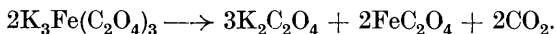


CXCVII.—*The Photolysis of Potassium Ferrioxalate Solutions. Part I. Experimental.*

By ARTHUR JOHN ALLMAND and WALTER WESTON WEBB.

WHEN aqueous solutions of potassium ferrioxalate are insolated by light from a quartz-mercury lamp, decomposition takes place as follows :



The difficultly soluble ferrous oxalate is precipitated, but this can be prevented if a sufficient concentration of potassium oxalate be added to the original solution. No quantitative investigation of this reaction has been hitherto carried out, although the corresponding photolyses of potassium cobaltioxalate (Vranek, *Z. Elektrochem.*, 1917, **23**, 336) and of potassium manganioxalate (Ghosh and Kappanna, *J. Indian Chem. Soc.*, 1926, **3**, 127) have received attention. Draper (*Phil. Mag.*, 1857, **14**, 161) showed that solutions of ferric oxalate itself undergo a similar decomposition in light, and suggested its application in photometry; and work has also been published on the closely related interaction between solutions of ferric chloride and oxalic acid in light, more particularly by Lemoine (*Ann. Chim.*, 1895, **6**, 433) and, very recently, by Kornfeld (*Z. Elektrochem.*, 1928, **34**, 598). Kornfeld's results are of quite a different nature from ours, whereas Lemoine's are, in some respects, similar. Experiments are in progress in this laboratory on the factors which cause the one type of reaction to change over to the other. In the meantime, the present paper contains essentially the results of an investigation of the energetics of the potassium ferrioxalate decomposition, which are discussed in the succeeding paper.

Preliminary Experiments.—As it was hoped to experiment with solutions of the free ferrioxalic acid, ferric oxalate was prepared by the action of an excess of freshly precipitated and washed ferric hydroxide on aqueous oxalic acid. A week's standing at the ordinary temperature with occasional shaking was necessary for neutralisation. After filtration from the excess of ferric hydroxide, the greenish-yellow solution was evaporated on the water-bath. The syrup produced finally set to a yellowish-green, transparent, hygroscopic solid, which gave analyses corresponding closely to the formula $\text{Fe}_2(\text{C}_2\text{O}_4)_3$. The ferrioxalate was prepared by mixing solutions of potassium oxalate and ferric chloride in the molecular ratio 3 : 1, and precipitating the salt with alcohol. The emerald-green crystalline powder, once recrystallised, on analysis corresponded closely to the formula $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$.

Preliminary insolutions of solutions of these substances were then

undertaken in order to determine the conditions for avoiding precipitation of ferrous oxalate, important for the success of quantitative energy measurements. Solutions of ferric oxalate (0.02—0.06*M*) in oxalic acid (0.1—0.7*M*) invariably precipitated this solid; so did solutions containing potassium ferrioxalate alone, but when enough potassium oxalate was present, precipitation was prevented. The concentrations of these two components were varied between the limits of 0.01—0.08*M* and 0.1—0.8*M*, respectively. Except for the mixture 0.08*M*- $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ + 0.1*M*- $\text{K}_2\text{C}_2\text{O}_4$, there was no visible precipitation of ferrous oxalate. All our further insolation experiments were carried out with solutions of the ferrioxalate containing a sufficient excess of potassium oxalate.

In order to obtain some idea of the nature of the ions present in these solutions, conductivity measurements were carried out at 25.2°. The results, for which no great accuracy is claimed, are in Tables I and II. Satisfactory data for the most dilute ferrioxalate solutions were only obtained if light was carefully excluded to avoid photolysis.

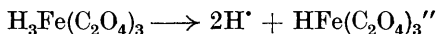
TABLE I.

| $\text{H}_3\text{Fe}(\text{C}_2\text{O}_4)_3$. | |
|---|---------|
| Molarity. | μ . |
| 0.05256 | 740.5 |
| 0.02628 | 777.0 |
| 0.01314 | 819.0 |
| 0.00657 | 849.2 |
| 0.00328 | 858.2 |
| 0.00164 | 858.3 |

TABLE II.

| $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$. | |
|---|---------|
| Molarity. | μ . |
| 0.02 | 312 |
| 0.01 | 339 |
| 0.004 | 357 |
| 0.001 | 410 |
| 0.0004 | 424 |
| 0.0002 | 436 |

