CXCVIII.—*The Photolysis of Potassium Ferrioxalate Solutions. Part II. Discussion.*

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Summary of Experimental Results.

The main results of this work, together with relevant observations of other experimenters, can be summarised as follows :

(*a*) The quantum efficiency in the photolysis of potassium ferrioxalate by monochromatic light between the wave-length limits of 313—436 μμ is of the order of unity, and decreases with increase of wave-length (Part I, Table V). Table I contains the figures, together with values of γ previously observed for similar reactions.

Table I.

Decomposition of	313 μμ.	365 μμ.	405 μμ.	436 μμ.	488 μμ.
$K_3Fe(C_2O_4)_3$	1·59	1·16	0·91	0·89	—
$K_3Co(C_2O_4)_3$ (Vranek)	—	1·5	0·9	0·6	—
$K_3Mn(C_2O_4)_3$ (Ghosh and Kappanna)	—	—	—	—	1·28

(*b*) Between the limits 0·02—0·06*M*, γ is independent of the concentration of the photolyte (Part I, Table V, i and ii). The same holds for potassium cobaltioxalate between limits of 0·0002—0·005*M*.

(*c*) With 0·02*M*-solutions, γ is independent of the degree of decomposition between the limits 3·42—32·1% (Part I, Tables V, i, and IX). It would therefore appear that the accumulation of ferrous oxalate does not retard the reaction apart from its internal light-filter effect. Some results reported by Baur (*Z. physikal. Chem.*, 1908, **63**, 683), to the effect that the ferrioxalate decomposition in light finally comes to a complete standstill, were shown later (Schaper, *ibid.*, 1910, **72**, 308) to be due to faulty methods of analysis. The retardation of the reaction observed by him was certainly due to the internal light-filter action of the ferrous oxalate. In the case of the cobaltioxalate, Vranek observed that, as the solutions became more dilute, the unimolecular coefficients tended to fall off and to give way to bimolecular coefficients.

(*d*) γ is slightly lowered by the addition of an excess of potassium oxalate, which also retards the photolysis of the cobaltioxalate, but has no effect with the manganioxalate.

(*e*) γ is slightly raised by the addition of all other strong electrolytes tried, at the concentrations used (Part I, Table VI). In the case of the cobaltioxalate, Vranek showed that the addition of small amounts of hydrochloric or sulphuric acid had no effect, whilst Jaeger and Berger (*Rec. trav. chim.*, 1921, **40**, 153), in agreement with our work, found an accelerating effect produced by potassium, sodium, and lithium chlorides, of the same order as we observe.

(*f*) For light of $\lambda = 365$ $\mu\mu$ containing a proportion of $\lambda = 405$ $\mu\mu$, γ is independent of the intensity, whether continuous or average intermittent, over a range of 15 : 1 (Part I, Tables IX, X). Proportionality between rate and intensity was found for the cobaltioxalate (white light) and, approximately, for the manganioxalate (continuous blue band).

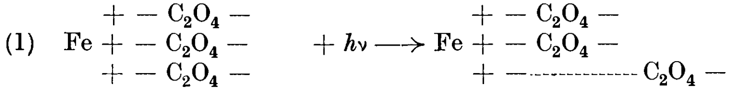
(*g*) With active absorbed light composed of a continuous band lying between 390—460 $\mu\mu$, with its head at about 420 $\mu\mu$, the degree of decomposition probably closely corresponds with that calculated on the assumption of the additive action of the different rays, but may be lower than this figure. The former result is to be anticipated from the relation found between intensity and velocity.

(*h*) If the absorbed active light be composed of varying proportions of two or more of the three mercury lines at 365, 405, and 436 $\mu\mu$, then the degree of decomposition is 25—30% higher than the figure corresponding to an additive effect of the different wavelengths (Part I, Table VIII).

