

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 291]

THE PHOTOCHEMICAL REDUCTION OF FERRIC IRON IN TRI-IODIDE SOLUTION

BY S. FREDERICK RAVITZ AND ROSCOE G. DICKINSON

RECEIVED JULY 3, 1931

PUBLISHED SEPTEMBER 5, 1931

Introduction

Investigations of the effect of light on the equilibrium¹ $2\text{Fe}^{+++} + 2\text{I}^- = \text{I}_2 + 2\text{Fe}^{++}$ have shown that visible or near ultraviolet displaces the equilibrium to the left and does so at such a rate that two equivalents of titratable iodine are consumed per einstein absorbed. In a recent paper² the authors described the effect of light on ferrocyanide-ferricyanide iodine-iodide equilibrium solutions in which the equilibrium is so displaced by light 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 suitably 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 as 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 ion 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 sulfuric acid, 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% potassium chromate and 1 cm. of 6% copper sulfate. The potassium chromate removed practically all radiation below 5000 Å., while the copper sulfate removed the infra-red. The change in iodine concentration in each solution was followed by with-

¹ (a) Sasaki, *Z. anorg. Chem.*, **122**, 61 (1922); (b) Rideal and Williams, *J. Chem. Soc.*, **127**, 258 (1925); (c) Kistiakowsky, *THIS JOURNAL*, **49**, 976 (1927).

² Dickinson and Ravitz, *ibid.*, **52**, 4770 (1930).

drawing, 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 initial composition of the solution used was as follows: $\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, 0.0025 *f*; KI, 0.00785 *f*; I_2 , 0.002 *f*; and H_2SO_4 , 0.015 *f*. 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

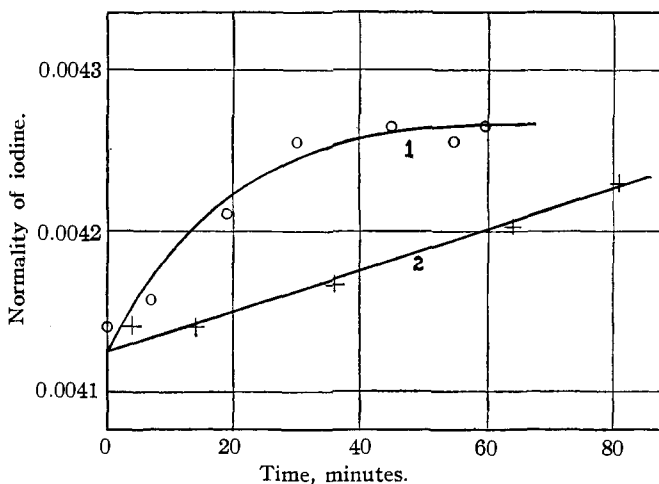


Fig. 1.—Change in iodine concentration with time for illuminated (1) and unilluminated (2) solutions of the same initial composition.

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 the experiments (fifty 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 temperature 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 formed 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, 10-cc. samples were simultaneously withdrawn from the illuminated and dark portions and pipetted into test-tubes containing potassium ferricyanide as described above. From a buret, 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 time were found. The results are shown in Table I

TABLE I
RESULTS OF EXPERIMENTS

Time of illumination, min.	Diff. in iodine concn. (milli-equiv./liter)	Diff. in ferrous concn. (milli-equiv./liter)
14	0.075	0.08
23	.12	.18
38	.16	.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 colloidal ferrous ferricyanide was formed were somewhat different in the two solutions matched. In view of these facts, the agreement between the amounts of ferrous iron and iodine produced 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 known³ 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 photochemical oxidation of ferrous iron. Sasaki illuminated solutions containing appreciable amounts of ferrous iron at the start and consequently always found a net disappearance of iodine. Similarly, the present results probably do not create any difficulty with Kistiakowsky's quantum yield determinations, for in those the ratio of ferrous to ferric iron present was sufficiently large so that the photochemical reduction could hardly have amounted to more than a few per cent. of the oxidation.

For the ferric iron reduction the same mechanisms may be offered as were suggested² in the case of the ferricyanide reduction. These mechanisms all involve reduction by the hypothetical ion I_2^- produced either in the primary absorption process or subsequently.

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.

PASADENA, CALIFORNIA

³ See, for example, Wagner, *Z. physik. Chem.*, **113**, 261 (1924).