THE PHOTOLYSIS OF POTASSIUM IODATE

BY J. HOWARD MATHEWS AND HARRY A. CURTIS

Introduction

Recently it was noted in this laboratory that potassium bromate apparently decomposes quite rapidly in light of short wave lengths. A quartz vessel containing a solution of potassium bromate and a little starch potassium iodide as an indicator became blue on a few seconds' exposure to the light from a quartz-mercury vapor lamp. Potassium chlorate and potassium iodate gave the same results. These reactions seemed so promising that it was decided to investigate them quantitatively if possible. The investigation has led to the consideration of several problems in photochemistry, and in one direction to a problem quite out of the field of photochemistry, as will be indicated below.

A few preliminary tests soon made it clear that potassium bromate alone does not decompose rapidly in solution, and that the observed result was due to the oxidation of the potassium iodide by the oxyhalogen salt under· the influence of light of short wave length. If potassium bromate solution were exposed for a few seconds and then removed from the light, it would give no blue color upon the addition of the potassium iodide-starch indicator. Nor would the starch-potassium iodide solution become blue on short exposure, although a longer exposure (a few minutes usually) would, of course, give blue, due to the well-known photo-oxidation of potassium iodide in the presence of air. The mixture of the two salts was far more sensitive to the light than either of them alone. The same was found to be true in the case of the iodate and chlorate.

It has been found that this reaction is an excellent one for lecture demonstration purposes, especially because of the fact that it is not very sensitive to the light of such wave lengths as ordinary glass will transmit. The details of this demonstration experiment are given below.

In the present paper only the photolysis of potassium iodate and its reaction with potassium iodide will be considered. Similar investigations with potassium chlorate and potassium bromate are under way in this laboratory and the results will appear later.

Lecture Demonstration Experiment in Photochemistry

Dissolve about one-tenth of a gram of potassium iodate in five hundred cc of distilled water. Add to this two cc of a one percent iodide solution and two cc of a one percent starch solution. Pour one-half of this mixture into a three hundred cc quartz flask and the other half into a similar flask of ordinary glass. Expose the two solutions at equal distances on either side of a quartz-mercury vapor lamp. In a few seconds the solution in the quartz flask will become a deep blue, while the solution in the glass flask remains quite colorless.

The amounts of reagents may be varied within very wide limits, the only effect being to change the time required for the appearance of the blue color. For example, the iodate used has been varied from 0.001 gram to one gram, and the iodide from 0.01 gram to one gram without changing the result except as to time. The variations in time required give no trouble practically, since the extreme change in the above limits was less than a minute using a "110-volt" lamp.

The effect of carbon dioxide on the reaction is large, as will be shown below, but with ordinary distilled water no trouble from this source has been experienced.

The Photolysis of Potassium Iodate

On long exposure to light of short wave lengths, potassium iodate in solution slowly decomposes, liberating iodine. The reaction may be followed by titrating the liberated iodine with standard sodium thiosulphate solution.

In the experiments described below, Merck's potassium iodate was used. This was recrystallized three times from distilled water, discarding each time the first portion of crystals to separate and the mother liquor. The purified iodate was tested for chlorate by converting to the iodide and then ap-

plying the chromyl chloride test for chlorine. Negative results were obtained on duplicate tests.

In determining the amount of iodine liberated, a 0.001 N solution of thiosulphate was used, this solution being always protected from carbon dioxide by a soda-lime tube. It was found best to add a slight excess of the standard thiosulphate in titrating, and then at once titrate back to a faint blue end point with standard iodine solution. In calculating the amount of thiosulphate required, a correction was always made for the amount of iodine required to give a faint blue end point in the volume of solution used. It would be desirable to determine also the amount of iodate actually decomposed by a direct determination of the potassium iodate content of the solution before and after illumination. A simple calculation shows, however, that the amount of iodate corresponding to the iodine liberated is not much larger than the unavoidable error which enters in the determination of the iodate. It was necessary, therefore, to depend entirely upon the iodine liberated as a measure of the progress of the reaction.

