15	—	0·249	22·25	12·0	5·17	5·82	1·13
0·587	—	0·566	22·58	11·2	4·01	5·41	1·35
0·073	—	1·43	21·67	10·6	4·43	5·14	1·16
0·439	—	1·01	17·67	10·5	3·73	5·08	1·36
—	0·716	0·374	45·50	16·0	6·92	7·75	1·12
—	0·177	1·11	22·25	7·52	3·86	3·63	0·94
0·735	0·131	—	20·17	6·24	2·94	3·01	1·02
0·223	0·548	—	47·50	12·4	5·53	6·00	1·08
7·61	1·15	—	4·37	15·5	6·47	7·50	1·16

With one exception, the observed velocities lie above those calculated, thus qualitatively confirming the earlier work. Quantitatively, the effects are somewhat smaller than those previously reported; for instance, with the G. 586 A filter, Allmand and Webb found a velocity 24% in excess of that calculated, whereas we only get 16%. We estimate our normal experimental error as not exceeding 5%. It may well, however, have been greater in this work with dichromatic light, so, although the effects in the cases of the second and fourth experiments in the table lie far outside this limit, it is clear that more precise experiments, including measurements of light actually absorbed, are desirable.

We have two further experiments to record under this head. The first was an attempt to see whether light which is inappreciably absorbed by the photolyte is capable of "stimulating" the molecules of the latter in the sense suggested by Allmand and Webb as an explanation of their "mixed light" effect, and thus causing an increased quantum efficiency. A solution of potassium ferrioxalate was insolated by two beams of monochromatic light, one, of 365 $\mu\mu$, entering the cell from the front, the other, of 546 $\mu\mu$, obtained from a second quartz-mercury lamp by using the filter combination described elsewhere (Allmand and Young, *loc. cit.*), entering from the back, through a second thermostat window. A slight increase in the velocity was observed when the green mercury line was allowed to enter the cell, but it amounted to only a few units %, and was within the probable experimental error.

The second experiment was a determination of the temperature coefficient of the reaction when using the G. 586 A filter already mentioned. Measurements at 22° and 52°, carried out just as those already described, led to the conclusion that the temperature coefficient is "negative." The actual values obtained, referred to a rise in temperature of 10°, were 0·95, 0·96, and 0·98. In every case, the fraction decomposed was about 12%. The absorption of the active wave-lengths was practically complete. The small correction due to the rather higher proportion of active light absorbed by the ferrioxalate at the higher temperature has not been made—its effect would be to depress the mean figure of 0·96 still lower. This remarkable result will be further investigated, and is given at present with due reserve. If confirmed, and found to be characteristic of photolysis with polychromatic light, it will clearly have an important bearing on the mechanism of such reactions.

A discussion of the different temperature coefficients recorded in this paper has already appeared elsewhere (Young and Style, *Trans. Faraday Soc.*, 1931, **27**, 493).

The Photo-reduction of Ferric Chloride by Oxalic Acid in Aqueous Solution.

We have already mentioned that an investigation of this reaction by Kornfeld has given results which differ completely from those obtained by Allmand and Webb for the photolysis of potassium ferrioxalate. In particular, she finds that the reaction (*a*) obeys the $I^{0\cdot5}$ law, whether with white light or with the monochromatic mercury lamp lines; (*b*) is a chain reaction with measured γ values as high as 600; (*c*) is retarded by ferrous ions and, in consequence, very soon comes to a standstill, at all events in monochromatic light. This last statement is particularly striking, for in a careful study of the same reaction by Lemoine (*Ann. Chim.*, 1895, **6**, 433, particularly pp. 482 *et seq.*), there is no indication of any such effect; indeed the author states (p. 433) that the solution "se décompose jusqu'à épuisement." Using the same general technique as employed above, we have done a few experiments in order to test these conclusions of Kornfeld, but are unable to confirm any of them under our conditions of work.

(i) *The Effect of Intensity.*—A solution of composition $0\cdot0523M\text{-FeCl}_3 + 0\cdot0162M\text{-H}_2\text{C}_2\text{O}_4$ was insolated in the full light of the quartz–mercury lamp, the intensity of the beam being varied by wire-gauze screens which had been calibrated by means of a thermopile and galvanometer. Care was naturally taken to avoid any projection of the pattern of the screens used on the reaction cell, *i.e.*, to obtain a true intensity variation. The degree of decomposition was about 10% in every case. Table V contains the results, which show proportionality between velocity and intensity.

TABLE V.

Relative intensity.	Percentage of oxalic acid oxidised per hour.	$\frac{\text{Velocity}}{\text{Intensity}}$.
0·16	1·23	7·7
0·35	2·83	8·1
0·48	3·89	8·1
1·00	7·5	7·5

(ii) *The Quantum Efficiency.*—A single determination was carried out in the usual manner at 22° with 365 $\mu\mu$ light, the initial composition of the solution being as above. For a degree of decomposition of 7·95%, γ, uncorrected for light absorbed by the ferrous salt produced, was found to be 0·49.

(iii) *The Course of the Reaction and the Influence of Added Ferrous Salt.*—The same solution was used and insolated in the full light of the lamp for various lengths of time, the whole contents of the cell being subsequently analysed. Table VI (*a*) contains the results. Complete reaction of all oxalic acid would correspond to a decrease in titre of 16·87 c.c. of titanous chloride solution.

TABLE VI.