It is difficult to reconcile these data. As the hydrogen-ion mobility at 25.2° is about 350, the figures for the acid suggest (1) that the dissociation constants for the first two stages (K_1 , K_2) are high, but for the third stage (K_3) comparatively low, (2) that dissociation in accordance with the equation



is practically complete at 0.003*M*, and (3) that the observed limiting molecular conductivity value of about 860 corresponds to a mobility of $\frac{1}{2}\text{HFe}(\text{C}_2\text{O}_4)_3''$ of about 80 [compare $l=95$ for $\frac{1}{4}\text{Fe}(\text{CN})_6''''$ at 18°]. But if K_3 is so low, then there should be appreciable hydrolysis of the ferrioxalate ions in potassium ferrioxalate solutions, which suggests itself as a possible cause of the steady rise in μ for the salt at dilutions considerably greater than those at which μ for the acid is already practically constant. An attempt was made to calculate K_3 and the degree of hydrolysis of the salt from the experimental data and the known value of K_w , assuming (*a*) that primary dissociation of the salt into potassium and ferrioxalate ions is complete

at 0.0002M, and (b) that the l values for H^+ , K^+ , and OH^- are 350, 75, and 220 respectively, and those for $\frac{1}{3}Fe(C_2O_4)_3'''$ and $\frac{1}{2}HFe(C_2O_4)_3''$ are identical; this, however, led to the results (i) that l for the complex ions is about 70.3 and not 80, (ii) that K_3 is fairly high (7×10^{-2}), and (iii) that hydrolysis of the salt at 0.0002M is quite negligible. Whilst these conclusions are naturally in accordance with the particular conductivity measurements from which they were derived, they are quite at variance with the general trend of the data, leading, as they do, to the conclusion that, at the greatest dilutions, μ for the acid should still be rising, whilst μ for the salt should be nearly constant. On the whole, we think that the data for the free acid solutions (made by mixing ferric oxalate and oxalic acid solutions in the molecular ratio 1 : 3) must be in error, and that the potassium ferrioxalate solutions ionise by steps, without hydrolysis, the value of l for $\frac{1}{3}Fe(C_2O_4)_3'''$ being at least 80, if not higher. In any case, such solutions, as also those of the free acid, are practically free from ferric ions, as shown by the absence of any coloration with ammonium thiocyanate solution.

Analytical Method.—We first investigated the possibility of using the method employed by Lemoine (*loc. cit.*) for insolated mixtures of ferric chloride and oxalic acid, *viz.*, precipitation of unchanged ferric iron and of oxalic acid by an excess of calcium carbonate, and titration of the acidified filtrate for ferrous iron by permanganate. With ferric chloride-oxalic acid mixtures, the results were not particularly satisfactory, low figures for ferrous iron always being obtained. These were at first ascribed to oxidation of the neutral solution during filtration, and an improvement was effected by carrying out precipitation, filtration, and washing in an atmosphere of nitrogen. Even then the results were low, a fact attributed to adsorption of ferrous ions on the large amount of precipitate present. The next method tried was reduction of the ferric iron remaining after the reaction to the ferrous condition, followed by titration of the whole solution with permanganate. The employment of zinc and sulphuric acid was found to be impossible owing to the reduction of some of the oxalic acid present to glyoxylic acid. The use of hydrogen sulphide proved very tedious, so recourse was finally had to direct titration of residual ferric iron by a dilute hydrochloric acid solution of titanous chloride, using thiocyanate as indicator, and working in an atmosphere of carbon dioxide. This method proved successful. A series of experiments showed that potassium oxalate, whatever its concentration, had no effect on the results.

Extinction Coefficients.—These were determined for both potassium ferri- and ferro-oxalate, in order to correct for any internal light-filter effect of the latter when formed during reaction. The

apparatus used comprised an ultra-violet spectrometer (Hilger), thermopile (Hilger), and galvanometer (Paschen, of maximum sensitivity 10^{-10} amp. per mm. deflexion with scale at 1 m.). The light source was a quartz-mercury lamp, and the absorption cells were constructed from rectangular glass blocks and crystal-quartz plates, as previously described (J., 1925, **127**, 829). A 5-cm. water cell of the same type was placed in front of the lamp to reduce the purely thermal effect of the beam. When in use, the absorption cells were mounted on a sliding carriage between two water-cooled copper screens, each provided with a variable aperture and a water-cooled shutter. A ratchet arrangement allowed of different parts of the surface of the cell being in turn interposed between the beam of light and the slit of the spectrometer. This was found very necessary when working with dilute solutions which were subject to appreciable photolysis during the time required for making the measurements. The intensity of the radiation was controlled, when required, by varying the distance between the lamp and the spectrometer—occasionally a quartz lens was necessary between the lamp and the first screen in order to raise the intensity sufficiently. All definitive measurements were made at night, in order to reduce to a minimum electrical and, particularly, mechanical disturbances, which rendered impossible the use in the daytime of the Paschen galvanometer at full sensitivity.