In each of the experiments described below, two hundred cc of tenth normal potassium iodate solution were used. Because of the small amount of iodine liberated it was necessary to titrate the whole solution after each period of illumination. This rendered the investigation rather a long and tedious one.

Apparatus Used

The following arrangement of apparatus shown, in part, in Fig. 1, has proved very satisfactory in studying photochemical reactions in solution.

The quartz-mercury vapor lamp A, is mounted over a water thermostat, B, provided with thermometer, electric temperature regulator, etc. The quartz flask C, containing the reaction mixture, is mounted as near the lamp as desired, and kept at constant temperature by allowing water from the perforated ring D, to flow down over it. This water is taken from the thermostat and delivered to the perforated ring by

a small centrifugal pump, E, driven by an electric motor. The reaction mixture in C is agitated by the stirrer F, which is driven by the pulley G, the latter being carried on an extension of the shaft operating the large stirrer in the thermostat.
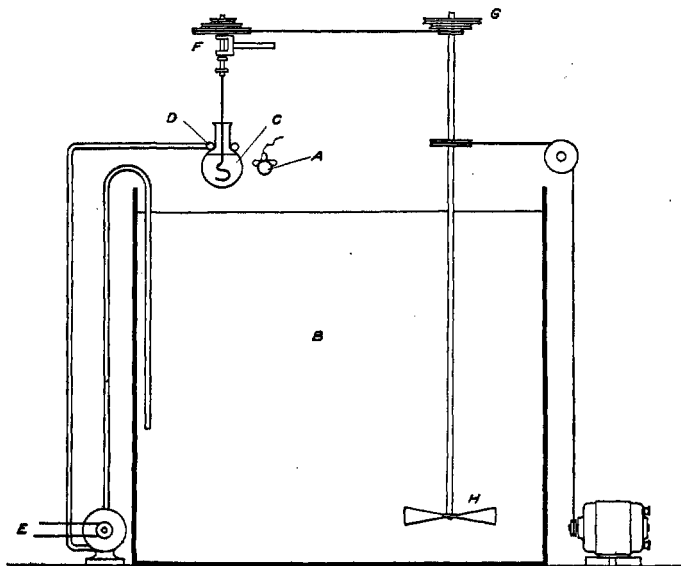

Fig. 1

When the flask C is to be left open to the air, an ordinary glass stirrer may be used. It is often desirable, however, to keep the solution in the flask C out of contact with air, or saturated with some particular gas. In the latter case the excellent device proposed by Plotnikow may be substituted for the simple stirrer. This device is shown in Fig. 2, where the quartz reaction flask C is drawn on a larger scale.

The apparatus is set up without the mercury in the seal L, and the gas to be used is delivered through the tube M until all the air in C has been replaced. Mercury is then poured in to make the seal, and the three-way cock N is turned so as to bring the gas burette O; filled also with the gas to be used, in connection with the flask C. By means of the leveling

tube the pressure in the flask C may be kept constant at any
pressure near that of the atmosphere. If the stirrer be ro-
tated at a high speed, gas will be drawn in through the hole P,
and thrown out into the liquid, keeping the latter always
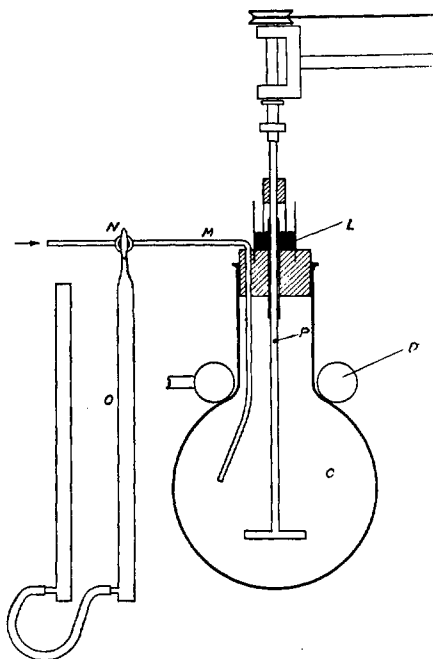saturated with the gas.

