proximately 0.05%. For the viscometer used the time of outflow for water was approximately 1000 sec., while the stop-watch used was accurate to 0.2 sec. An error of 0.4 sec. in time would thus introduce an error of 0.04%. If the weighings involved were accurate to only 1 mg., then the errors of weighing for the pycnometer used (about 25 g. capacity) would amount to only 0.004%. According to the "International Critical Tables," Vol. V, p. 10, the change in viscosity of water per 0.01° at 25° is approximately 0.02%. Thus the appreciable errors will total not more than 0.06% and it is believed that an error of 0.05% represents the reasonable degree of precision of results obtained.

It should be noted that the values recorded for the water–*n*-propyl alcohol system are probably the least accurate of the conductance data, since the solvent corrections for this system are unusually large.

Summary

1. Measurements have been made of the conductivities of lithium nitrate in the mixed solvents containing various proportions of the following components: water, ethyl alcohol, *n*-propyl alcohol and isopropyl alcohol.

2. Viscosity and density determinations have also been made on the same pure solvent systems.

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THE EFFECT OF LIGHT ON THE FERROCYANIDE–FERRICYANIDE IODINE–IODIDE EQUILIBRIUM

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It is well known that ferric salts oxidize iodides in aqueous solution at a moderate rate and that ultimately an equilibrium, $2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2$, is reached. Sasaki[1] investigated the effect of light on systems containing the substances involved in this equilibrium. Using sunlight and light from an incandescent lamp, he found that the illuminated systems always contained less titratable iodine than similar unilluminated systems. He further adduced evidence that the effect of the light was a displacement of the equilibrium rather than some other mode of disappearance of iodine. Further photochemical experiments were made by Rideal and Williams[2] who concluded, among other things, that the region of visible photoactive radiation was within the range 5500–6500 Å., and that one quantum of absorbed radiant energy caused one molecule of iodine to react. However,

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[1] N. Sasaki, *Z. anorg. Chem.*, **122**, 61 (1922).

[2] E. K. Rideal and E. G. Williams, *J. Chem. Soc.*, **127**, 258 (1925).

Kistiakowsky[3] extended these experiments and concluded that radiations of the wave lengths 5460, 4360 and 3660 Å. were all effective; determinations of the quantum yield showed a disappearance of approximately one molecule of iodine per quantum absorbed at each of these three wave lengths.

In systems containing the ions $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{=\,=}$ instead of the ions Fe^{+++} and Fe^{++}, the thermal rates of reaction are again moderate, and directly measurable equilibria are again attained. The reaction may be expressed by the equation $2Fe(CN)_6^{\equiv} + 2I^- \rightleftharpoons 2Fe(CN)_6^{=\,=} + I_2$. Both the kinetics and the equilibria in these systems have been the subject of considerable study.[4] We have found that such systems are sensitive to light not absorbed by the complex cyanides. However, preliminary experiments showed that when light was directed into an equilibrium mixture containing the complex cyanides, free iodine was produced rather than consumed. The present paper describes experiments in which the light sensitivity of solutions containing the complex ions is compared with that of solutions containing the simple ions.

Apparatus

The source of illumination was a 500-watt lamp whose filament covered an area about 1.3 cm. square. The lamp was controlled with the aid of a variable resistance and an ammeter in series with it; the lamp current was maintained constant at 4.3 amperes. Light from this lamp passed through a 6% copper sulfate solution in a flat cell, 1 cm. thick; this filter absorbed the infra-red. This cell was fastened to the front of the thermostat, which was a large flat-sided glass jar, so as to leave a pocket 3 cm. in thickness between the cell and the jar. In this pocket was placed a second filter mounted on a sheet of brass with a rectangular opening; this filter served to isolate the desired spectral region. The pocket was filled with water to minimize reflection losses. The reaction cell which contained the solution to be illuminated was a flat-sided bottle, the face of which was 4.5 × 10 cm., and the thickness 2.86 cm. This reaction cell was silvered externally except on the face toward the lamp. The thermostat with its attached filters was contained in a box provided with a shutter and thermal insulation. Arrangement was made so that the lamp and cell could, from one experiment to another, be brought into the same positions. The experiments were carried out at 0°; to permit this, the thermostat was kept well packed with clean ice except in front of the reaction cell, which was close to the thermostat wall. Water was circulated from bottom to top of the thermostat by an air lift. Ice was also kept in the upper part of the filter pocket.