The absorption of a 0.25*M*-potassium oxalate solution was first measured in a 0.5-cm. cell, as an excess of this salt was present during all quantitative insolutions. The wave-lengths of the lines used and the transmissions (compared with water as 100) were as follows :

| | | | | | | | | |
|----------------------|------|------|------|------|------|-----|-----|-----|
| Line, $\mu\mu$ | 365 | 313 | 303 | 290 | 280 | 265 | 254 | 248 |
| Transmission, % | 99.3 | 96.6 | 93.6 | 81.9 | 64.4 | 6.2 | 0 | 0 |

Preliminary experiments with potassium ferrioxalate solutions showed that a 0.049*M*-solution in a 5-mm. layer absorbed practically all incident light between 405 $\mu\mu$ and 249 $\mu\mu$ (the limit of possible measurement with our experimental arrangement) and also the bulk of the blue 436 $\mu\mu$ line, but hardly affected the mercury green and yellow lines. In order to obtain satisfactory values for extinction coefficients by this method, it is desirable that the cells should transmit between one- and two-thirds of the incident light. Consequently, several preliminary measurements were carried out until the dilutions and thicknesses required for this were found. (It was during these experiments that the necessity, mentioned above, of reducing to a minimum the exposure to light of the more dilute solutions was discovered.) These conditions having been determined, the definitive readings were made, including some on solu-

tions containing various added quantities of potassium oxalate. The results are in Table III, of which the last column contains the molecular extinction coefficient of potassium ferrioxalate, calculated from the equation $\log_{10} I_0/I = kcd$, c being expressed in mols./litre and d in cm.

TABLE III.

| Line, $\mu\mu$. | Cell. | Conc. of $K_3Fe(C_2O_4)_3$. | Conc. of $K_2C_2O_4$. | Ratio of concs. | k . |
|---------------------|---------|---------------------------------|---------------------------|--------------------|-------|
| 313 | 0.5 cm. | 0.000196 | — | — | 1620 |
| | 1.0 | 0.000125 | — | — | 1573 |
| 365 | 0.5 | 0.00125 | — | — | 698 |
| | 0.5 | 0.00125 | 0.025 | 20 | 720 |
| | 0.5 | 0.00125 | 0.25 | 200 | 722 |
| | 0.5 | 0.00025 | 0.05 | 200 | 737 |
| | 0.5 | 0.00098 | — | — | 722 |
| 405 | 2.0 | 0.00125 | — | — | 125 |
| | 0.5 | 0.0049 | — | — | 123 |
| | 1.0 | 0.00196 | — | — | 112 |
| | 2.0 | 0.00125 | 0.025 | 20 | 119 |
| | 2.0 | 0.00125 | 0.25 | 200 | 127 |
| 436 | 0.5 | 0.0245 | — | — | 20.7 |
| | 1.0 | 0.025 | — | — | 20.2 |

Similar experiments were carried out with potassium ferro-oxalate solutions, containing in every case an excess of potassium oxalate, and prepared by insolating solutions of the ferrioxalate (in absence of oxygen, see later) to complete decomposition, as shown by a negative test with thiocyanate solution after subsequent strong acidification. The final results are summarised in Table IV.

TABLE IV.

| Line, $\mu\mu$. | Cell. | Conc. of $K_2Fe(C_2O_4)_2$. | Conc. of $K_2C_2O_4$. | Ratio of concs. | k . |
|---------------------|---------|---------------------------------|---------------------------|--------------------|-------|
| 313 | 1.0 cm. | 0.00125 | 0.026 | 21 | 105 |
| 365 | 2.0 | 0.00125 | 0.251 | 201 | 155 |
| | 2.0 | 0.001 | 0.051 | 51 | 146 |
| | 0.5 | 0.005 | 0.255 | 51 | 143 |
| | 0.5 | 0.005 | 0.105 | 21 | 143 |
| | 1.0 | 0.00125 | 0.026 | 21 | 117 |
| | 2.0 | 0.001 | 0.021 | 21 | 107 |
| 405 | 0.5 | 0.005 | 0.255 | 51 | 117 |
| | 2.0 | 0.001 | 0.051 | 51 | 105 |
| | 0.5 | 0.005 | 0.105 | 21 | 96 |
| | 2.0 | 0.00125 | 0.026 | 21 | 76 |
| | 2.0 | 0.00125 | 0.026 | 21 | 70 |
| 436 | 0.5 | 0.005 | 0.255 | 51 | 65 |
| | 0.5 | 0.005 | 0.105 | 21 | 56 |
| | 2.0 | 0.00125 | 0.026 | 21 | 38 |

