A. PHOTOCHEMICAL REACTIONS INVOLVING TRI-IODIDE ION

B. THE PHOTOCHEMICAL REACTION BETWEEN

IODINE MONOCHLORIDE AND HYDROGEN

Thesis by

S. Frederick Ravitz

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

By Roscoe G. Dickinson and S. Frederick Ravitz

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,

[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 $Fe(CN)_6^=$ 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 $2Fe(CN)_6^= + 2I^- \rightleftharpoons 2Fe(CN)_6^{--} + I_2$. 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

[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.

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
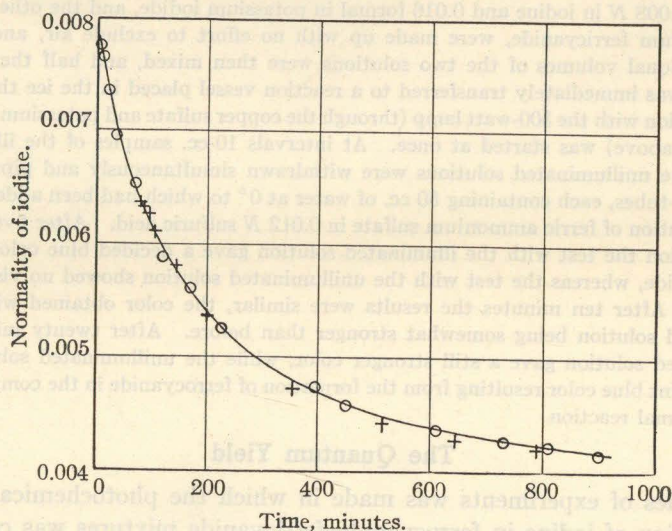

Fig. 1.—Comparison of change of iodine concentration with the time for two solutions of the same composition, one (circles) having been removed from equilibrium by dilution, the other (crosses) having been illuminated. The curve is drawn through the circles.

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.

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.

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

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

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

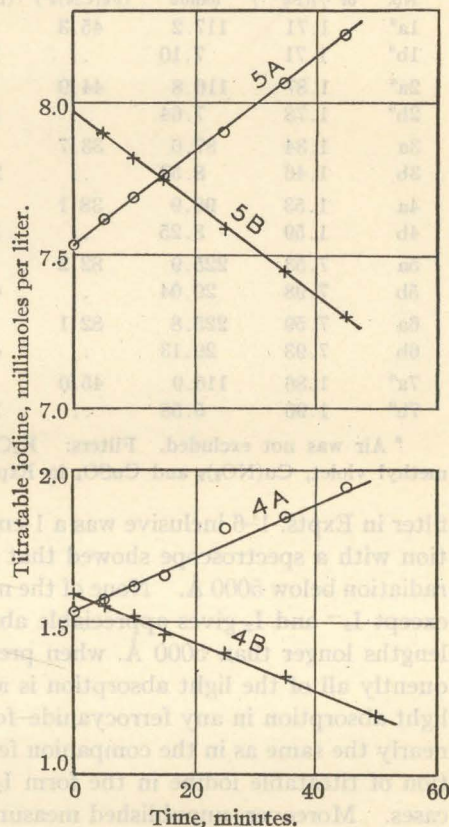[6] G. Jones and M. L. Hartmann, THIS JOURNAL, **37**, 241 (1915).

TABLE I

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

	Concentrations in millimoles per liter					Rate of production	
No.	Titratable iodine = $\frac{1}{2}(Fe(CN)_6^{---})$ or $\frac{1}{2}(Fe^{++})$	Total iodide	$(Fe(CN)_6^{=})$	(Fe^{+++})	$\frac{(I_3^-)}{(I_2)+(I_3^-)}$	of titratable iodine, milli-moles/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.
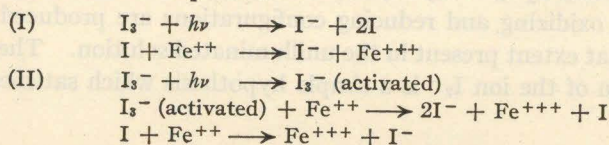
filter in Expts. 1–6 inclusive was a 1-cm. layer of 16% solution. Examination with a spectroscope showed that this filter removed substantially all radiation below 5000 Å. None of the materials involved in the experiments except I_3^- and I_2 gives appreciable absorption of visual radiation of wave lengths 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.
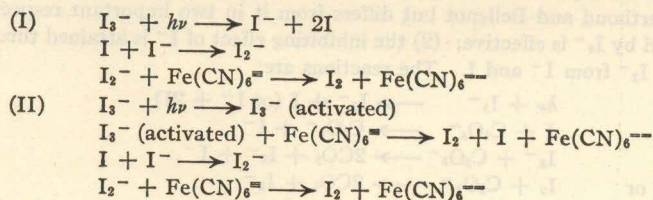
Discussion

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
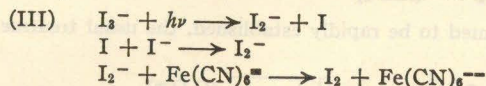
(I) $I_3^- + h\nu \longrightarrow I^- + 2I$
           $I + Fe^{++} \longrightarrow I^- + Fe^{+++}$

(II) $I_3^- + h\nu \longrightarrow I_3^-$ (activated)
           I_3^- (activated) $+ Fe^{++} \longrightarrow 2I^- + Fe^{+++} + I$
           $I + Fe^{++} \longrightarrow Fe^{+++} + I^-$

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

$$2Fe^{+++} + 2I^- \longrightarrow 2Fe^{++} + I_2 \qquad \text{and}$$
$$2Fe(CN)_6^{\equiv} + 2I^- \longrightarrow 2Fe(CN)_6^{\equiv\equiv} + I_2$$
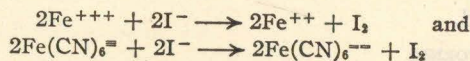
and for this purpose has been attributed both oxidizing and reducing properties. If it be introduced here, the following mechanisms of ferricyanide reduction result

(I) $I_3^- + h\nu \longrightarrow I^- + 2I$
           $I + I^- \longrightarrow I_2^-$
           $I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv\equiv}$

(II) $I_3^- + h\nu \longrightarrow I_3^-$ (activated)
           I_3^- (activated) $+ Fe(CN)_6^{\equiv} \longrightarrow I_2 + I + Fe(CN)_6^{\equiv\equiv}$
           $I + I^- \longrightarrow I_2^-$
           $I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv\equiv}$

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

(III) $I_3^- + h\nu \longrightarrow I_2^- + I$
           $I + I^- \longrightarrow I_2^-$
           $I_2^- + Fe(CN)_6^{\equiv} \longrightarrow I_2 + Fe(CN)_6^{\equiv\equiv}$

[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.
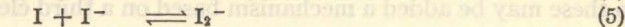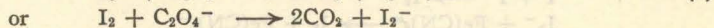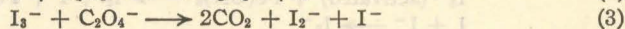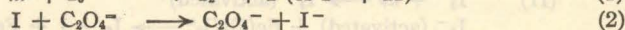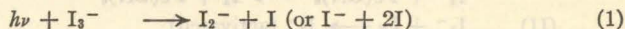
Summary

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:

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

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

$$-\frac{d(C_2O_4^-)}{dt} = k_2 K_5 \sqrt{\frac{k_1}{k_4} I_0 (I_2^-)} \frac{(C_2O_4^-)}{(I^-)}$$

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

A.

PHOTOCHEMICAL REACTIONS INVOLVING TRI-IODIDE ION

II.   The Photochemical Reduction of Ferric

   Iron in Tri-iodide Solution.

INTRODUCTION.

Investigations of the effect of light on the equilibrium[1]

$$2 Fe^{+++} + 2 I^- \rightleftharpoons 2 Fe^{++} + I_2$$

have shown that visible or near ultra violet displaces the equi-
librium to the left and does so at such a rate that two equivalents
of titratable iodine are consumed per einstein absorbed. In a recent
paper[2] the authors described the effect of light on ferrocyanide-
ferricyanide iodine-iodide equilibrium solutions in which the equi-
librium is so displaced that two equivalents of iodine are formed
per einstein absorbed. This result showed that absorption of light
by tri-iodide ion leads to configurations having both oxidizing and
reducing properties, and suggested that under suitable chosen conditions
photochemical reduction of ferric ion might be observed. The present
paper describes experiments in which this result was obtained.

EXPERIMENTAL PART.