Analytical Method

The solutions to be analyzed, whether ferrous-ferric iodine-iodide mixtures or ferrocyanide-ferricyanide iodine-iodide mixtures, were ordinarily not greatly removed

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[3] G. B. Kistiakowsky, This Journal, **49**, 976 (1927).

[4] F. G. Donnan and R. Le Rossignol, *J. Chem. Soc.*, **83**, 703 (1903); G. Just, *Z. physik. Chem.*, **63**, 513 (1908); C. Wagner, *ibid.*, **113**, 261 (1924); V. K. La Mer and K. Sandved, This Journal, **50**, 2656 (1928); V. K. La Mer and H. B. Friedman, *ibid.*, **52**, 876 (1930).

from equilibrium. They were analyzed for free iodine by the following method: from a 0.1 *N* thiosulfate solution, a solution of convenient strength, usually 0.004 *N*, was freshly prepared by dilution. Five cc. of this solution was pipetted into 50 cc. of water and starch was added. A sample of the solution to be analyzed was withdrawn from the reaction cell into a 10-cc. graduated pipet. The solution was then immediately run from this pipet into the thiosulfate solution to the appearance of a blue color, permanent on stirring. The elapsed time between the withdrawal of the sample and the attainment of the end-point was less than two minutes, and most of the solution analyzed was discharged into the thiosulfate in considerably less time. The suitability of this method for the titration of solutions containing ferrocyanide and ferricyanide has been discussed by La Mer and Friedman and by La Mer and Sandved.[5]

The Nature of the Photochemical Reaction

As mentioned above, when light is directed into a ferrocyanide–ferricyanide iodide–iodide equilibrium mixture, the concentration of titratable iodine increases. We have supposed that this increase in iodine concentration arises from a displacement of the equilibrium, *i. e.*, from the oxidation of iodide by ferricyanide. If this be the case then a solution which has been removed from equilibrium by shining in light should, when placed in the dark, return to equilibrium at the same rate as a solution of the same composition which has been equally removed from equilibrium by some other method, for example, by the dilution of a more concentrated equilibrium solution. We have tested this by the following experiment, which was carried out in an atmosphere of nitrogen in order to eliminate possible oxidation by dissolved air.

Tank nitrogen which had been bubbled through two bottles of strong alkaline pyrogallol solution and one bottle of water was used. All flasks used were first filled with nitrogen by filling them with water and displacing the water with nitrogen. Solutions were made up of distilled water which had been boiled for several minutes and allowed to cool with a fairly strong stream of nitrogen passing through it; the solutions were transferred from one flask to another by the use of nitrogen pressure.

Sixteen grams of C. P. potassium ferricyanide was dissolved in about 100 cc. of water, filtered into a 500-cc. volumetric flask, and a vigorous stream of nitrogen was passed through the solution for several minutes; 20.00 g. of C. P. potassium iodide was likewise dissolved in about 100 cc. of water and nitrogen was passed through this solution for several minutes. It was then transferred to the volumetric flask and water was added to the 500-cc. mark. The resulting mixture was transferred to an Erlenmeyer flask and nitrogen was passed through it for about ten minutes, during which time very little iodine was formed. The mixture was then carefully packed with ice and allowed to stand for several days at 0° until equilibrium was practically attained.

To 250 cc. of the resulting equilibrium solution at 0° an equal volume of oxygen-free water (previously cooled to 0°) was added. The flask containing the resulting solution was packed in ice water and allowed to stand in the dark. Samples of this diluted solution were withdrawn at intervals by forcing the solution into the 10-cc. graduated pipet with nitrogen pressure, and were titrated by the method described above. The results of these titrations are plotted as circles in Fig. 1.

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[5] V. K. La Mer and H. B. Friedman, THIS JOURNAL, **52**, 877 (1930); V. K. La Mer and K. Sandved, *ibid.*, **50**, 2659 (1928).

After about twenty-four hours, this diluted solution had nearly reached equilibrium; 160 cc. of it was then transferred to the reaction vessel in the ice thermostat and illuminated for three hours through the copper sulfate filter and a 1-cm. layer of 16% potassium chromate solution. Immediately upon ceasing the illumination the solution was placed in the dark and samples were withdrawn at intervals and titrated as before.