It will be noticed that, whilst k for the ferrioxalate rises rapidly with decrease of wave-length, the curve for the ferro-oxalate is flatter, and k shows signs of passing through a maximum in the

region 313—365 μ . The correction for the internal light-filter effect is obviously a very important one at 436 μ and becomes less as wave-length decreases. The effect of added potassium oxalate differs markedly in the two cases; whereas the k values of the ferrioxalate remain practically unaffected, those for the ferro-oxalate are considerably increased by the addition, as they also are by increase in concentration. This is in accord with what is known of the relative stability of the two complex ions.

Effect of Oxygen on the Reaction.—The photolysis of Eder's solution (Jodlbauer and Tappeiner, *Ber.*, 1905, **38**, 2602), of ferric oxalate (Jodlbauer, *Z. physikal. Chem.*, 1907, **59**, 513), and of other ferric salts of organic acids (Winther and Oxholt-Howe, *Z. wiss. Phot.*, 1914, **14**, 196) is stated to be retarded by oxygen. On the other hand, the photoreaction between uranyl nitrate and oxalic acid is not thus affected (Boll and Henri, *Compt. rend.*, 1914, **158**, 32). Indeed, the last authors found oxygen to take part in the reaction, oxidising the uranous salt as the latter was produced by photolysis. To test its action in the present case, experiments were carried out, a solution of composition $0.03M\text{-K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 + 0.09M\text{-K}_2\text{C}_2\text{O}_4$ being used. This was contained in a cell with plane quartz ends, and insulated by the full light of a quartz-mercury lamp brought to a focus by a quartz lens. In the first experiment, the solution was air-free, and carbon dioxide was kept continuously bubbling through it; in 3 hours, the decomposition was 17.4%. A further identical sample, containing dissolved air, was insulated under identical conditions, except that the carbon dioxide stream was dispensed with. The decomposition was then 15.9%. Finally, a third sample was insulated in the same fashion, but with a current of oxygen bubbled continuously through it. The titanous chloride titre after the experiment was unchanged.

This complete inhibition of the reaction, as followed, was either real, or merely apparent and due to the reoxidation by the oxygen of the ferrous salt formed by insolation, as found by Boll and Henri for the uranyl nitrate-oxalic acid reaction. To test this point, the last experiment was repeated in a somewhat modified form. The oxygen stream, before entering the cell, was freed from carbon dioxide by a column of soda-lime, and, on leaving the cell, passed through a U-tube containing a mixture of glass-wool and phosphoric oxide (to hold up any spray containing potassium oxalate) and into a test-tube containing baryta water, protected by a soda-lime guard tube at the end of the train. A blank experiment (no insolation) gave no indication of any precipitate in the baryta. When insolation was commenced, gradual formation of such a precipitate was noticed. This was very marked after an hour's run, and, on test,

proved to consist of barium carbonate. While oxygen may or may not retard the reaction (we did not investigate the matter further), it certainly affects our method of following it, and was consequently rigorously excluded during quantitative work.

Apparatus for Quantum Efficiency Determinations.—The optical system, mercury-vapour lamps, and methods of thermopile calibration and of energy measurement were identical with those used by us in our work on the photolysis of sodium hypochlorite solutions (*Z. physikal. Chem.*, 1928, **131**, 189). The insolation cell was of the type used in the extinction measurements, drilled out of a block of glass (10 × 10 × 1 cm.), with plane parallel crystal-quartz plates cemented by hard pitch on to the two ends of the central cavity (7.5 cm. in diameter). Two vertical channels in the top of the glass block gave access to the interior of the cell, and into each was cemented a glass tube. One of the latter (B), situated in the centre of the cell, ended flush with the upper surface of the cylindrical central cavity; the other (A), passing through a hole nearer the side of the cell, was drawn out to a fine tip, and curved so as to reach practically to the bottom of the cell. A steady stream of carbon dioxide from a Kipp generator passed through a splash-trap, a flow-meter, a bubbler containing titanous chloride solution to remove traces of oxygen and of acid, a water bubbler, and then into the cell *via* a ground glass joint and A, leaving *via* B (another ground joint), and passing out to the air through a water bubbler. This simple arrangement, which proved very satisfactory in practice, guaranteed the absence of oxygen during the insolation and also effected stirring. It may be added that all solutions were made from previously boiled, air-free water, saturated with carbon dioxide when still warm, and were freshly prepared for each run.