Fig. 2

Rate of Photolysis of Potassium Iodate Solution in the Presence of Air

In Table I, and in Fig. 3, are given the data for the pho-
tolysis of tenth normal potassium iodate solution, the flask
C being left open to the air. Two hundred cc of tenth normal
iodate solution were used each time, and the temperature
held at 30°. In titrating with the thiosulphate solution as
dilute as 0.001 N it is not to be expected that duplicate de-
terminations will yield exactly the same titer, nor that a

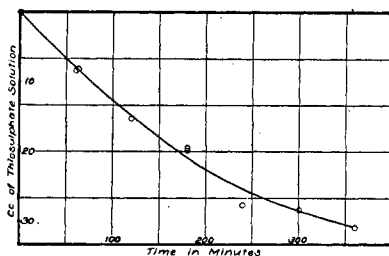very smooth curve will result when these numbers are plotted on as large a scale as has been used in Fig. 3.

Fig. 3

TABLE I

Time in minutes	cc Na$_2$S$_2$O$_3$	Time in minutes	cc Na$_2$S$_2$O$_3$
61	8.4	180	19.7
63	8.2	240	27.6
120	15.3	300	28.3
180	19.4	360	30.9

The Influence of Oxygen on the Photolysis of Potassium Iodate Solution

In attempting to follow the reaction between a mixture of potassium iodate and potassium iodide under the influence of light, it was not possible at first to get concordant results. It was finally noticed that the rate of the reaction could be greatly increased by shaking the reaction mixture with air before insolating it. This fact seemed to indicate that the oxygen of the air was disturbing the reaction, and suggested at once the possibility that the photolysis of the iodate alone was also influenced by air. To decide this point regarding the iodate, a solution of potassium iodate was prepared in water which had been boiled for an hour and then cooled in an atmosphere of pure nitrogen. The reaction flask was fitted with a stirrer carrying a mercury seal and was filled with pure nitrogen. The iodate solution was then forced into the flask and the excess of nitrogen allowed to escape through the mercury seal, so that the reaction flask finally

contained an air-free solution of potassium iodate under an atmosphere of nitrogen. (The rather elaborate apparatus for accomplishing the above result is not described, for reasons which appear below.) The iodate solution was now insolated for 168 minutes, and it was found that it required 11 cc of the standard thiosulphate solution to titrate the liberated iodine, whereas the amount interpolated from Fig. 3 for 168 minutes is about 19 cc. This result apparently indicated that air influences the reaction, but it seemed strange that the effect was not greater than was actually found. Many attempts were now made to prepare an iodate solution so free from air that no decomposition of the iodate would occur on insolation. Long-continued boiling of the solution under reduced pressure before illumination would always greatly reduce the rate of photolysis, and on two occasions no iodine was obtained, although several similar experiments gave positive results, the amount of iodine being always very small, however. The fact that the decomposition could be reduced so nearly to zero seemed to indicate that no decomposition would occur if the last trace of air could be removed from the solution, but it seemed impossible to do this. As will appear later, our efforts were directed toward the removal of a substance which takes no part in the reaction.

Finding it impossible to obtain checking results by this plan, it was decided to keep the concentration of the oxygen constant by keeping the solution always saturated with oxygen. The Plotnikow saturation device was, therefore, substituted for the ordinary stirrer and pure oxygen used. It was now found that no decomposition occurred. The next step was obvious; substitution of carbon dioxide for oxygen gave positive results at once.