The results of this series of titrations are shown as crosses in Fig. 1; the time origin for the plot relating to the illuminated solution was so chosen that the first point (highest iodine concentration) fell on the curve relating to the unilluminated solution. If the effect of light was simply the displacement of equilibrium, then the concentrations of *all* materials should be the same in the two solutions at this point. It may be seen from Fig. 1 that these two solutions returned toward equilibrium at the same rate at all times. Moreover, the final iodine concentration arrived at was the same in each case; twenty-nine hours after the beginning of each experiment that for the illuminated solution had become 0.00396 and that for the unilluminated solution, 0.00398 *N*.

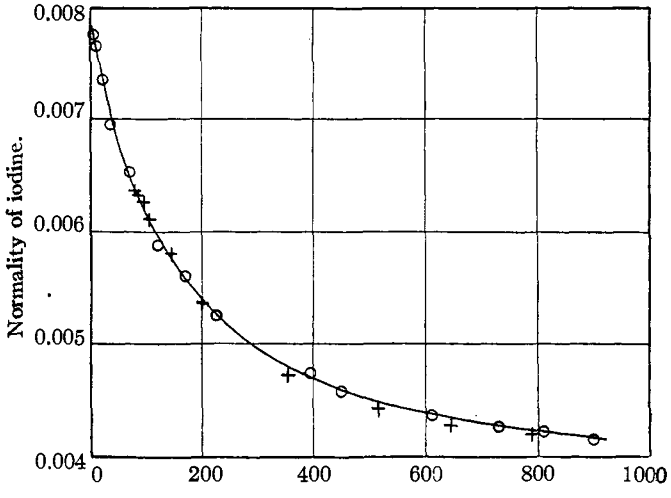

Fig. 1.—Comparison of change of iodine concentration with the time for two solutions of the same composition, one (circles) having been removed from equilibrium by dilution, the other (crosses) having been illuminated. The curve is drawn through the circles.

When similar experiments were carried out without the precaution of excluding air, the coincidence of the two curves was not so complete and was especially incomplete if the illumination was a prolonged one; a solution which had been given twenty hours' illumination finally came in the dark to an equilibrium concentration of iodine about 12% lower than that of a corresponding unilluminated solution.

In the experiments of Fig. 1, the concentration of the iodine before illumination was 0.00398 *N;* the equivalent concentration of the ferrocyanide (since the solution was made up from ferricyanide and iodide) was the same. During illumination, the iodine concentration rose to 0.00636 *N*, an increase of 60%. If this increase were not due to a shift in the equilibrium, the illuminated solution would then not be expected to contain the same amount of ferrocyanide as the unilluminated solution of equal iodine concentration prepared by dilution, and an equality in the rate of return to equilibrium would not be expected, nor should the same equilibrium concentration of iodine be reached in the two cases. We take the observed equality as evidence that the photochemical reaction with the radiation used is a reduction of ferricyanide to ferrocyanide by iodide.

Further evidence that this is the case is furnished by the following experiment in which the formation of ferrocyanide on illumination is shown directly. Two solutions, the first 0.008 *N* in iodine and 0.016 formal in potassium iodide, and the other 0.010 *M* in potassium ferricyanide, were made up with no effort to exclude air, and brought to 0°. Equal volumes of the two solutions were then mixed, and half the resulting solution was immediately transferred to a reaction vessel placed in the ice thermostat. Illumination with the 500-watt lamp (through the copper sulfate and potassium chromate filters as above) was started at once. At intervals 10-cc. samples of the illuminated and of the unilluminated solutions were withdrawn simultaneously and pipetted into large test-tubes, each containing 50 cc. of water at 0° to which had been added 2 cc. of a 2% solution of ferric ammonium sulfate in 0.012 *N* sulfuric acid. After five minutes' illumination the test with the illuminated solution gave a decided blue color of ferric ferrocyanide, whereas the test with the unilluminated solution showed no visible trace of blue. After ten minutes the results were similar, the color obtained with the illuminated solution being somewhat stronger than before. After twenty minutes the illuminated solution gave a still stronger color, while the unilluminated solution now gave a faint blue color resulting from the formation of ferrocyanide in the comparatively slow thermal reaction.