In calculating the values of γ given later, all necessary corrections were applied for reflexion from quartz surfaces, for gradual change of total absorption with time, and for change in proportion of effective absorption, due to the formation of increasing amounts of ferro-oxalate. The last correction was very small with the 313 and 365 $\mu\mu$ rays, but considerable with the 436 $\mu\mu$ line. Thus, at the end of a run with this line, about one-third of the total light absorbed was normally being taken up by the ferro-oxalate.

Monochromatic Light Filters.—The transmissions of a number of filters were examined, the same apparatus being used as in the extinction-coefficient work. Those involving solutions were set up in cells of the same general construction as used in the latter experiments. The filters finally employed were as follows, transmissions being expressed as percentages of light incident on the complete filter :

| Mercury line. | Filter. | Transmission. |
|---------------|--|--|
| 313 $\mu\mu$ | 0.5 Cm. of 0.00376% <i>p</i> -nitrosodimethylaniline + 0.0486% K_2CrO_4 . Crystal quartz end plates. | 303 $\mu\mu$ 10% 313 28 546 80.5 579 86.5 |
| 365 $\mu\mu$ | Corning glass filter, G. 586-AW, 0.73 cm. thick. | 14% |
| 405 $\mu\mu$ | (a) 0.5 Cm. of 0.02% quinine bisulphate; (b) 0.5 cm. of 0.0125% Diamant Fuchsin. Two compartment cell. Glass end and separating plates. | 26% |
| 436 $\mu\mu$ | (a) 0.5 Cm. of 4% quinine bisulphate; (b) 0.5 cm. of 0.085% Victoria Blue (Cassella). Compound cell as for 405 $\mu\mu$. | 59% plus trace of red light. |

In the case of the 313 $\mu\mu$ filter, the green and yellow lines were completely transmitted, and the two shorter lines completely absorbed, by the potassium ferrioxalate solutions. As, however, the ratio of absorbed to unabsorbed radiation was low, it was thought more accurate not to determine the former by direct measurement, as in the other cases, but to calculate it from the total intensity of the filtered beam, the energy distribution in the unfiltered beam, and the filter transmissions just given. The 365 $\mu\mu$ and 405 $\mu\mu$ filters passed no measurable amount of any other ray. The maximum intensity obtained with the 365 $\mu\mu$ filter, when concentrated on the 2 cm. Moll thermopile, was about 2 H.K. The red light passed by the blue filter was shown to be unabsorbed by the ferrioxalate solutions. It may be added that a large number of measurements were carried out, solutions of Diamant Fuchsin being used as filter for the 365 $\mu\mu$ ray, but were found to be useless owing to a gradual change in the filter due to the action of light.

Effect of Potassium Oxalate on Rate of Reaction.—By use of monochromatic 365 $\mu\mu$ light, duplicate insolutions were carried out with 0.03*M*-potassium ferrioxalate plus either 0.09*M*- or 0.72*M*-potassium oxalate solutions. The percentage decompositions after 3 hours' insolation were 17.30, 17.40 and 15.65, 15.70, respectively. An eight-fold increase in the potassium oxalate concentration thus causes a fall in velocity of nearly 10%. In all the γ measurements given subsequently, the concentration of added potassium oxalate was kept at 0.18*M*.

Results of Quantum-efficiency Determinations with Monochromatic Light.

The first point tested was the effect of the concentration of potassium ferrioxalate. Measurements were carried out with both 365 $\mu\mu$ and 436 $\mu\mu$ light. The results are in Table V, (i) and (ii), where $\gamma = \frac{28470}{\lambda} \cdot \frac{\text{mols. decomposed}}{\text{cals. absorbed}}$, λ being expressed in terms of μ .

TABLE V.

| Expt. No. | Conc. of $K_3Fe(C_2O_4)_3$. | Duration of insolation, hours. | Decomposition, %. | Mean active absorption (cals./hour). | Mols. decomposed per hour $\times 10^6$. | γ . |
|----------------------|------------------------------|--------------------------------|-------------------|--------------------------------------|---|------------|
| (i) 365 $\mu\mu$. | | | | | | |
| 1 | 0.02 | 19.33 | 10.6 | 0.315 | 4.76 | 1.18 |
| 2 | 0.02 | 22.33 | 11.8 | 0.291 | 4.42 | 1.18 |
| 3 | 0.04 | 23.33 | 7.52 | 0.364 | 5.35 | 1.15 |
| 4 | 0.06 | 21.25 | 3.42 | 0.296 | 4.18 | 1.11 |
| 5 | 0.06 | 41.17 | 6.72 | 0.280 | 4.225 | 1.17 |
| (ii) 436 $\mu\mu$. | | | | | | |
| 6 | 0.02 | 21.50 | 14.1 | 0.412 | 5.69 | 0.90 |
| 7 | 0.04 | 21.66 | 9.20 | 0.553 | 7.34 | 0.87 |
| 8 | 0.06 | 44.66 | 11.1 | 0.467 | 6.48 | 0.91 |
| (iii) 405 $\mu\mu$. | | | | | | |
| 9 | 0.02 | 22.33 | 12.2 | 0.364 | 4.70 | 0.91 |
| (iv) 313 $\mu\mu$. | | | | | | |
| 10 | 0.02 | 41.58 | 23.0 | 0.272 | 4.77 | 1.59 |