The choice of experimental conditions was governed by the
following considerations. The concentrations of all materials
involved should be kept so small as convenient in order to reduce the
rates of the thermal reactions; the thermal reactions would be
further suppressed by working at $0°$. The concentration of ferrous
iron should be small compared with that of ferric; otherwise, the
usual observation of a net photochemical oxidation of ferrous iron
would be expected. The concentration of titratable iodine should,
however, not be too small since this material furnishes the light-
absorbing constituent. The following procedure was accordingly
adopted: A dilute solution of ferric ammonium alum, acidified with
H_2SO_4 was mixed with a dilute solution of iodine in potassium iodide,
both solutions having been previously cooled to $0°$. The resulting

solution was immediately separated into two parts, one of which was placed in the dark and the other illuminated in an ice thermostat as previously described[2]. The light used was that from a 500-watt projection lamp filtered through 1 cm. of 16% K_2CrO_4 and 1 cm. of 6% $CuSO_4$. The change in iodine concentration in each solution was followed by withdrawing, from time to time, portions which were titrated against freshly prepared 0.004 n. thiosulfate. In some experiments the solutions were made up and handled under an atmosphere of nitrogen; this, however, did not alter the results.

In Fig. 1 are shown the results of a typical experiment in which oxygen was excluded. The concentrations of iodine in the illuminated(1) and unilluminated(2) solutions are plotted against the time. It may be seen that the iodine concentration increased more rapidly at first in the illuminated than in the unilluminated solution, but subsequently did so less rapidly when sufficient ferrous ion had been formed to make its rate of photochemical oxidation appreciable. All experiments of this type yielded similar results, and we have attributed them to a photochemical oxidation of iodide by ferric iron, I_3^- being the light absorber. However, in view of the fact that the differences between the illuminated and unilluminated solutions were not large, we have sought confirmation of this conclusion in an attempt to detect more rapid development of ferrous ion in the illuminated solution.

For this purpose a solution was made up and divided as described above. At intervals, 10 cc. samples of the illuminated and unilluminated solutions were simultaneously withdrawn and pipetted into large test tubes, each containing 40 cc. of water at 0° to which had been added 2 cc. of 2% potassium ferricyanide. Throughout

12.

INITIAL COMPOSITION OF SOLUTION:

$Fe_2(NH_4)_2(SO_4)_2 \cdot 24 H_2O$ 0.00250 formal

KI .00785 "

I_2 .0020 "

H_2SO_4 .015 "

O   ILLUMINATED SOLUTION

+   DARK SOLUTION

(1)

(2)

0.0043

.0042

.0041

.0040

TITRATABLE IODINE, EQUIV. PER LITER

0   20   40   60   80
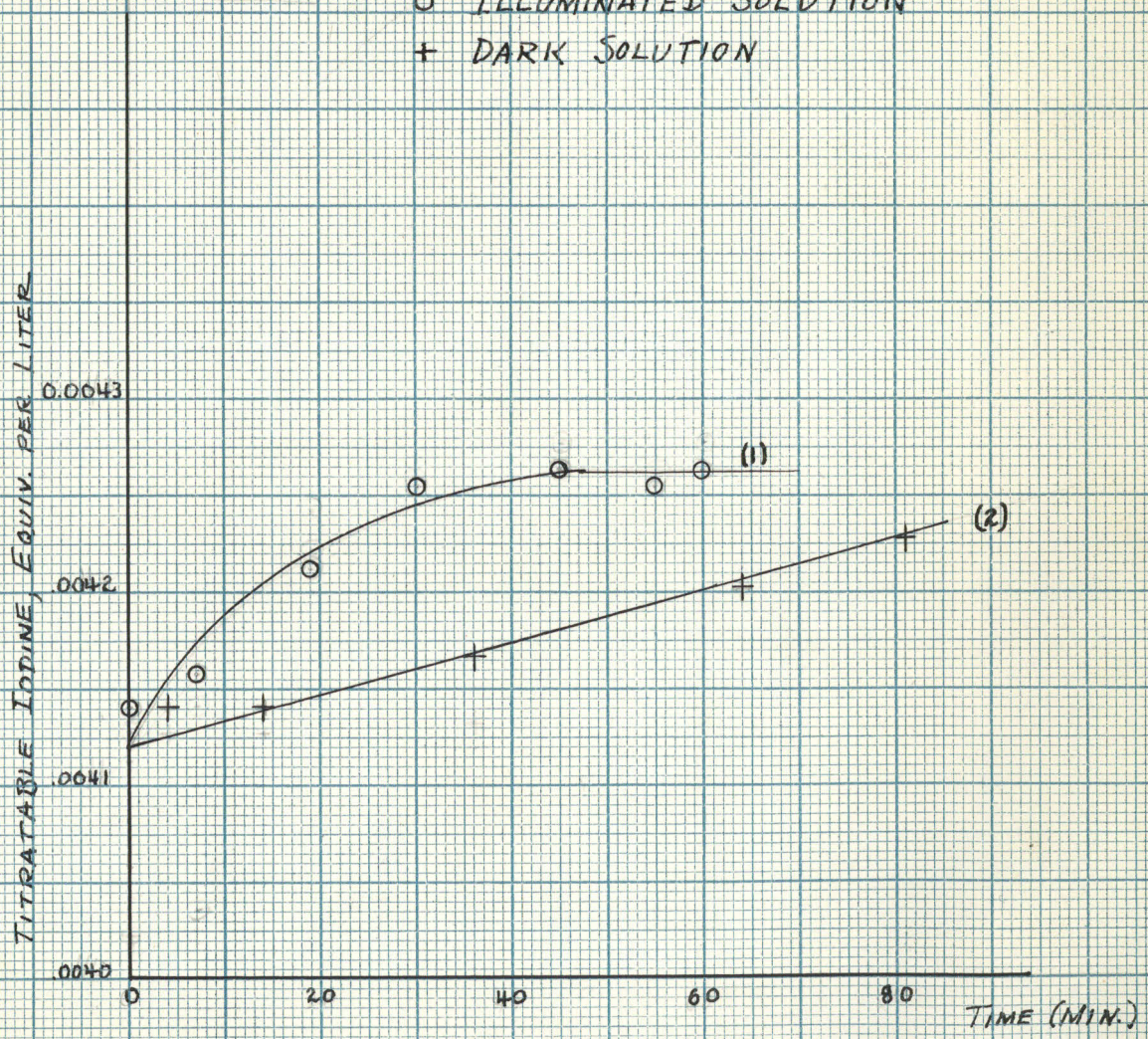
TIME (MIN.)

FIG. 1

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the experiment (50 minutes) the illuminated solution produced a
decidedly stronger blue color of ferrous ferricyanide than did the
unilluminated. This experiment, showing the photochemical formation
of ferrous iron, is then in agreement with those in which the iodine
was followed and seems hardly to be open to the possibility that the
result was produced by traces of oxygen. That the more rapid reaction
in the illuminated solution was not due simply to a higher tempera-
ture resulting from the illumination was shown by an experiment in
which the unilluminated solution was purposely kept at a higher
temperature (5°) than the illuminated (a thermometer in the illuminated
solution read below 0.5° throughout). The results of this experiment
were similar to those of the preceding.

Finally an experiment was performed to determine whether
ferrous iron and iodine were found in equivalent amounts by the
illumination. A solution was made up as in the preceding experiments
and the iodine concentrations in both the illuminated and unilluminated
portions followed by withdrawing samples for titration. Alternating
with the thiosulfate titrations, 10cc. samples were simultaneously
withdrawn from the illuminated and dark portions and pipetted into
test tubes containing potassium ferricyanide as described above. From
a burette, 0.001 n. ferrous ammonium sulfate solution was immediately
titrated into the test tube to which had been added the unilluminated
sample until the color matched that produced by the illuminated sample.
From this, the differences in ferrous iron concentration in the two
solutions were calculated; by plotting the results of the thiosulfate
titrations, the differences in iodine concentrations at the same times
were found. The results are shown in Table I.

Table I.

Time of illum-ination (min.)	Dif. in iodine conc. (milli-equiv./liter)	Dif. in ferrous conc. (milli-equiv./liter)
14	0.075	0.08
23	.12	.18
38	.15	.24
53	.17	.23

It may be noted that (1) the differences between the iodine titrations were small (about 0.2 cc.), (2) a color match was depended on for the ferrous determinations, and (3) the conditions under which the collodial ferrous ferricyanide was formed were somewhat different in the two solutions matched. In view of these facts, the agreement is as good as could be expected and shows that, at least as to order of magnitude, the iodine and ferrous iron are produced on illumination in equivalent amounts.

We have also attempted to show a photochemical reduction of iodine by ferrocyanide by illuminating a very dilute solution of potassium iodide, iodine and potassium ferrocyanide. However, the attempts have not been successful. The thermal rates in these solutions were so fast as to mask any effects of the order of magnitude of those described above.