There are one or two similar remarkable cases in the literature. Kuhn (*J. Chim. phys.*, 1926, **23**, 521) finds γ for the decomposition of ammonia by light of average wave-length 208 $\mu\mu$ to fall from 0·4—0·5 to 0·1 as the degree of monochromatism of the light is increased. According to Padoa and Vita (*Gazzetta*, 1926, **56**, 164), the relative velocities of combination of hydrogen and chlorine in a beam of white light, and in the same beam spectrally dispersed, show similar relations. Some discrepant observations of Henri and Wurmser (*Compt. rend.*, 1913, **156**, 1012; **157**, 126) on hydrogen peroxide decomposition, which, at first sight, look as if they might be explained in this way, are probably capable of another interpretation (unpublished work by A. J. Allmand and D. W. G. Style).

General Theory of Results.

The majority of our results appear capable of a simple interpretation. We suggest that the primary result of the absorption of a light quantum is the activation of a ferrioxalate ion, a process regarded as involving the partial dislocation of the union between the ferric ion and one of its attached oxalate ions, thus



$$(1)\quad \mathrm{Fe}\begin{array}{l} + - C_2O_4 - \\ + - C_2O_4 - \\ + - C_2O_4 - \end{array} + h\nu \longrightarrow \mathrm{Fe}\begin{array}{l} + - C_2O_4 - \\ + - C_2O_4 - \\ + \cdots\cdots\cdots C_2O_4 - \end{array}$$

This activated ion is assumed to have a life long in comparison with the average time required (in solutions of the concentrations used by us) for a collision to take place between it and an unactivated ferrioxalate ion. When collision takes place, we assume either degradation to heat of the absorbed energy or, if the degree of dislocation of the activated ion be sufficient, reaction according to the equation

$$(2)\ \underset{\text{(activated)}}{Fe(C_2O_4)_3'''} + \underset{\text{(unactivated)}}{Fe(C_2O_4)_3'''} \longrightarrow 2Fe(C_2O_4)_2'' + C_2O_4'' + 2CO_2.$$

The proportion of absorbing ions giving fruitful collisions will naturally increase with the size of the quantum, and the maximum quantum efficiency possible will be seen to be 2.

This mechanism is in accord with the results given under (*a*), (*b*), (*c*), (*f*), and (*g*) above, including the increase in the order of the reaction observed by Vranek in his very dilute cobaltioxalate solutions. With regard to (*d*) and (*e*), neutral-salt action in photolysis is yet far from being understood (compare Kistiakowsky, "Photochemical Processes," 1928, pp. 192—194), and we have no particular suggestion to make, unless perhaps that the retarding effect of potassium oxalate may be looked on as due to the oxalate ions opposing the weakening of the $Fe^{\cdot\cdot\cdot}$–C_2O_4'' bond (*i.e.*, electron transfer from C_2O_4'' to $Fe^{\cdot\cdot\cdot}$), just as they would hinder the splitting off of C_2O_4'' ions in accordance with an equation such as

$$(3)\ Fe(C_2O_4)_3''' \longrightarrow Fe(C_2O_4)_2' + C_2O_4'',$$

where $Fe(C_2O_4)_2'$ represents another (hypothetical) type of ferrioxalate ion.

We prefer activation, as the primary result of quantum absorption, to actual dissociation as follows :

$$(4)\ Fe(C_2O_4)_3''' + h\nu \longrightarrow Fe(C_2O_4)_2'' + C_2O_4'$$

followed by

$$(5)\ C_2O_4' + Fe(C_2O_4)_3''' \longrightarrow Fe(C_2O_4)_2'' + C_2O_4'' + 2CO_2,$$

in view of the experimental fact that the accumulation of ferrous oxalate does not retard the reaction as might be expected if the correct primary mechanism were represented by (4).

Special Theory for Results with " Mixed " Light.