The Effect of Carbon Dioxide on the Photolysis of Potassium Iodate Solution

Carbon dioxide greatly increases the rate of photolysis of potassium iodate in solution. Table II and the solid-line curve of Fig. 4 present the data for the decomposition of po-

tassium iodate in a solution kept saturated with carbon dioxide. The broken-line curve of Fig. 4 represents the rate of photolysis of the potassium iodate when the solution was exposed to the air, the curve being here plotted on the same scale as used for the solid-line curve.
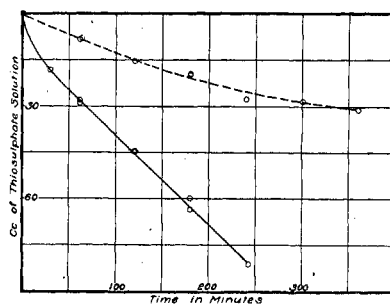

Fig. 4

TABLE II

Time in minutes	cc thiosulphate	Time in minutes	cc thiosulphate
30	18.3	180	59.8
30	18.4	180	63.2
62	28.7	243	81.1
62	28.2	—	—
120	44.3	—	—
122	44.5	—	—

Order of the Reaction when Carbon Dioxide is Present

Inspection of Fig. 4 shows that the amount of iodine liberated is a linear function of the time of insolation, *i. e.*, the reaction apparently does not follow the mass law.[1] While it is true that the decomposition here is practically linear with respect to time of insolation, it is not permissible to draw conclusions regarding the order of the reaction from such data as are available in Table II, a point which the following consideration will make clear: For the two hundred cc of

---

[1] This case is sometimes loosely expressed by saying that the reaction is of the zero order, *i. e.*, the rate of reaction is independent of the concentration.

tenth normal iodate solution it would require twenty liters of the standard thiosulphate solution to titrate the iodine if it were all liberated. Since the maximum amount of thiosulphate solution actually required for any titration was less than one hundred cc, it is evident that less than one two-hundredth of the total amount of iodate was decomposed during the longest period of insolation, *i. e.*, for the purposes of the mass law calculations, the iodate concentration of the iodate would be considered as constant, and this makes the rate constant, regardless of the order of the reaction. The fact that it is not possible to judge correctly the order of a reaction when the amount transposed is very small as compared with the total amount present must be especially noted in photochemical research where, on account of the small effect of light on most reactions, the amount of material transformed in the photochemical reaction is apt to be but a small fraction of the total amount present. It was pointed out in our paper on the photolysis of hydrogen peroxide[1] that the decomposition of the peroxide is a linear function of the time of insolation when the concentration of the peroxide is higher than about 1.5 percent, although the reaction is clearly of the first order when the concentration is small.

Knowing the effect of carbon dioxide on the photolysis of the iodate, it is now possible to explain the decomposition curve obtained when the flask was left open to the air (Fig. 3). The iodate solution would absorb carbon dioxide from the air but slowly, while the amount in the solution would grow less, since the carbon dioxide is certainly used in the reaction. The rate of photolysis would, therefore, decrease, a fact which was very puzzling when the data for Fig. 3 were first obtained. By keeping the solution always saturated with carbon dioxide, this factor became constant and the decomposition curve then became a straight line, as was to be expected from the relatively small amount of decomposition.

---

[1] Jour. Phys. Chem., **18**, 166 (1914).

The Reaction between Potassium Iodate, Potassium Iodide and Carbon Dioxide in the Absence of Light

From a solution containing both potassium iodate and potassium iodide, carbon dioxide at once liberated iodine. This fact is not often mentioned in the literature, and has been entirely neglected in certain investigations of the reaction between these salts in the presence of other acids. For example, Dushman,[1] in his study of the reaction between these salts in the presence of acetic acid, kept all his solutions under an atmosphere of carbon dioxide and must, therefore, have had the effect of carbonic acid superposed upon that of acetic acid. In fact, with carbon dioxide in the solution the acetic acid may be omitted entirely and the reaction will still proceed rapidly. We have studied the reaction between potassium iodate, potassium iodide and carbon dioxide; the results of this investigation will appear later, since they do not fall under the head of photochemical research with which the present paper deals. The investigation is mentioned here because of its bearing on the problem of the photolysis of potassium iodate, since a knowledge of the reaction between potassium iodate and potassium iodide in the presence of carbon dioxide makes it possible to formulate what appears to be a logical explanation of the photolysis of potassium iodate and the influence of carbon dioxide upon this reaction.