DISCUSSION.

In general, when a solution containing ferrous and ferric iron, iodine and iodide is under illumination, four reactions may be presumed to be occurring, namely, a photochemical and a thermal oxidation of ferrous iron and a photochemical and a thermal reduction of ferric iron. The two thermal reactions are well known[3], as is

also the photochemical oxidation of ferrous iron[1] . The photochemical
reduction of ferric iron, demonstrated in the present paper, has not
previously been found. The existence of this reaction is, however, not
in disagreement with previous experimental work, for the specific rate
of the reaction is apparently much lower than that of the photo-
chemical oxidation of ferrous iron. Sasaki illuminated solutions
containing appreciable amounts of ferrous iron at the start and conse-
quently always found a net disappearance of iodine. Similarly, the
present results probably do not create any difficulty with Kistiakowski's
quantum yield determinations; for in these the ratio of ferrous to
ferric iron present was sufficiently large so that the photochemical re-
duction could hardly have amounted to more than a few per cent of
the oxidation.

SUMMARY.

It has been found that when solutions containing iodine, ferric iron, and iodide ion are illuminated immediately after being prepared, iodine and ferrous iron in approximately equivalent amounts, are at first formed more rapidly than in similar unilluminated solutions, indicating that the effect of light is to increase the rate of reduction of ferric iron by iodide. After a short time, however, the illuminated solutions reach a steady state, owing to the fact that the photochemical oxidation by iodine of the ferrous iron formed becomes appreciable.

Attempts to observe a greater rate of oxidation of ferrocyanide by iodine in illuminated solutions containing ferrocyanide ion, iodide ion, and iodine, than in corresponding unilluminated solutions, were unsuccessful. The thermal rates, however, were so rapid that they would have masked any effects of the order of magnitude of those observed in the photochemical reduction of ferric iron by iodide.

REFERENCES

1. (a) Saski, Zeit.anorg.Chem., 122, 61 (1922);
   (b) Rideal and Williams, J.Chem.Soc., 127, 258 (1925);
   (c) Kistiakowski, J.Am.Chem.Soc., 49, 976 (1927).

2. Dickinson and Ravitz, J.Am.Chem.Soc., 52, 4270 (1930).
        (Part A - I of this Thesis)

3. See, for example, Wagner, Zeit.phys.Chem., 113, 261 (1924).

B.

THE PHOTOCHEMICAL REACTION BETWEEN

IODINE MONOCHLORIDE AND HYDROGEN

INTRODUCTION

The photochemical reactions between hydrogen and the halogens have been the object of considerable study. At the time this work was started no investigation had been reported of the behavior of hydrogen with a mixed halogen, such as iodine monochloride, under the influence of light, so it was thought of interest to study that behavior. Also it was hoped that this might give some information regarding the mechanism of the hydrogen-chlorine reaction. Rollefson[1] gave reasons for believing that only excited chlorine atoms can start the latter reaction, the normal atoms being without effect. Unfortunately, it is not yet definitely known whether iodine monochloride dissociates optically into two normal atoms or into a normal iodine atom and an excited chlorine atom. Gibson and Ramsperger,[2] who investigated the absorption spectrum of ICl, at first interpreted their results as indicating dissociation into normal atoms, but later Gibson[3] decided that dissociation into a normal iodine atom and an excited chlorine atom was more probably the case.

Shortly after the present work had been started and a definite photochemical reaction found, Rollefson and Lindquist[4] reported that "it is not possible to bring about the formation of hydrogen chloride by the optical dissociation of iodine monochloride in hydrogen, either in the presence or absence of chlorine molecules". However, Mellor and Iredale,[5] and also Ashley and West,[6]

shortly afterwards stated that they observed a fairly rapid photo-chemical reaction between ICl and hydrogen. To date, though, no quantitative information concerning this reaction has appeared in the literature.

PRELIMINARY EXPERIMENTS.

In order to determine whether iodine monochloride and hydrogen would react under the influence of light some simple qualitative experiments were made with some ICl furnished by Dr. D. M. Yost. A small glass bulb was filled with ICl in the manner in which Victor Meyer bulbs are usually filled, and placed, along with a heavy piece of glass rod, in a large cylindrical glass tube. The latter was filled with hydrogen at atmospheric pressure and then sealed off at both ends; by shaking the tube the glass rod was made to break the bulb of ICl. The tube, which was not quite saturated with I Cl, was placed in a water thermostat and illuminated at room temperature with a 500-watt projection lamp. Within five minutes small crystals of iodine could be seen separating out on the walls of the flasks. Upon breaking the tube open after the illumination, white fumes appeared, indicating the presence of hydrogen chloride or hydrogen iodide. Several such experiments were made with different amounts of ICl and at different temperatures, but all gave substantially the same results. Also mixtures of ICl and hydrogen kept in the dark showed no signs of reaction even after a week.

Two possible reactions between ICl and hydrogen suggest themselves:

I. $H_2 + 2 ICl = 2 HCl + I_2$

2. $H_2 + ICl = HCl + HI$.
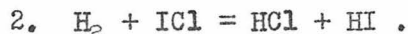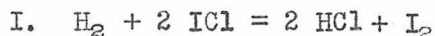
However, experiments made by Dr. H. C. Ramsperger of this laboratory showed that HI and ICl react to form hydrogen chloride and iodine so rapidly that the rate cannot be followed. Hence, if any HI is formed it is used up immediately, so equation 1 would represent the over-all reaction. The possibility of photochemical reaction between hydrogen and the iodine formed is eliminated by the fact that Coehn and Stuckardt[7] and Bowen[8] found that even at temperatures as high as 270° illumination of mixtures of hydrogen and iodine in glass vessels produced no reaction.

PREPARATION OF IODINE MONOCHLORIDE

Iodine monochloride is usually prepared by passing chlorine over iodine until the solid has completely liquified, and then fractionally distilling the product. This method, however, is open to serious objection since it is known that the vapors of ICl are richer in chlorine than is the solid, giving rise to a product containing more than the stoichiometric proportion of chlorine.[9] To overcome this difficulty, the ICl used in the experiments to follow was prepared by directly combining weighed quantities of chlorine and iodine.

Purification of Iodine.

The best available commercial iodine, the manufacturer's analysis of which gave the iodine content as 99.97%, was used. This was purified by mixing intimately 50 grams of it with 15 grams of c.p. potassium iodide and 15 grams of c.p. calcium oxide, and subliming the iodine from the mixture at a temperature never over 75°C. The first and last portions of the sublimate were discarded, and the remainder, about 40 grams, was resublimed in vacuo at temperatures below 70° through a series of U-tubes.

Purification of Chlorine.

Tank chlorine was purified by passing it through the following all-glass chain: (1) a wash bottle, 16 cm. deep, filled with glass beads and containing a saturated solution of potassium permanganate; (2) a similar wash bottle containing distilled water; (3) another similar wash bottle containing concentrated sulfuric acid; (4) a U-tube filled with glass-wool; and (5) a long tube filled with dessichlora.

Preparation of the Iodine Monochloride.