The Quantum Yield

A series of experiments was made in which the photochemical rate of production of iodine in ferrocyanide–ferricyanide mixtures was compared with the rate of disappearance of iodine in ferrous–ferric mixtures. In carrying this out, a pair of solutions, one of each kind, was made up and the solutions allowed to come substantially to equilibrium at 0°; the concentrations were so chosen that the titratable iodine content was about the same in each. The ferrocyanide–ferricyanide solutions were all made up as described in the previous section, by starting with 16.00 g. of potassium ferricyanide and 20.00 g. of potassium iodide; in different experiments, the extent of dilution was varied. The ferrous–ferric solutions were made up by dissolving 4.82 g. of ferrous ammonium sulfate and 0.66 g. of ammonium sulfate in water containing 4.2 cc. of 6 *N* sulfuric acid; to this was added a solution of 3.74 g. of potassium iodide and the resulting solution diluted so as to give the desired free iodine concentration. The solutions were successively exposed in the same reaction cell under the same conditions. During each exposure samples with withdrawn from time to time and titrated.

The results of two typical pairs of such experiments are shown plotted in Fig. 2. The abscissas are the time of exposure in minutes and the ordinates are the concentration of titratable iodine in millimoles per liter. Only at the beginning of each exposure can the rate of change of iodine concentration be considered to be due to light alone; when sufficient departure from thermal equilibrium has been attained, the thermal reverse reaction should lower the rate of change of iodine concentration. We have sought to decrease this difficulty by working at 0°. With exposures of one hour, in our apparatus, no appreciable change in rate was observable; consequently, as in Fig. 2, a straight line has been taken as the best representation of the data.

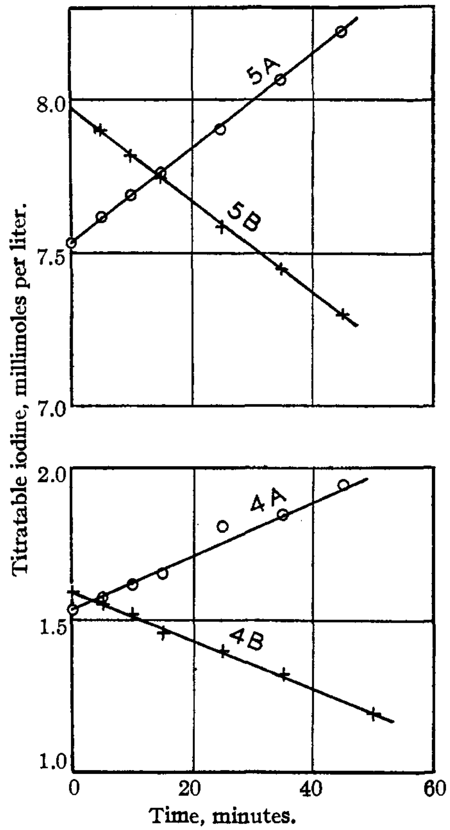

Fig. 2.—Change of iodine concentration with the time in ferrocyanide–ferricyanide solutions (circles) and in ferrous-ferric solutions (crosses) under the same illumination.

The results of all pairs of experiments are summarized in Table I. The concentrations, given throughout in millimoles per liter, apply to the beginning of exposure. In Col. 2 is given the concentration of titratable iodine; this is equal (since the solutions were made up from iodide and ferricyanide or ferric iron) to one-half the millimolal concentration of ferrocyanide or ferrous iron as the case may be. The total iodide, given in Col. 3, is the iodide taken minus the milliequivalents of titratable iodine. The concentrations of ferricyanide or ferric iron in Cols. 4 and 5 are similarly obtained from the titratable iodine and the amounts of ferricyanide or ferric iron taken. In Col. 6 is given the fraction of the titratable iodine existing as I_3^-. This was obtained using the equilibrium constant $(I^-) \times (I_2)/(I_3^-) = 0.000686$, which is the value obtained by Jones and Hartmann[6] in 0.1 *N* potassium iodide. Although the solutions involved here are by no means perfect, the calculations suffice to show that most of the titratable iodine was in the form of I_3^-.

The potassium chromate filter used in addition to the copper sulfate

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[6] G. Jones and M. L. Hartmann, This Journal, 37, 241 (1915).