It is clear that γ is independent of the concentration of the photolyte between the limits worked with. Consequently, one run only was carried out with the 313 $\mu\mu$ and 405 $\mu\mu$ filters, of which the results are in Table V, (iii) and (iv).

Attention was next turned to the effect of the addition of various strong electrolytes on γ . All measurements were carried out with the 365 $\mu\mu$ line, and with solutions of composition 0.02M- $K_3Fe(C_2O_4)_3$ + 0.18M- $K_2C_2O_4$. The duration of insolation was normally about 20 hours. The concentrations of the two acids used were considerably higher than those of the neutral salts. The addition of smaller concentrations (about 0.2M) led to the precipitation of ferrous oxalate on insolation. The results are in Table VI. It is clear that, in every case, an increase in the value of γ has followed the addition of the electrolyte.

TABLE VI.

| Expt. No. | Added electrolyte. | Conc. of added electrolyte. | Mean active absorption (cals./hour). | Mols. decomposed per hour $\times 10^6$. | γ . |
|-----------|--------------------|-----------------------------|--------------------------------------|---|------------|
| 11 | H_2SO_4 | 1.0M | 0.392 | 6.76 | 1.35 |
| 12 | HCl | 2.0 | 0.378 | 5.72 | 1.18 |
| 13 | K_2SO_4 | 0.2 | 0.273 | 4.5 | 1.29 |
| 14 | KCl | 0.2 | 0.469 | 7.39 | 1.23 |
| 15 | NaCl | 0.2 | 0.433 | 7.1 | 1.27 |
| 16 | LiCl | 0.2 | 0.425 | 7.17 | 1.32 |
| 17 | LiCl | 0.2 | 0.362 | 5.87 | 1.26 |
| 18 | Check—no addition | | 0.389 | 5.72 | 1.14 |

Experiments with Non-homogeneous ("Mixed") Light.

Padoa and Vita (*Gazzetta*, 1924, **54**, 147) recently published some interesting results on the photolysis of ferric chloride-oxalic acid solutions, according to which, in this reaction, the sum of the effects of a series of spectral regions is greater than the effect of the same light undispersed. Kornfeld (*loc. cit.*) has since shown that, in accordance with this result, the rate of this reaction is proportional to the square root of the light intensity. We have done similar experiments with potassium ferrioxalate solutions and, as will be seen, under certain conditions, have obtained precisely the opposite result to that of Padoa and Vita.

Most of our work was carried out with the quartz-mercury lamp and Corning glass filters which transmitted considerable fractions of two or more of the 365, 405, and 436 $\mu\mu$ lines. One insolation was carried out with a metal-filament lamp. Data with regard to the filters are in Table VII. The transmissions were determined by the same method as previously.

TABLE VII.

| Filter. | Transmission. | | Remarks. |
|-------------------------------|---------------|------|---|
| | % | | |
| G. 586-A. 3.59 mm. thick. | 365 $\mu\mu$ | 77 | Used in Expts. 19, 25—29. |
| | 405 | 22 | |
| | 436 | | |
| G. 86-B. 4.00 mm. thick. | 365 $\mu\mu$ | 84 | Also transmits 546 and 579 $\mu\mu$ lines, unabsorbed by reaction solution. Used in Expt. 22. |
| | 405 | 91.5 | |
| | 436 | 89 | |
| G. 50. 4.72 mm. thick. | 365 $\mu\mu$ | 42.3 | Used in Expt. 20. |
| | 405 | 78.5 | |
| | 436 | 66.5 | |
| G. 552-Py. 4.00 mm. thick. | 365 $\mu\mu$ | 3 | Used in Expt. 21. |
| | 405 | 60.5 | |
| | 436 | 71 | |
| G. 53-C. 3.5 mm. thick. | 365 $\mu\mu$ | 5 | Used with metal-filament lamp (Expt. 24). See Fig. 1 for detail of trans- mission. |
| | 405 | 35 | |
| | 436 | 20 | |