A weighed glass bulb was filled with about 3.5 cc. of chlorine as follows (see fig. 1): Chlorine from the purifying chain passed through the small glass tube F into the weighed bulb G, where it was liquified with liquid air. Care was taken to keep the end of tube F above the surface of the liquid chlorine, and to keep the chlorine flowing fast enough so that it issued out through the calcium chloride tube at all times. The latter tube served to
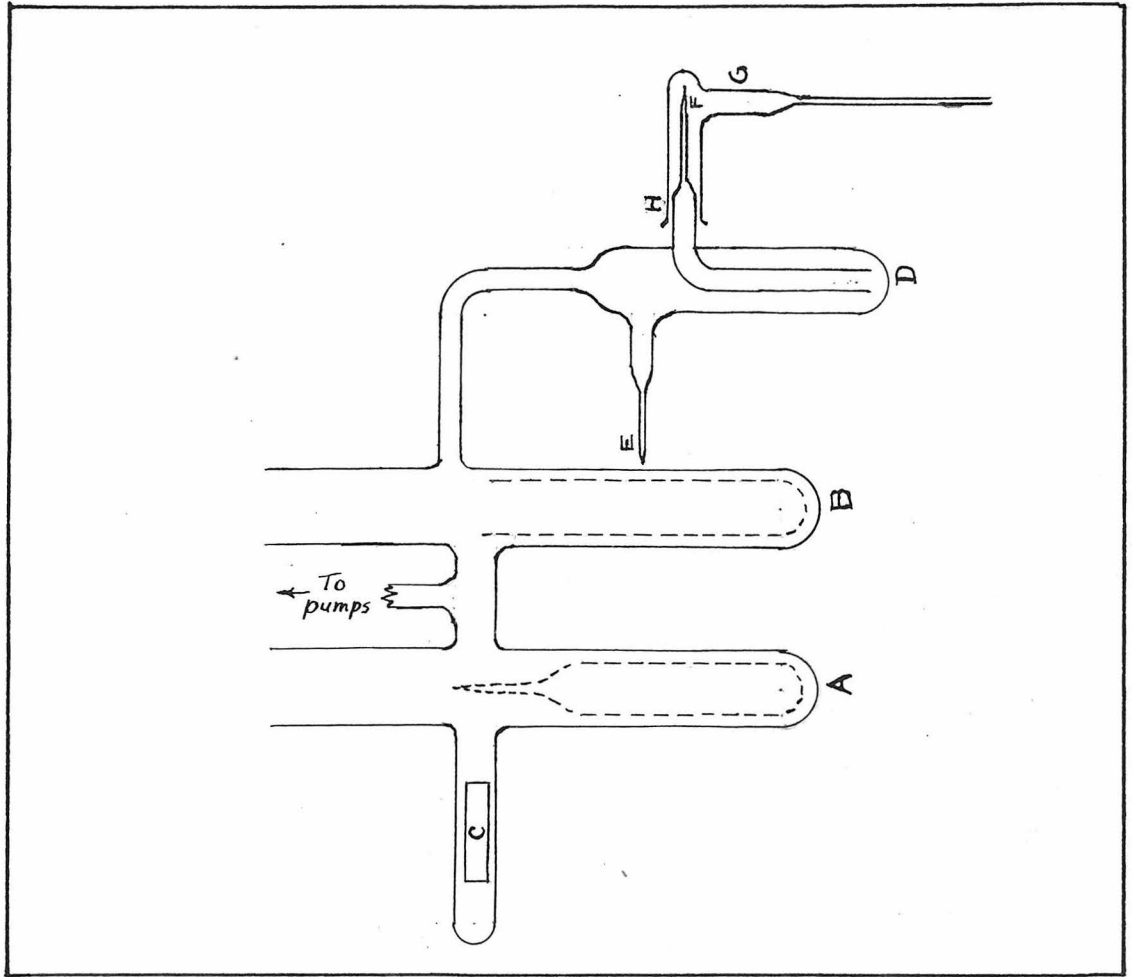
The image contains two figures with labels.

Fig. 2.

Cl₂ →

CaCl₂ tube

a, b, c —
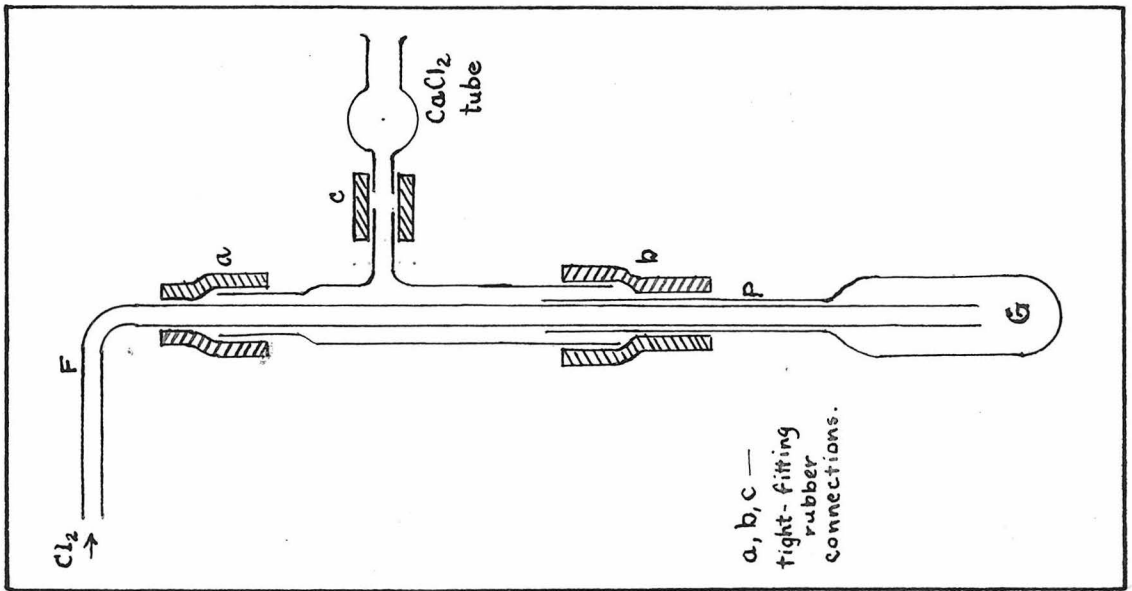tight-fitting
rubber
connections.

Fig. 1

prevent the condensation of atmospheric moisture in G. When the desired amount of chlorine had been liquified, the end of tube F was drawn up to a point above P, at which point the neck of bulb G was sealed off to a fairly long capillary. The bulb of liquid chlorine was allowed to come to room temperature, and was then weighed, together with the sealed off neck. The difference between this weight and the original weight of the bulb gave the weight of the chlorine. This was 4.8434 grams.

The weight of iodine stoichiometrically equivalent to 4.8434 grams of chlorine is 17.3357 grams. To allow for evaporation, 10 mg. more than this weight of the purified iodine was weighed out into a glass tube closed at one end.

For the combination of the iodine and the chlorine, the reaction chamber shown in figure 2 was made. The bulb of chlorine was placed in arm A, the tube of iodine in arm B, and the tops of the two arms were sealed off. The system was then pumped down as rapidly as possible and the reaction chamber sealed off from the pumps. The arm containing the chlorine was immersed in a carbon dioxide-ether freezing mixture until the chlorine was frozen, and then by moderately shaking the apparatus, the heavy glass hammer C was made to break the tip of the chlorine bulb. The chlorine was allowed to evaporate slowly, and when it had all evaporated, the mixture of iodine and chlorine was repeatedly distilled from one portion of the apparatus to another to insure complete reaction. Finally every trace of the mixture was condensed in the container D, which was then sealed off from the rest of the system.

The ICl container was so designed that small quantities of the liquid could be transfered without contamination. This was done in the following manner: The ends of the capillary tips E and F were broken off and the section G (which was ground to fit at H) was attached. By blowing (through a calcium chloride tube) at E, a few drops of ICl were forced into G, through which the liquid passed into a weighed length of 1.5 mm. tubing, the closed end of which was drawn to an easily breakable capillary. When filled with the desired amount of ICl, the open end of the small tube was sealed off and the tube of ICl was weighed together with its sealed-off piece. After the desired number of tubes had been filled, the tips E and F of the container were again sealed off.

METHOD OF TITRATION.

Since the photochemical reaction is $2ICl + H_2 = 2HCl + I_2$, it can be followed by determination of total free halogen present (i.e., $ICl + I_2$) and of acid. This was done by (a) dissolving the sample in potassium iodide solution and titrating to an endpoint with thiosulfate solution, then (b) adding potassium iodate and titrating the iodine thus liberated with more thiosulfate. The reactions involved are:

(a) $ICl + KI = I_2 + KCl$

(b) $6 H^+ + IO_3^- + 5 I^- = 3I_2 + 3 H_2O$,
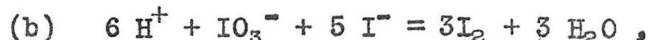
hence each equivalent of ICl and each equivalent of acid gives one equivalent of titratable iodine. From the equation for the photochemical reaction, it is evident that for every two equivalents of ICl used up, one of acid and one of iodine are formed, so that the total number of equivalents of thiosulfate used for both

the free halogen and the acid should be equal to the number of equivalents of ICl originally present. If "a" represents the number of ccs. of thiosulfate solution used for the titration of free halogen, and "b" the number used for the acid, then $\frac{2b}{a+b}$ is the fraction of ICl which has reacted.

This method of analysis was tested as follows: a number of tubes were filled with ICl as described in the preceding section, but were made with breakable tips at each end. A file scratch was made across the center of each tube, and it was then placed in a flask containing 15 cc. of 30% KI solution. The tube was broken at the file scratch by placing it across a glass rod and striking it sharply with another glass rod; the tips were also broken with a glass rod. 0.1039 n. thiosulfate solution was run in until an endpoint was reached with starch solution as an indicator, then 5cc. of 3% potassium iodate solution were added and more thiosulfate solution was run in until an endpoint was reached again. In some experiments definite amounts of standard HCl solution were added before titrating. Blanks made on the potassium iodate showed that neither contained any acid or any free halogen. The results are shown in table I.