Theory of the Photolysis of Potassium Iodate in a Solution Containing Carbon Dioxide

Potassium iodate decomposes under the influence of light, yielding oxygen and potassium iodide. The iodide formed is at once oxidized by the potassium iodate in the presence of the carbon dioxide. In a solution saturated with carbon dioxide, the speed of the second reaction is far higher than that of the first, so that the reaction velocity measured will be that of the photolysis of potassium iodate. The equations might be written:

$$KIO_3 = KI + 3O$$
$$5KI + KIO_3 + 6CO_2 + 3H_2O = 6KHCO_3 + 6I$$
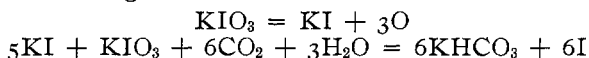
[1] Jour. Phys. Chem., **8**, 453 (1904).

If this theory be the correct one, oxygen should be liberated, and even though the amount of potassium iodate decomposed be small, there should be an appreciable volume of oxygen liberated. To test this point experimentally, a solution of potassium iodate was insolated in a quartz flask so arranged as to collect any gas which might be liberated. When this was done, there was a slow but steady accumulation of gas which on testing was found to be insoluble in sodium hydroxide solution but readily soluble in alkaline pyrogallol.

Concerning the Influence of Light on the Reaction between Potassium Iodate and Potassium Iodide in the Presence of Carbon Dioxide

Light increases the speed of this reaction, but it has not been possible so far to make any progress toward a quantitative examination of the reaction. The number of variable factors is so large as to make the problem extremely complex. Potassium iodide alone is decomposed by light, the reaction being affected by oxygen and possibly also by carbon dioxide; potassium iodate is decomposed by light, the reaction being affected by carbon dioxide; potassium iodate and potassium iodide react if carbon dioxide be present, the reaction being conditioned by at least three concentrations. Combine all these variables in one reaction, and then add the effect of light on the whole mixture, and the problem becomes so complex that progress toward a quantitative study of the photochemical reaction involved seems almost hopeless. The reaction, however, is an excellent one for demonstrating the role of wave length in photochemical reactions, as has been pointed out.

Summary

1. An apparatus suitable for the study of photochemical reactions in solution has been described.

2. A lecture demonstration experiment suitable for showing the role of wave length of the light used in photochemical reactions has been described.

3. The photolysis of potassium iodate in solution has been studied quantitatively, with the results enumerated under Nos. 4, 5, 6, 7, below.

4. When the photolysis of potassium iodate is carried out with the solution exposed to air, the rate of photolysis slowly decreases.

5. Iodine is not liberated when the insolated solution is kept saturated with oxygen.

6. Carbon dioxide greatly increases the rate of photolysis of potassium iodate in solution.

7. The rate of photolysis of potassium iodate in a solution kept saturated with carbon dioxide is linear when the amount of iodine liberated is small compared with the total amount present in the iodate. Under such circumstances it is not possible to determine correctly the order of the reaction involved.

8. A theory of the way in which the photolysis of potassium iodate occurs has been suggested.

9. Light accelerates the reaction between potassium iodate, potassium iodide and carbon dioxide, but the reaction is very complex in the presence of light and has not been investigated quantitatively.

NOTE.—Since preparing the above article for publication, the paper by Oertel[1] on the photolysis of chlorates, bromates and iodates has come to our attention through the pages of *Chemical Abstracts*, the original article having escaped our notice. Oertel has pursued the investigation along quite different lines from those followed in the present paper, but we take this opportunity to give reference to his paper.

Laboratory of Physical Chemistry
University of Wisconsin
May, 1914

[1] Biochem. Zeit., **60**, 480 (1914); Chem. Abstr., **8**, 1746 (1914).