To explain the results recorded under (*h*) is difficult. As it is the average quantum efficiency which is raised, and not the absorption of the light rays used, the first possibility which suggests itself is that those ferrioxalate ions A*, which have absorbed a particular quantum, $h\nu_1$, but which are only *subactivated, i.e.*, insufficiently activated to react on collision with a normal ferrioxalate ion A, can nevertheless react on collision with an ion A** which has been subactivated by absorption of a light quantum of different size $h\nu_2$. But there are several objections to this view. Such collisions between two activated ions would require their mean lives to be far longer than it is necessary to assume for the purpose of explaining the great majority of our experimental results. If, moreover, collisions between A* and A** ions are fruitful, it would seem natural to expect a similar result to follow collision between two A* or two A** ions, in which case there should be no such increase in γ when passing from monochromatic light to " mixed " light as is actually found. If collisions between two activated ions essentially represent the mechanism of the reaction in *all* cases, collisions between A* and A** being more fruitful than collisions between two A* or two A** ions, the maximum γ value to be anticipated would be unity, unless indeed the collision mechanism be of the type

$$(6)\ 2A^* \longrightarrow 2Fe(C_2O_4)_2'' + 2C_2O_4'$$

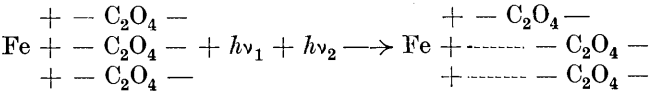
followed by (5). But, apart from the objection already raised to the actual splitting off of C_2O_4' ions as a result of primary light absorption, the formation of two such very reactive ions by a bimolecular collision would appear less probable than the production of C_2O_4'' and $2CO_2$.

The strongest objection to any hypothesis involving some kind of interaction between two ions subactivated by light absorption is perhaps the magnitude of the effect. For example, in Expt. 19 (Part I), the average quantum efficiency for absorbed light, of which 90·7% represents 365 μμ and 9·3% 405 μμ quanta, is almost 24% greater than the calculated figure. It can readily be shown that, even if every ion subactivated by absorption of a 405 μμ quantum (A*—5% of total absorbing ions) were to collide fruitfully with a similar ion subactivated by absorption of a 365 μμ quantum (A**—38% of total absorbing ions), the decomposition would only be 9% above the normal figure if the result of the collision were

$$(7)\ A^* + A^{**} \longrightarrow 2Fe(C_2O_4)_2'' + C_2O_4'' + 2CO_2,$$

or 18% if the collision were to take place on the lines of the improbable equation (6), followed by (5). In addition, as k_{365} is considerably higher than k_{405} (Part I, Tables III, IV), A* and A** ions will not be formed in the same ratio throughout the whole of the absorbing region of the photolyte; in the foremost layers there will be a heavy preponderance of A** ions and in the deeper layers a preponderance of A* ions, which would render the likelihood of A*–A** collisions still more remote.

Another suggestion, made in one form or another by Padoa and Vita (*Gazzetta*, 1924, **54**, 127), Kuhn (*loc. cit.*), and Henri and Wurmser (*J. Physique*, 1927, **8**, 289), is that of successive absorption by the one ion of two different quanta, $h\nu_1$ and $h\nu_2$, followed by a highly efficient activation and reaction in accordance with

(8) 

$$\mathrm{Fe}\begin{array}{l}+-\mathrm{C_2O_4}-\\+-\mathrm{C_2O_4}-\\+-\mathrm{C_2O_4}-\end{array}+h\nu_1+h\nu_2\longrightarrow\mathrm{Fe}\begin{array}{l}+-\mathrm{C_2O_4}-\\+\cdots\cdots-\mathrm{C_2O_4}-\\+\cdots\cdots-\mathrm{C_2O_4}-\end{array}$$

succeeded by (in stages)

$$\begin{array}{llll}(9)\ \mathrm{Fe(C_2O_4)_3'''} & +\ 3\mathrm{Fe(C_2O_4)_3'''} & \longrightarrow & 4\mathrm{Fe(C_2O_4)_2''}+2\mathrm{C_2O_4''}\\ \text{(doubly activated)} & \text{(unactivated)} & & +\ 4\mathrm{CO_2}\end{array}$$

Such a mechanism would, however, imply that ions which had already absorbed the quantum $h\nu_1$ would have a very high extinction coefficient for light of frequency ν_2. This would mean that the total absorption of the photolyte towards the mixed light would be greater than the sum of its absorption for the separate components. This we found not to be the case, the point being tested during experiments with 436 $\mu\mu$ light, where absorption was incomplete.