It will be noted that in experiments 2, 3, and 4 some acid was found, although none was added, and that the percentages of ICl are somewhat low. In these experiments the broken off tips retained a little of the ICl so that it could not react with the KI, and due to the deep color of the solution, this was not noticed until several ccs. of thiosulfate solution had been added. The

Table I.

Expt. No.	Wt. ICl used	ICl found Wt.	ICl found %	Vol. acid added	Vol. thio for acid. Calc.	Vol. thio for acid. Found	Vol. thio for acid. %
1	0.2421	0.2417	99.83	none	none	none	
2	.1821	.1803	99.00	"	"	0.18	
3	.2411	.2362	98.00	"	"	.70	
4	.2021	.2012	99.55	"	"	.01	
5	.1799	.1801	100.07	"	"	none	
6	.1865	.1868	100.14	"	"	"	
7	.2054	.2050	99.84	10.00	9.23	9.23	100.00
8	.2007	.1999	99.61	15.00	13.85	13.83	99.87

small capillary tips were then crushed with a glass rod and the
titration continued. Since it is known that chlorine oxidizes
tetrathionate to sulfate[10], these results are probably due to a
similar oxidation by ICl of the tetrathionate produced by the
reaction between iodine and thiosulfate, according to the equation

$$10 \ H_2O + 14 \ ICl + S_4O_6^{=} = 4 \ SO_4^{=} + 7 \ I_2 + 14 \ Cl^{-} + 20 \ H^{+} \ .$$
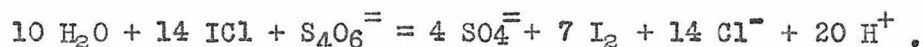
Evidently for every twenty-eight equivalents of ICl reacting in
this manner, only fourteen will appear in the free halogen titra-
tion; the other fourteen will appear as twenty equivalents of
acid. Hence, if x is the number of equivalents of thiosulfate used
for the first endpoint, and y the number used for the acid, then
if no acid were initially present, the actual number of equiva-
lents of ICl is $x + \frac{14}{20} \ y$. Making this correction gave the

following results*:

Table Ia.

Expt. No.	Wt. ICl used.	ICl found (uncorr.) Wt.	%	ICl found (corrected) Wt.	%
2.	0.1821	0.1803	99.00	0.1813	99.60
3.	.2411	.2362	98.00	.2404	99.72
4.	.2021	.2012	99.55	.2013	99.59

In all subsequent experiments, special care was taken that all the ICl was dissolved by the KI solution before any thiosulfate was added.

Tables I and Ia indicate that the ICl is very pure, the mean of the eight values(using the corrected values for 2, 3 and 4) being 99.80%, with an average deviation of 0.17%. Experiments 7 and 8 show that the method outlined for determining acid is quite satisfactory.

PRELIMINARY QUANTITATIVE EXPERIMENTS.

A number of preliminary photochemical experiments were made before it was found possible to make the analyses after illumination agree with the amounts of iodine monochloride used. Only after the apparatus shown in figure 3 was adopted, were satisfactory results obtained.

————————

* More striking are the results obtained (with a different sample of ICl) in another series of titrations for which it was necessary to make a similar correction:

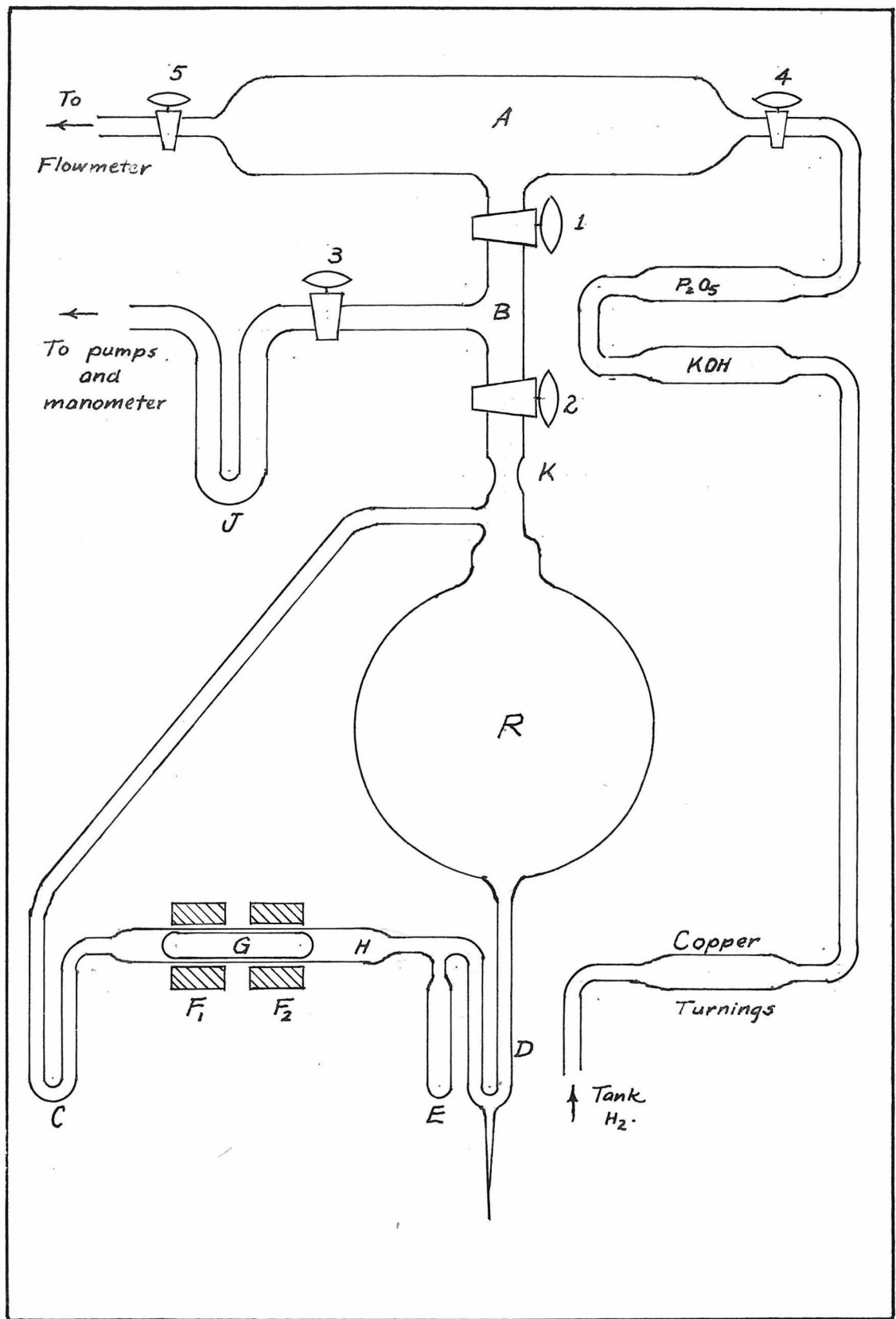| % ICl. Apparent:	94.58	98.63	98.70	101.0	101.0	101.2
Corrected:	100.6	100.7	101.0	101.0	101.0	101.2

FIGURE 3.

Tank hydrogen was passed through the purifying chain
(consisting of tubes of copper turnings, potassium hydroxide
sticks, and phosphorus pentoxide respectively, as shown) into
the reservoir A, and out through a flowmeter. This purifying chain
served to remove oxygen and moisture from the hydrogen. The
hydrogen was allowed to flow through the reservoir for several
hours to sweep out all the air, then for at least two hours with
the tube of copper turnings strongly heated, before being used.
The ICl, contained in a small tube with a breakable tip, was
introduced by means of the side-arm E. This side-arm also con-
tained a small piece of iron rod sealed in a glass tube, which,
by means of a small solenoid, could be made to break the tip of
the ICl tube whenever desired. The reaction vessel R was constructed
from a one liter round-bottomed flask, and had a diameter of about
12 cm. F_1, F_2, G and H constituted an automatic circulating
device. G was a plunger of thin walled glass tubing, 16 cm. long,
in which was sealed a 14.5 cm. length of steel rod about 4 mm. in
diameter, and which fitted very closely, yet freely, within tube H;
the latter was about 42 cm. long. F_1 and F_2 were solenoids,
each 3 inches long and 1 inch in diameter, and each wound with 3500
turns of no. 24 enamel-covered copper wire. By mechanically
alternating the current from one solenoid to the other, the plunger
G could be made to oscillate back and forth through almost the
full length of H about once a second, and quite effective cir-
culation of the gas was thus obtained.