Time, hours.	Decrease in titre of solution, c.c.	Time, hours.	Decrease in titre of solution, c.c.
	(*a*)		(*b*)
0·48	0·92	1·92	3·15
1·68	3·55	14·2	15·35
4·61	7·73		
16·0	15·92		

Two similar experiments were carried out with solutions to which some ferrous ammonium sulphate had been added at the start, the initial ferrous sulphate concentrations being in both cases 0·00362*M*, those of ferric chloride and of oxalic acid remaining unaltered. The results are given in Table VI (*b*). If the four points of Table VI (*a*) be plotted, they fall on a normal curve showing no signs of autoretardation, and indicating that the reaction would be complete after about 22 hours. Whilst the first point in Table VI (*b*) might, by itself, be taken as affording evidence of retardation by $Fe^{\cdot\cdot}$ ions, the second falls well on the curve corresponding to Table VI (*a*), and it is probable that the ferrous salt has no other than a small internal light-filter effect. A second series of experiments gave results confirming those recorded in Table VI.

As stated, we followed the course of the reaction by titration with titanous chloride, whilst Kornfeld, except for very dilute solutions, used Lemoine's method, which Allmand and Webb found to be unsatisfactory, giving too low ferrous salt titration figures, and therefore too small values for the extent of reaction. It would, however, seem unlikely that this could be the cause of the discrepancy. Kornfeld's experiments with dispersed monochromatic light were probably carried out with considerably lower intensities than was the case in our work, and as she finds the maximum amount transformed (independent of concentration) to be proportional to the square root of the absorbed energy, this might perhaps be responsible for the difference between the nature of her results and those of Lemoine and our own. But it could hardly account for the difference between the results of our work and hers when using the full light of the quartz–mercury lamp (an $I^{1\cdot 0}$ and an $I^{0\cdot 5}$ reaction respectively).

We carried out two further experiments on this reaction. Three samples of a solution were insolated separately and successively with monochromatic light of wave-lengths 365 μμ and 546 μμ and with both beams simultaneously, using the experimental arrangement already described. The results indicated the action of the two rays to be additive or nearly so; if not additive, the sum of the effects of the two rays taken singly is rather *greater* than their effect in conjunction, in qualitative agreement with the results of Padoa and Vita (*Gazzetta*, 1924, **54**, 147). There is certainly no sign of the reverse effect as found in the case of potassium ferrioxalate photolysis. It may be mentioned that, in the present reaction and under our experimental conditions, the total effect of the 546 μμ mercury line was two to three times that of the 365 μμ line.

We also determined the temperature coefficients for these two lines, using a solution 0·0933*M*-$FeCl_3$ + 0·0162*M*-$H_2C_2O_4$. For 546 μμ, a correction due to increased extinction coefficient at 52° compared with 22° was necessary, the absorptions with a 5-cm. cell being respectively 0·843 and 0·819 of the incident light. The 365 μμ radiation was completely absorbed, and the temperature coefficient, referred to 10°, was 1·030. For 546 μμ, the uncorrected figure was 1·14, and, corrected for the increased absorption, 1·10.

We have not done sufficient experimental work to justify a detailed discussion of this reaction. It may, however, be pointed out that the mechanism

(1) $Fe^{\cdots} + h\nu \longrightarrow Fe^{\cdots *}$
(2) $Fe^{\cdots *} + C_2O_4'' \longrightarrow Fe^{\cdot\cdot} + C_2O_4'$
or (2*a*) $Fe^{\cdots *} + H_2C_2O_4 \longrightarrow Fe^{\cdot\cdot} + 2H^{\cdot} + C_2O_4'$
(3) $C_2O_4' + Fe^{\cdots} \longrightarrow Fe^{\cdot\cdot} + 2CO_2$

would account for our results. The unstable C_2O_4' ion is that postulated by Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307) as intermediate product in the iodine–potassium oxalate reaction. The corresponding mechanism for the photolysis of potassium ferrioxalate, *viz.*,

(*a*) $Fe(C_2O_4)_3''' + h\nu \longrightarrow Fe(C_2O_4)_2'' + C_2O_4'$
(*b*) $C_2O_4' + Fe(C_2O_4)_3''' \longrightarrow Fe(C_2O_4)_2'' + C_2O_4'' + 2CO_2$

was rejected by Allmand and Webb, on the ground that accumulation of ferrous oxalate in the solution during the experiment is not found to retard the reaction by reversal of (*a*). A similar objection, *i.e.*, no sign of reversal of (2), could of course be raised in the present instance. The validity of this view is, however, doubtful when it is realised that Berthoud and Bellenot explain the mechanism of the iodine–potassium oxalate reaction very satisfactorily by ascribing to the C_2O_4' ion reducing, but not oxidising, properties. Moreover, chloride ions retard the present reaction (Lemoine, *loc. cit.*, pp. 515, 516), but accelerate the decomposition of potassium ferrioxalate (Allmand and Webb, *loc. cit.*), and evidence exists which points to this difference in behaviour being associated with photo-reactions whose primary stages are respectively the activation and the decomposition of the absorbing molecule. On the whole, we suggest the above schemes as representing most satisfactorily the reactions discussed in this paper.

Summary.

1. The temperature coefficients of the quantum efficiencies in the photolysis of aqueous potassium ferrioxalate solutions were determined for light of wave-lengths 313 μμ, 365 μμ, 405 μμ, and 436 μμ. They are small, and rise with increasing wave-length.

2. In qualitative agreement with earlier work, it is found that the effect of two monochromatic rays acting simultaneously is greater than the sum of their effects when acting separately. Under such conditions, the temperature coefficient is " negative."

3. In disagreement with the published work of Kornfeld, the photo-reduction of ferric chloride by oxalic acid in aqueous solution is found to proceed at a rate proportional to the intensity, not to be retarded by ferrous ions, and to have a quantum efficiency of the order of unity.

4. The results are briefly discussed.

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