The actual experiments were carried through as before, with the necessary modifications required by the use of mixed light. Knowing the energy distribution in the unfiltered beam and the transmission of the filter, the energy distribution in the filtered beam could be calculated. This, combined with the known extinctions of the photolyte for the different wave-lengths, enabled the distribution of the active absorbed energy to be calculated, correction being made for the progressively increasing absorption of the potassium ferrioxalate. The total absorbed intensity was directly measured as before, and corrected for the ferrous salt in order to obtain the total active absorbed energy. Experiments lasted 15—20 hours.

A solution of composition $0.02M\text{-K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 + 0.18M\text{-K}_2\text{C}_2\text{O}_4$ was used throughout.

For the experiments made with the quartz-mercury lamp, we have calculated from our data the number of quanta corresponding to each of the wave-lengths 365, 405, and 436 $\mu\mu$ absorbed per hour, and, using the γ values previously determined for monochromatic light of these wave-lengths (Table V), have thus obtained the decomposition that would have taken place per hour if the total effect of the light were simply the sum of the effects of its separate components. With these figures we have compared the actual decompositions found experimentally. Our results are in Table VIII (Expts. 19—22).

TABLE VIII.

| Expt. No. | Total mean active absorption (cals./hr.) | Fractional distribution of active absorbed energy. | | | Duration of insolation (hours). | Decomposition, %. | Mols. decomposed per hour $\times 10^5$. | |
|-----------|--|--|----------------|----------------|---------------------------------|-------------------|---|--------|
| | | 365 $\mu\mu$. | 405 $\mu\mu$. | 436 $\mu\mu$. | | | Calc. | Found. |
| 19 | 0.802 | 0.914 | 0.085 | — | 19.00 | 32.1 | 1.18 | 1.46 |
| 20 | 0.517 | 0.458 | 0.294 | 0.248 | 17.58 | 19.3 | 0.73 | 0.95 |
| 21 | 0.425 | 0.057 | 0.458 | 0.484 | 15.83 | 14.0 | 0.57 | 0.73 |
| 22 | 0.750 | 0.593 | 0.202 | 0.205 | 17.78 | 27.9 | 1.07 | 1.34 |
| 23 | 0.512 | 1.000 | — | — | 16.08 | 13.2 | 0.76 | 0.71 |
| 24 | 0.379 | — | — | — | 20.00 | 9.5 | 0.51 | 0.41 |

In Exp. 24, with a metal-filament lamp (of 2000 c.p., and water-cooled), a graphic method was employed for obtaining the average energy distribution with wave-length of the absorbed active light. This is best illustrated by Fig. 1, in which the significance of the different curves, all plotted with λ along the abscissa, is as follows :

Curve a. Relative energy distribution in the beam of white light over the active part of the spectrum, determined by the thermopile-galvanometer method, and corrected for the variation in dispersion of the quartz prism with wave-length.

Curve b. Percentage transmission of Corning filter G.53 c, determined with the continuous light source.

Curve c. Average percentage absorption of incident light by photolyte.

Curve d. Average percentage absorption due to the potassium ferrioxalate.

Curve e. Relative energy distribution in filtered light (combination of curves *a* and *b*).

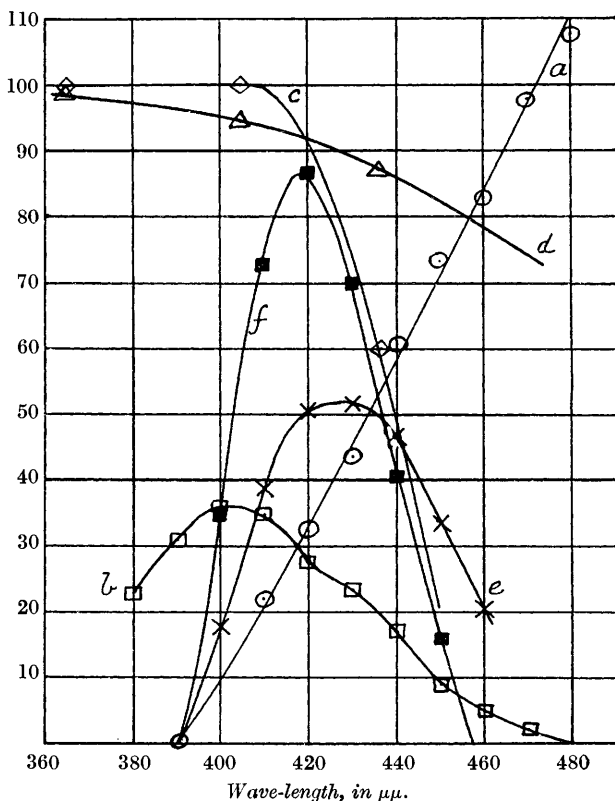
Curve f. Relative average distribution of active absorbed energy (combination of curves *c*, *d*, and *e*).