The system was filled with the reaction mixture in the
following manner: The apparatus was completely evacuated below

stopcock 1. Liquid air was placed at U-trap J to condense out mercury vapor from the system, and then at U-traps C and D. The ICl in the bulb in arm E was completely solidified with liquid air, then the tip of the ICl bulb was broken. When all the ICl had distilled into C and D, the arm E was sealed off. Any air introduced by the ICl bulb was pumped off, and the hydrogen was let into the reaction flask from the reservoir A by means of the "doser" B, which was the space between stopcocks 1, 2 and 3. When the desired amount of hydrogen had been introduced, the reaction vessel was sealed off at the constriction K. The volume of the reservoir A had been directly determined before assembling the apparatus by measuring the volume of water which it could hold, and found to be 255 cc. By expanding air from A into B, and into the volume below stopcock 2, before and after sealing off at K, and measuring the resulting pressures on the manometer, the following volumes had been calculated: B, 37.0 cc.; total volume below stopcock 2, about 1155 cc.; volume of reaction system (below constriction K), about 1150 cc. From these volumes and the weight of ICl used, the partial pressures of ICl and of hydrogen could be determined.

After the hydrogen had been introduced and the reaction system sealed off, the liquid air was removed from the U-traps and the ICl allowed to evaporate into the flask. The latter was then illuminated with a 500-watt projection lamp whose filament was 17 cm. from the surface of the flask. During the illumination, water at 15° C. was kept at the U-trap D, and the circulating pump was operated continuously; considerable iodine always condensed

out at D. At the end of the illumination, liquid air was placed at D and the pump operated rapidly for at least an hour to condense out all the ICl, I_2 and HCl. The trap D was then sealed off and the condensed materials titrated.

Two runs were made in this manner under exactly the same conditions with approximately the same amounts of ICl, but greatly different hydrogen pressures. The time of illumination was four hours in each case. A marked dependence on the hydrogen pressure was shown. The results are given in table II.

Table II.

| | Wt. ICl used. | Initial pressures. | | Vol. 0.1039 n. thio (cc.) | | | | % ICl Consumed % |
		ICl	H_2	For free halogen.	For acid	Total. Found	Calc.	
1.	0.1304	13.0	60	14.00	1.32	15.32	15.45 99.2	17.3
2.	.1457	14.5	330	11.55	5.65	17.20	17.28 99.6	65.7

FINAL PHOTOCHEMICAL EXPERIMENTS.

The method described in the preceding section, although it could undoubtedly be applied, is hardly practical for an extended series of experiments. The principal objection is that only one single measurement can be made with a particular mixture of ICl and hydrogen. The fact that fairly long illuminations are required, even with unmonochromatized light from a 500-watt lamp, would make the process exceedingly slow and tedious, and this would be much more the case if monochromatic light were used. Accordingly, an entirely different analytical procedure was adopted, and it was decided to follow the rate of the reaction by measuring, by means of a photo-cell, the change in the absorption of light by the ICl as the reaction proceeded.

Reaction System.

The reaction system used was similar to that shown in figure 3, except that a better manometer than that used previously was attached at the "doser" B, and a liquid air trap was inserted between stopcock 2 and the constriction K. The purpose of this trap was to catch mercury vapor, and any condensable materials which might be carried into the reaction vessel by the hydrogen. The volume of the system below the constriction was determined very carefully by expansion of air from A into B, and into the part of the system below stopcock 2 before and after sealing off at the constriction; the resulting pressures were measured on the new manometer. The volume was found to be 1163 cc.

The hydrogen and the ICl were introduced into the system in exactly the same manner as before. However, the pressure of the hydrogen, instead of being determined from the volume relations, was read directly on the manometer before sealing the reaction flask off at the constriction.

Optical System.

The light source consisted of a quartz mercury vapor arc lamp which was always operated at a current of 4.0 amperes, and with a potential drop of 33 volts across the electrodes. The lamp was housed in a wooden box 33 cm. high, 20 cm. wide, and 25 cm. long. The box was open at the top and back, and had a rectangular hole 6.5 x 14 cm. in the front, in front of which was mounted a shutter. Across the hole, inside the box, was fastened a brass filter compartment, 3.5 cm. thick, with glass windows 6 x 9 cm. Water was

flowed through this filter compartment continuously while the lamp was running. By placing the lower part of the lamp in a horizontal V-shaped slot cut in a piece of heavy brass which was fastened permanently to the box, the lamp could always be replaced in exactly the same position, very close to the filter compartment.

To isolate the mercury blue line, 4358 Å, a filter consisting of a 2 mm. thick piece of Noviol A glass and a 3 mm. thick piece of Cornung G-585 glass, with a 1 cm. layer of 6% $CuSO_4$ solution between them, was used. This filter was mounted over a square hole, 4.75 cm. on a side, in a strip of brass which slid smoothly into the filter compartment.
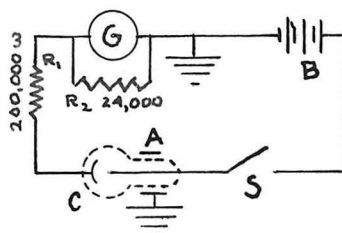
The photocell circuit was as follows:

Fig. 4

The Burt sodium photocell C was mounted on a Bakelite socket in a closed box 20 cm. high, 12 cm. wide, and 12 cm. long, which had a 1.9 cm. diameter hole in the front. The socket, and the two binding posts which passed through the side of the box, were cast in sulfur plugs to insulate them completely from the box. The photocell had a grounded metal guard ring, A, fastened tightly around its neck. A high sensitivity galvanometer, G, was used. It had a resistance of 595 ohms and a sensitivity of 11,300 megohms. It was protected by the 200,000 ohm resistance, R_1, and was almost critically damped by the 24,000 ohm resistance, R_2. The source of

potential, B, was two 45-volt B batteries; these were mounted on paraffin blocks. The switch, **5**, consisted of two small pools of mercury in a block of paraffin, with a removable wire bridge. Wherever it was necessary to suspend the connecting wires, they were suspended from paraffin blocks. All the above insulating precautions were very necessary. Before they were taken, numerous leaks manifested themselves in the electrical circuit, but these disappeared one by one as the various precautions were taken, and were finally entirely eliminated.

The boxes containing the photocell and the mercury lamp were firmly fastened to a rigid base, facing each other at a distance of 14 cm. apart. The base was mounted on brass runners so that the entire assemblage could be slid forward and back. Two stops were arranged so that in one position there was a free path between the two boxes, while in the other, the reaction flask came directly between them.

The entire reaction system, except for the front and back of the reaction flask itself, was painted with optical black to prevent the entrance of stray light.

Experimental Procedure.

During all measurements of light transmissions with the photocell, a brass diaphragm, 2.5 cm. in diameter, was always inserted in the filter compartment. This was done to reduce the galvanometer deflections to the desired amount, and also to insure that the only light reaching the photocell was that passing through the center of the spherical flask where the windows could be considered as essentially plane and parallel.

Before filling the reaction flask with hydrogen and iodine
monochloride, a determination was made of the ratio of the light
intensities with and without the flask in the path of the light beam.
This was done in the following manner: first, with a free path
between the two boxes, the shutter was opened. At the end of thirty
seconds, the galvanometer was read and the shutter closed. At the
end of another thirty second period, the galvanometer was again
read and the shutter opened; then, a third reading was made after
thirty seconds with the shutter open. The difference between the
average of the two galvanometer readings with the shutter open and
that with the shutter closed gave the light intensity in arbitrary
units. Next, the optical assemblage was pushed into place with the
flask in the light path, and the readings repeated. This was
continued until three measurements had been made with a free path,
and two with the flask in the path of the light. The mean of the
two latter measurements, divided by the mean of the three former,
gave the transmission of the empty flask, which was 0.876.

All transmission determinations were made in the above
manner, except that usually only two measurements were made with
a free light path, and one with the flask in the path of the light.
If I represents the intensity measured through the flask, and I_f the
intensity with a free light path, then $0.876 I_f$ would be the intensity
I_o measured through the flask if empty, and $\frac{I}{I_o} \left(= \frac{I}{0.876 I_f} \right)$ the
actual transmission.

The reaction system was filled with ICl and hydrogen as
previously described, and a transmission measurement made before
starting an illumination in order to determine an absorption

coefficient for the ICl. The 2.5 cm. diaphragm was then withdrawn
and the flask illuminated. During the illumination, the automatic
circulating pump was operated continuously, and U-trap D was kept
immersed in a Dewar flask full of water at a definite temperature,
somewhat below room temperature, in order to keep the iodine
formed during the photochemical reaction at a definite and rather
low pressure. Transmission measurements were made at intervals
of about 15 minutes.

Experimental Results.