No other way has occurred to us for correlating the increased γ values with the fact that the *absorbed* light is mixed and not homogeneous. We therefore make the following tentative suggestion.

If the extreme view of the nature of a light quantum be taken, *viz.*, that it is a discrete corpuscle of energy, then all known facts concerning light absorption and its dependence on concentration, wave-length, and nature of absorbent (extinction coefficient), suggest that, when a stream of such quanta enters an absorbing solution, there will be on the average an enormous number of " encounters " between the quanta and the molecules of the absorbing substance before absorption takes place, even in media of high extinction coefficient. The majority of these encounters will not result in absorption, and the light quantum passes on normally unchanged. Hitherto, it would appear to have been assumed that the molecules which undergo such " collisions " with the light quanta are also unchanged, unless they, quite exceptionally, absorb the quantum. Recently, however, the discovery of the Raman effect (*Indian J.*

Physics, 1928, **2**, 387, 399) gives reason for doubting this to be the case. Raman has shown, for example, that a beam of monochromatic 436 $\mu\mu$ light, passed through pure carbon tetrachloride, undergoes modification, slight in degree but profound in nature, in that the emergent beam is found no longer to be monochromatic, but to contain weak components of both longer and shorter closely adjacent wave-lengths. The accepted explanation, which is in accordance with the effect of temperature on the intensities of these new components, is that small transfers of energy have taken place between the light quanta and the tetrachloride molecules; the latter give up energy to the quanta if at a particularly high energy level, and take up energy from the quanta if of particularly low energy level. No absorption in the ordinary sense results from such encounters, but nevertheless there is energy transfer between quantum and molecule.

We suggest that the existence of the Raman effect indicates that some kind of energy interaction may take place between light quantum and molecule even during encounters which do not result either in absorption, in the ordinary sense, or in a transfer of energy between molecule and quantum, as in the Raman effect. The result of the disturbance in the molecule caused by the encounter may be possibly a momentary transfer of energy to the molecule from neighbouring molecules of solvent, or perhaps, in the case of a complex absorbing unit, such as the ferrioxalate ion, merely a redistribution of the energy of the molecule itself within its different degrees of freedom. We imagine what we term " stimulation " of the molecules by light to be possible *without appreciable absorption of light*. The degree of such " stimulation " would be slight in comparison with the " activation " produced by the absorption of a light quantum, and the mean life of such stimulated molecules might be expected to be proportionately long. Moreover, they are being continuously produced in large numbers as long as insolation is continued.

If this be granted, there appear to be two possibilities of application to the present case. Possibly collision between a stimulated and a subactivated ferrioxalate ion may result in chemical action, thereby leading to a higher γ value than would be the case if no " stimulated " ions were to exist; or possibly, a subactivated ion (already assumed to be of comparatively long life) may, by encounter with a light quantum, be " stimulated," and thereby turned into a fully activated ion, which then reacts with a normal ion on collision. It is, of course, necessary to assume that such interaction between subactivated ions and either stimulated ions or light quanta only takes place when the frequencies involved in subactivation and stimulation are different, and for this reason we prefer the second of the two mechanisms just suggested; for it would appear natural that a molecule which had already absorbed a quantum $h\nu_1$, and had thereby become activated (or subactivated), should no longer possess the favourable configuration or energy distribution which had made possible the exceptional process of quantum absorption, and therefore, whilst not responding to stimulation by another quantum of the same size, might, on the other hand, well be capable of responding to an encounter with a quantum, $h\nu_2$, of another size. And if the readiness of stimulation, by light of frequency ν_2, of a molecule already subactivated by absorption of a quantum $h\nu_1$, be perhaps a function of the difference between ν_1 and ν_2, being greater the further apart the two frequencies (always provided that ν_2 can effect stimulation), then the absence of any unusual effect when using a continuous band of light would be explicable.

The *ad hoc* nature of the above suggestion is recognised, and further experimental work is being carried out in this laboratory on the subject.

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