The total average active energy absorbed per hour was distributed, at 10 $\mu\mu$ intervals, over the region 400—450 $\mu\mu$ in accordance with Fig. 1f, and the decomposition to be expected on the

assumption of additive relations was calculated as in Expts. 19—22. This result, together with the experimentally found figure, is given under Expt. 24 in Table VIII.

It will be seen that, when complex light is used consisting of varying proportions of two or three of the mercury lines, the amount of decomposition actually found is consistently greater, by 25—30%, than that calculated on the basis of additivity. This result is the

FIG. 1.



reverse of that found by Padoa and Vita, working with a ferric chloride-oxalic acid mixture and using a strip of continuous spectrum. Expt. 23, with monochromatic $365 \mu\mu$ light (filter G.586 A.-W.) was carried out as a check. It will be noticed that it gave a smaller decomposition than that calculated from the results of the earlier measurements with the $365 \mu\mu$ line ($\gamma = 1.08$ as against the former mean of 1.16—see Table V, i). This only makes the results of Expts. 19—22 still more remarkable in comparison.

When, however, a continuous region of the spectrum (390—460 $\mu\mu$) was used, as was the case with Padoa and Vita, the experimentally found value was lower, by about 20%, than the calculated figure. Except in as far as this experiment does not give the increased chemical effect found in Expts. 19—22, we lay no great stress on the result, as three factors may enter, absent or much less important in Expts. 19—22, and all liable to cause error: (1) appreciable amounts of infra-red radiation may be present in the filtered light and be absorbed by the photolyte; (2) the absolute and relative energy values of the filament-lamp radiation are much more liable to fluctuation than is the case with the mercury lamp; (3) the extinction coefficients of the potassium ferri- and ferro-oxalates were not determined by us for wave-lengths longer than 436 $\mu\mu$.

Effect of Intensity and of Intermittent Light.—Just as the results of Padoa and Vita suggested to Kornfeld that the velocity of the reaction in question might vary as $I_0^{\frac{1}{2}}$, so the results of Expts. 19—22 might be held to indicate that, under certain conditions, the rate of the present reaction would be proportional to I_0^2 . We tested this point, using the mercury lamp and the G.586.A Corning filter, this being chosen because its high transmission allowed of a considerable variation in I_0 . This variation was effected by an iris diaphragm, the apparatus being so arranged that a change in the diaphragm aperture did not appreciably affect the cross-section of the beam passing through the cell. The results are in Table IX.

TABLE IX.

| Expt. No. | Decomposition, %. | Mean active absorption (cals./hour). | Mols. decomposed per hour $\times 10^5$. | Mols. decomposed per calorie absorbed $\times 10^5$. |
|-----------|-------------------|--------------------------------------|---|---|
| 25 | 15.1 | 3.57 | 6.53 | 1.83 |
| 19 | 32.1 | 0.802 | 1.46 | 1.82 |
| 26 | 8.2 | 0.246 | 0.452 | 1.83 |

Finally, experiments were carried out in which the light beam was interrupted by an electrically driven rotating disc, from which two 90° sectors had been removed, alternating with two solid sectors. The average intensity of light passing the sector was thus half the total intensity in the beam. The same G.586.A filter was employed, and the average absorbed intensity measured as before. Table X

TABLE X.

| Expt. No. | Insolations per min. | Decomposition, %. | Mean active absorption (cals./hour). | Mols. decomposed per hour $\times 10^5$. | Mols. decomposed per calorie absorbed $\times 10^5$. |
|-----------|----------------------|-------------------|--------------------------------------|---|---|
| 27 | 1470 | 10.3 | 1.87 | 3.24 | 1.73 |
| 28 | 750 | 9.3 | 1.58 | 2.69 | 1.70 |
| 29 | 540 | 14.5 | 0.370 | 0.636 | 1.72 |

shows that, as was anticipated after the preceding results, the specific photochemical effect is practically the same as with continuous light, and exhibits no sign of alteration with variation in sector speed. It must therefore be concluded that the decomposition of potassium ferrioxalate solutions under our experimental conditions proceeds at a rate proportional to the first power of the light intensity.

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