Five series of measurements were made with the reaction
flask filled with 0.1144 grams of ICl, and 596 mm. of hydrogen. The
weight of ICl used corresponded to an initial ICl pressure of
14.03 mm. Since the hydrogen is so largely in excess, it can be
regarded as constant throughout the run. The initial value of the
transmission was 0.2029. Assuming Beer's law to be obeyed,
$\log \frac{I}{I_o} = - kp$. In this case, $\log \frac{I}{I_o}$ is -0.6927 and p is 14.03 mm.,
so k = 0.04937. This value was used in calculating the pressures
of iodine monochloride throughout the run. The results of the
experiments are shown in table III. The temperature of the reaction
flask was 23° throughout.

Plotting the partial pressures of ICl against $\Sigma I_o \Delta t$
gave the curves shown in figure 5. The values used for I_o were
the means of the values obtained at the beginning and end of each
time interval. Since the points are somewhat irregular, a straight
line was chosen as the best curve in each case. It was found that
on dividing the slope of each curve by the average value of the
fraction of light absorbed during the particular run, the resulting

TABLE III

$$P_{H_2} = 596 \text{ mm.}$$

	Time (min)	I/I_0	I_0	P_{ICl} mm	$(1-I/I_0)$	$I_0 t$	Temp. of I_2 Trap	P_{I_2} mm
A.	0	0.3288	9.31	9.79	0.6712	0	17°C	1.54
	14	.3358	9.14	9.60	.6642	129		
	29	.3413	8.99	9.46	.6587	265		
	44	.3549	9.32	9.14	.6451	402		
	59	.3655	8.95	8.85	.6345	540		
B.	0	0.4054	9.05	7.94	0.5946	0	17°	1.54
	15	.4180	9.31	7.67	.5820	138		
	32	.4244	9.24	7.54	.5756	295		
	45	.4370	9.25	7.28	.5630	415		
	61	.4465	9.27	7.09	.5535	563		
	75	.4572	8.97	6.88	.5428	691		
C.	0	0.6079	8.83	4.38	0.3921	0	15°	1.28
	15	.6193	8.70	4.22	.3807	132		
	30	.6239	8.90	4.15	.3761	264		
	45	.6378	8.69	3.96	.3622	396		
	60	.6491	8.97	3.80	.3509	528		
	75	.6624	8.98	3.62	.3376	663		
D.	0	0.7509	9.61	2.52	0.2491	0	10°	0.0808
	16	.7558	9.42	2.46	.2442	152		
	30	.7675	9.34	2.33	.2325	283		
	45	.7809	9.36	2.18	.2191	423		
	60	.7903	9.24	2.07	.2097	562		
	75	.7954	9.81	2.01	.2046	705		
E.	0	0.8121	8.76	1.83	0.1879	0	10°	0.0808
	15	.8224	9.03	1.72	.1776	133		
	30	.8285	9.67	1.66	.1715	273		
	45	.8337	9.69	1.60	.1663	418		
	60	.8464	9.57	1.47	.1536	563		
	75	.8582	9.58	1.35	.1418	707		

FIG. 5

Partial Pressure of ICl (MM.)
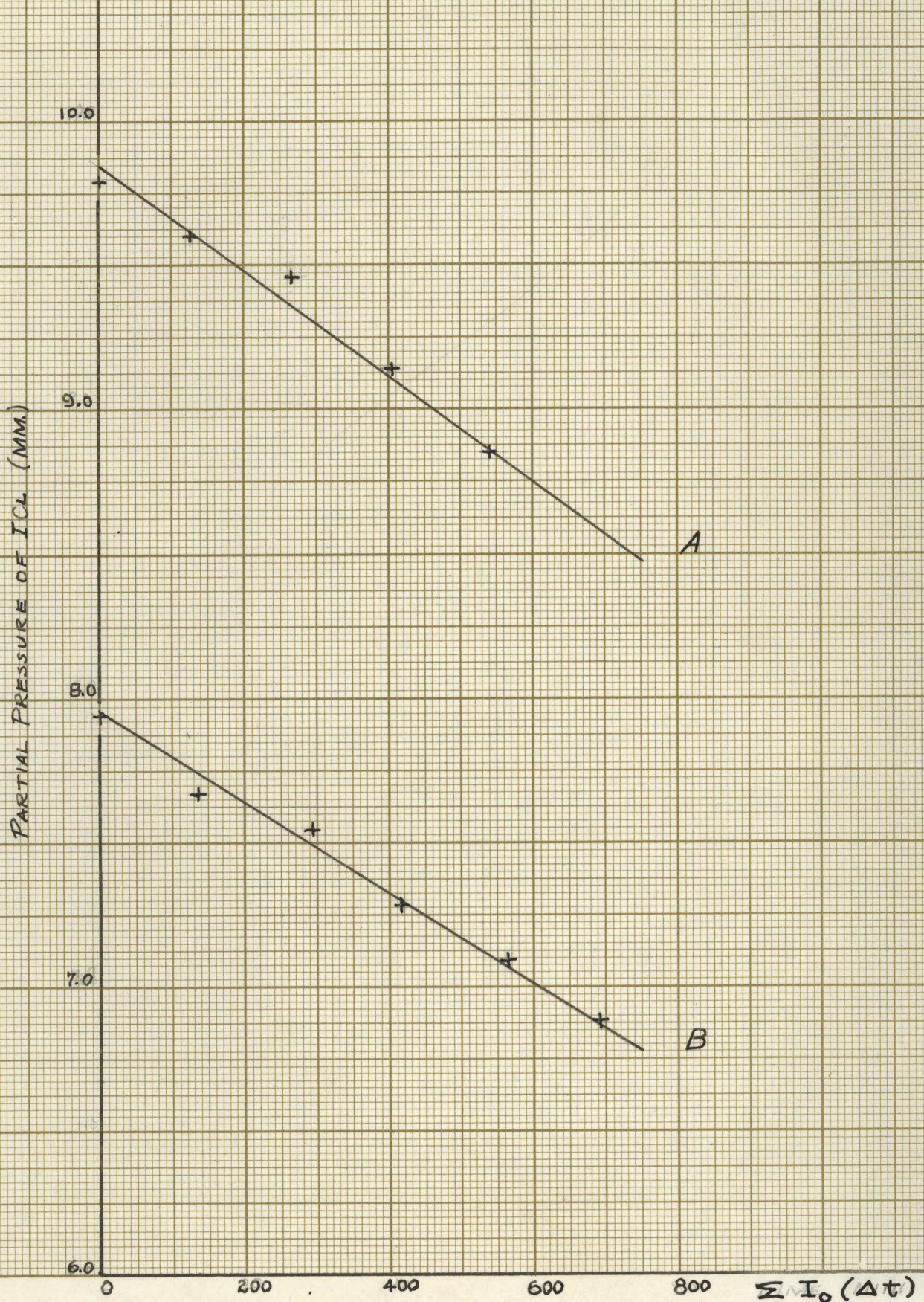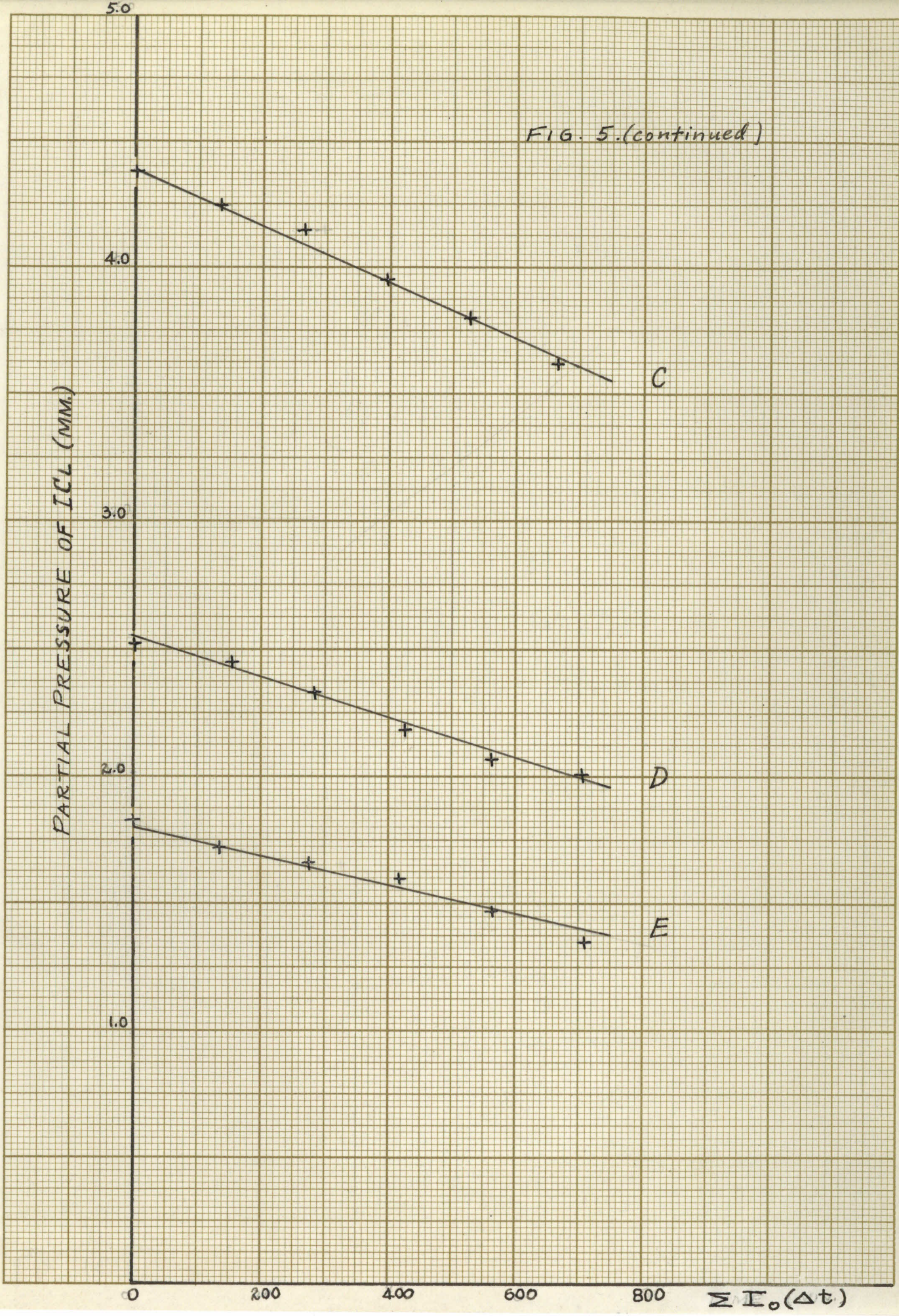
$\Sigma I_0 (\Delta t)$