TABLE I

RELATIVE RATES OF PRODUCTION OF IODINE IN FERROUS–FERRIC AND IN FERROCYANIDE–FERRICYANIDE SOLUTIONS

	Concentrations in millimoles per liter						
No.	Titratable iodine = $^1/_2(Fe(CN)_6^{----})$ or $^1/_2(Fe^{++})$	Total iodide	$(Fe(CN)_6^{\equiv})$	(Fe^{+++})	$\frac{(I_3^-)}{(I_2) + (I_3^-)}$	Rate of production of titratable iodine, millimoles/liter-min.	Ratio of rates
1a[a]	1.71	117.2	45.3	..	0.995	+0.0108	1.03
1b[a]	1.71	7.10	..	1.25	.889	− .0105	
2a[a]	1.87	116.8	44.9	..	.995	+ .0111	1.03
2b[a]	1.78	7.64	..	1.51	.899	− .0108	
3a	1.34	87.6	33.7	..	.993	+ .0085	1.08
3b	1.46	8.52	..	2.26	.912	− .0079	
4a	1.53	98.9	38.1	..	.994	+ .0086	1.07
4b	1.59	8.25	..	1.99	.906	− .0080	
5a	7.53	225.9	82.2	..	.997	+ .0152	1.00
5b	7.98	29.04	..	4.04	.969	− .0151	
6a	7.59	225.8	82.1	..	.997	+ .0152	1.07
6b	7.93	29.13	..	4.13	.968	− .0142	
7a[a]	1.86	116.9	45.0	..	.995	+ .0008	0.16
7b[a]	1.96	5.58	..	1.08	.893	− .0050	

[a] Air was not excluded. Filters: K_2CrO_4 and $CuSO_4$ in Expts. 1–6 inclusive; methyl violet, $Cu(NO_3)_2$ and $CuSO_4$ in Expt. 7.

filter in Expts. 1–6 inclusive was a 1-cm. layer of 16% solution. Examination with a spectroscope showed that this filter removed substantially all radiation below 5000 Å. None of the materials involved in the experiments except I_3^- and I_2 gives appreciable absorption of visual radiation of wave lengths longer than 5000 Å. when present in the amounts used. Consequently all of the light absorption is attributed to I_3^- and I_2. The total light absorption in any ferrocyanide–ferricyanide solution must have been nearly the same as in the companion ferrous–ferric solution, for the proportion of titratable iodine in the form I_2 was not large even in these latter cases. Moreover, unpublished measurements made by Mr. C. F. Carlson in this Laboratory have shown that the absorption coefficient of I_2 is the same as that of I_3^- at about 5500 Å., and that the absorption coefficients do not change rapidly in this neighborhood.

In Col. 8 of Table I are given the ratios of the rates of appearance of iodine in the ferricyanide solutions to the rates of disappearance in the companion ferric solutions. For Expts. 1–6 inclusive, where the light absorption was due simply to I_3^- (and I_2), the ratios are within a few per cent. of unity in all cases, *i. e.*, the quantum yield of the two reactions is substantially the same. If we may assume that the quantum yield in the ferrous–ferric solutions is the same at 0° as in Kistiakowsky's quantum yield determinations, we are led to conclude that in the ferricyanide reaction, one molecule of iodine is formed per quantum absorbed by I_3^-.

Experiment 7 was made using filters of methyl violet and copper nitrate solutions; the combination absorbed strongly above 5000 Å. and transmitted freely below 4700 Å. It accordingly transmitted radiation which was absorbable by ferricyanide as well as by I_3^-. In this case the rate in the ferricyanide solution fell considerably below that in the ferric solution. Apparently, then, absorption by ferricyanide leads to little, if any, production of iodine.

Discussion

In the present photochemical experiments resulting in the reduction of ferricyanide, the absorbing species was almost exclusively I_3^-. The formation of a theory of this reaction is hampered by lack of knowledge of the elementary act accompanying the light absorption. In reviewing the photochemical ferrous-ion oxidation, Kistiakowsky[7] considered two reaction mechanisms to be possible

$$\begin{array}{ll}
\text{(I)} & I_3^- + h\nu \longrightarrow I^- + 2I \\
 & I + Fe^{++} \longrightarrow I^- + Fe^{+++} \\
\text{(II)} & I_3^- + h\nu \longrightarrow I_3^- \text{ (activated)} \\
 & I_3^- \text{ (activated)} + Fe^{++} \longrightarrow 2I^- + Fe^{+++} + I \\
 & I + Fe^{++} \longrightarrow Fe^{+++} + I^-
\end{array}$$