FIG. 5. (continued)

values were fairly constant over the entire range, as shown in the following table:

Table IV

Run	$\dfrac{-dp}{d(\Sigma I_o \Delta t)}$	$1 - I/I_o$	Ratio
A	0.00186	0.6547	0.00284
B	.00160	.5686	.00282
C	.00112	.3833	.00292
D	.00078	.2265	.00344
E	.00058	.1663	.00324

The ratio is $\dfrac{\frac{-dp}{d(\Sigma I_o \Delta t)}}{1 - I/I_o}$. Since $-dp/dt$ is the rate of the reaction, while $I_o(1 - I/I_o)$ is proportional to the rate of absorption of light, it is evident that the constancy of this ratio indicates that the rate of the reaction is proportioal to the rate of absorption of light. Apparently, the rate of photochemical reaction, under the conditions studied, is independent of the concentrations of ICl (except insofar as it affects the absorption of light) and of the products of the reaction. Also, since the rate of reaction is proportional to the number of molecules of ICl decomposed per unit time, and the rate of absorption of light is proportional to the number of quanta absorbed per unit time, it follows that the number of molecules of ICl reacting per quantum of light absorbed, i.e., the quantum yield, is constant under the conditions of the experiments.

In the above consideration, the fraction of the total absorption which was due to iodine was taken as negligible. This is justified by the following calculation: When two absorbing species, both of which obey Beer's law, are present, the fraction x_1 of the absorption which is due to one of them is given by the expression $x_1 = \dfrac{A_1 c_1}{A_1 c_1 + A_2 c_2}$,

in which A_1 and A_2 are the respective absorption coefficients, and c_1 and c_2 the respective concentrations. Applying this expression to run E, in which iodine would have the greatest effect, it was found that about 3.0 % of the light absorption was due to iodine. The pressure taken for ICl was 1.35 mm., and that for iodine 0.0808 mm. (its vapor pressure at 10°). The absorption coefficient for ICl was calculated from the initial transmission measurement, and the initial ICl pressure, and found to be 75.7. That for iodine at the same wave-length had been determined by Wellman and Ravitz in this laboratory and found to be approximately 40. (Log_{10} $I/I_0 = -Acl$; c in mols per liter, l in centimeters.)

The Quantum Yield.

In order to obtain an idea of the order of magnitude of the quantum yield under the conditions studied, a Moll thermopile-galvanometer system was calibrated against a standard lamp, the directions furnished by the Bureau of Standards being carefully followed. The quartz window of the thermopile was removed during the calibration. It was found that each centimeter galvanometer deflection corresponded to 1.30 ergs/mm^2/sec. Next, the deflections produced by a steady light source, with and without a 7-ohm shunt across the galvanometer, were measured, and it was found that the ratio of the deflection without the shunt to that with the shunt was 2.39.

With conditions exactly the same as during the illuminations of the ICl-hydrogen mixture, but with the reaction flask out of the light path, the thermopile (with the quartz window in place) was placed at a position corresponding to the center of the exposed part of the flask; and average deflection of 21.3 cm. was observed, with

the 7-ohm shunt across the galvanometer. At a position 2.5 cm. to the right of the center the deflection was 12.1 cm., and at a position 2.5 cm. to the right of, and 2.5 cm. above the center it was 7.5 cm. Immediately following these measurements, the brass diaphragm was inserted in the filter compartment and a reading made with the photocell in the usual manner, an average deflection of 9.42 cm. being obtained. Assuming, for the purpose of calculation, an average of 20 cm. deflection with the thermopile for an area 2 cm. in radius about the center of the portion of the flask exposed to the light (the diameter of which was 8.0 cm.) and 9 cm. for the remaining area, a very approximate value of the quantum yield can be determined.

A deflection of 20 cm. with the shunt corresponds to one of 47.8 without the shunt, or 62.2 ergs/mm^2/sec., while an area 2 cm. in diameter is 1257 mm^2. Similarly, a 9 cm. deflection corresponds to 28.0 ergs/mm^2/sec., and the area receiving this is 3770 mm^2. Taking into account the transmission of the thermopile window, which is 90%, it is found that the amount of light reaching the surface of the flask was 2×10^5 ergs/sec., or 1.2×10^7 ergs/min. Since the deflection with the photocell was 9.42, a 1 cm. galvanometer deflection with the photocell corresponds to 1.27×10^6 ergs/min. at the surface of the flask.

In run A the average value of I_0 was 9.14 cm., corresponding to a value of 10.45 cm. with the flask out of the light beam. Hence during that run, $1.27 \times 10^6 \times 10.45$ or 1.33×10^7 ergs reached the surface of the flask. If it be assumed that 10% of the light is reflected at the surface, and that the average absorption, 65.5%, measured during run A (see Table IV) represents the average absorption throughout the cell during the run, then 7.83×10^6 ergs/min. are absorbed.

From Table IV, $\dfrac{-dp}{d(\Sigma I_o \Delta t)}$ for run A was 0.00186. Multiplying this by the average value, 9.14 cm., of I_o during the run gives $-dp/dt$ as 0.0170 mm/min., from which, assuming the perfect gas equation it is found that 1.07×10^{-6} mols of ICl were consumed per minute.

One einstein of light of wave length 4358 Å is 2.73×10^{12} ergs. Hence, in one minute, 1.07×10^{-6} mols of ICl reacted for every 7.83×10^{6} ergs, or 2.87×10^{-6} einsteins of light absorbed. This corresponds to a quantum yield of 0.37 molecules of ICl reacting per quantum absorbed.

This value for the quantum yield is undoubtedly a minimum, and the actual value may be several times larger. In the first place, the light intensities at the surface were probably less than the value taken. In the second place, since the flask was spherical with only a six inch radius, the reflection at the surface was certainly considerably greater than the 10% assumed. And finally, the absorption measured was through the longest possible path, whereas a fairly large amount of the light must have traversed a considerably shorter path.

SUMMARY

The effect of light on mixtures of iodine monochloride and hydrogen has been investigated, with the following results:

1. Iodine monochloride and hydrogen react under the influence of light to give hydrogen chloride and iodine.

2. The reaction is much faster at high hydrogen pressures than at low.

3. Evidence has been found that, at a constant hydrogen pressure of about 600 mm., the rate of the reaction is dependent only on the amount of light absorbed.

4. An approximate determination of the quantum yield *at the same hydrogen pressure* has been made, yielding a minimum value of 0.37 molecules of iodine monochloride decomposed per quantum of light absorbed.

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