Neither elementary act here provides very naturally for the reduction of $2Fe(CN)_6^{\equiv}$, but either can be made to do so by supplementing with the reaction $I + I^- \longrightarrow I_2^-$ and supposing that I_2^- (as well as I_3^- (activated) in II) can act as a reducing agent. The hypothetical ion I_2^- has been employed by Wagner[8] to account for the inhibiting effect of the products in the thermal reactions

$$\begin{array}{ll}
2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2 & \text{and} \\
2Fe(CN)_6^{\equiv} + 2I^- \longrightarrow 2Fe(CN)_6^{--} + I_2 &
\end{array}$$

and for this purpose has been attributed both oxidizing and reducing properties. If it be introduced here, the following mechanisms of ferricyanide reduction result

$$\begin{array}{ll}
\text{(I)} & I_3^- + h\nu \longrightarrow I^- + 2I \\
 & I + I^- \longrightarrow I_2^- \\
 & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{--} \\
\text{(II)} & I_3^- + h\nu \longrightarrow I_3^- \text{ (activated)} \\
 & I_3^- \text{ (activated)} + Fe(CN)_6^{\equiv} \longrightarrow I_2 + I + Fe(CN)_6^{--} \\
 & I + I^- \longrightarrow I_2^- \\
 & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{--}
\end{array}$$

To these may be added a mechanism based on a third elementary act

$$\begin{array}{ll}
\text{(III)} & I_3^- + h\nu \longrightarrow I_2^- + I \\
 & I + I^- \longrightarrow I_2^- \\
 & I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{--}
\end{array}$$

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[7] G. B. Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, **1928**, p. 65.

[8] C. Wagner, *Z. physik. Chem.*, **113**, 261 (1924).

Any of these mechanisms is readily reconciled with our present knowledge of the photochemical ferrous-ion oxidation.

In an investigation of the photochemical reaction between potassium oxalate and iodine in iodide solution, Berthoud and Bellenot[9] developed a mechanism of that reaction which led to their empirical kinetic expression; this mechanism supposed that light absorbed by I_2 (producing iodine atoms) was effective while light absorbed by I_3^- was ineffective. This mechanism would then rule out any elementary act in which iodine atoms are produced from I_3^-; this would eliminate I and III above. However, we are at present disinclined to accept this conclusion; for it is possible to set up a mechanism leading to the kinetic expression of Berthoud and Bellenot without assuming light absorbed by I_3^- to be ineffective.[10]

In conclusion we may say that whatever the elementary act accompanying light absorption by I_3^- may be, it is clear that in it or in the subsequent reactions both oxidizing and reducing configurations are produced which are not to a great extent present in the unilluminated solution. The tentative assumption of the ion I_2^- is a simple hypothesis which satisfies these requirements.

Summary

It is found that when a ferrocyanide–ferricyanide iodine–iodide solution is illuminated with light absorbable by I_3^- but not by the complex cyanides, reduction of ferricyanide and oxidation of iodide occurs. The quantum yield is found to be substantially the same as that in the oxidation of ferrous ion in iodine–iodide solutions. Some possible mechanisms of the reaction are discussed.

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[9] A. Berthoud and H. Bellenot, *J. chim. phys.*, **21**, 308 (1924); *Helv. Chim. Acta*, **7**, 307 (1924).

[10] This is accomplished, for example, by the following mechanism which is similar to that of Berthoud and Bellenot but differs from it in two important respects: (1) light absorbed by I_3^- is effective; (2) the inhibiting effect of I^- is attained through the formation of I_2^- from I^- and I. The reactions are:

$$h\nu + I_3^- \longrightarrow I_2^- + I \text{ (or } I^- + 2I) \qquad (1)$$
$$I + C_2O_4^{=} \longrightarrow C_2O_4^- + I^- \qquad (2)$$
$$I_3^- + C_2O_4^- \longrightarrow 2CO_2 + I_2^- + I^- \qquad (3)$$
$$\text{or} \quad I_2 + C_2O_4^- \longrightarrow 2CO_2 + I_2^-$$
$$I_2^- + I_2^- \longrightarrow I_3^- + I^- \qquad (4)$$
$$I + I^- \rightleftharpoons I_2^- \qquad (5)$$

If the equilibrium (5) is assumed to be rapidly established, the usual treatment leads to the expression

$$-\frac{d(C_2O_4^{=})}{dt} = k_2K_5\sqrt{\frac{k_1}{k_4}I_0\,(I_3^-)}\,\frac{(C_2O_4^{=})}{(I^-)}$$

for the case of low absorption, which agrees with that of Berthoud and Bellenot.