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THE PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE. I

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Introduction

Although the photochemical properties of hydrogen peroxide have been the subject of many researches, the effects of light on that class of oxygen compounds which can be considered as derivatives of hydrogen peroxide, namely the peroxide and peracid compounds, have received little attention. That they are sensitive to the light we first discovered in a previous investigation upon the mechanism of the photochemical reaction involved in acetophenone solutions of the alkali halides.[2]

A study of the oxidation and decomposition products intermediate between the acetophenone and the final product, benzoic acid, which might be responsible for some of the changes observed in that investigation, led to the preparation and exposure to the quartz mercury lamp of a variety of organic and inorganic peroxides and peracids. The organic compounds, perbenzoic acid, peracetic acid and benzoyl peroxide in benzene solutions, propionic peroxide in water solution and sodium perbenzoate in acetic acid solution were prepared and found to be photosensitive. Solutions of the inorganic compounds, persulfates, percarbonates, perchromates and monopersulfates were investigated and also found to be decomposed in the light.[3]

Of all of these, potassium persulfate, because of the possibility of its preparation in the pure state and of its stability when kept dry and in the dark, recommended itself the most highly for investigation; moreover, it possesses the added advantage of decomposing thermally in solution at such temperatures that the two types of reaction can be isolated and compared. That there is a thermal reaction which takes place in aqueous solutions of this salt has been recognized for some time and has been formulated as follows: $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + {}^1/_2\ O_2$. This reaction takes place to an appreciable extent only above 30°, is greatly accelerated by acids and is unimolecular.[4] The intermediate equilibria have also been studied[5] and those represented by the following reactions

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[1] This research was made possible by the award to the senior author of the Ernest Kempton Adams Research Fellowship of Columbia University.

[2] Morgan, Lammert and Crist, THIS JOURNAL, **46**, 1170 (1924).

[3] For the preparation of these inorganic compounds see the monograph by Price, "Per-acids and Their Salts," Longmans, Green and Co., London, **1912**.

[4] Ref. 3, p. 31.

[5] See, in addition to the references given in Ref. 3, Palm, *Z. anorg. Chem.*, **112**, 697 (1920).

found to exist: $K_2S_2O_8 + H_2O \rightleftharpoons K_2SO_5 + H_2SO_4$; $K_2SO_5 + H_2O \rightleftharpoons K_2SO_4 + H_2O_2$; $H_2O_2 \longrightarrow H_2O + O_2$.

A search of the literature showed that very little work had been done on the effect of light on solutions of this compound. Dhar,[6] in his effort to prove that all substances with high temperature coefficients for their thermal reactions would be light-sensitive, showed that such was the case with aqueous solutions of potassium persulfate, but no thorough study of the reaction was made. Kailan[7] has noted an effect of radium rays on potassium persulfate; Elbs and Neher[8] found that sunlight accelerated the decomposition of an aqueous 1 M sodium persulfate solution which was not measurably decomposed until a temperature of 35° was reached. In sunlight, however, the reaction is as rapid at 27° as it is at 85° in the dark, and is complete in 45 minutes.

The formation of certain peroxygen compounds has been found to be accelerated by ultraviolet radiation.[9]

Later in this paper it will be shown that the photochemical reaction can be represented in a manner similar to the final thermal reaction, namely, $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + {}^1/_2O_2$, but no evidence has been found of any intermediate equilibria. This comparative simplicity of reaction coupled with the fact that it proceeds under the influence of light whose wave lengths lie in a narrow band in the ultraviolet just above the transmission of ordinary transparent fused quartz, makes it a valuable reaction for actinometric use. For this reason the experimental methods are given in some detail in this paper, together with the reaction rate for the photochemical reaction and the effect of gases on it. In other papers to follow shortly we shall give the absorption spectra, effect of added electrolytes, temperature coefficients and theoretical calculations, made on the basis of these photochemical properties, and finally the applications of the reaction to radiometry.

Preparation of Materials

Potassium Persulfate.—Two preparations were used, one obtained by the electrolysis of potassium bisulfate in this Laboratory, the other a purified commercial product. The first was pure white, although some of the commercial samples had a red color that persisted in the crystals after repeated recrystallization. It was found that with ammonia present in the potassium bisulfate solution, a red color developed during the electrolysis, thus indicating the source of the color in the commercial salt since the more soluble ammonium bisulfate is used in its preparation. However, as the two preparations had the same photochemical properties, the second was used.

Potassium Sulfate.—A c. p., commercial salt was recrystallized twice.

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[6] Dhar, *Proc. Akad. Vetensk.*, **23**, 308 (1920).

[7] Kailan, *Monatsh.*, **44**, 35 (1923).

[8] Elbs and Neher, *Chem.-Z.*, **45**, 1113 (1921).

[9] Ellis and Wells, "The Chemical Action of Ultra-violet Rays," The Chemical Catalog Co., Inc., New York, **1925**, p. 154.

Ferrous Sulfate.—A C. P., commercial product was purified by recrystallization.

Sulfuric Acid.—A commercial "analyzed sulfuric acid" was used.

Potassium Permanganate.—Solutions were prepared and used with the usual precautions.

Oxygen, Nitrogen and Hydrogen.—The commercial compressed gases were used without further purification, after it had been shown that purification was unnecessary.

Sodium Oxalate.—The Bureau of Standards' preparation was used for standardizing the potassium permanganate.

Water.—Laboratory distilled water was redistilled from alkaline permanganate with steam escaping. Powdered manganese dioxide in addition to light-weight beads obviated the customary bumping.

The Analytical Method

After an experimental study of the several methods for the determination of persulfates, that one was selected in which the excess of ferrous sulfate beyond that necessary for the reduction of the persulfate (the solution was heated to 95° to hasten the reaction) was back-titrated with potassium permanganate solution. For the titration, an iodine flask containing the solution was placed on a white background with a yellow tungsten lamp to one side, the room being darkened. The color change at the end-point for the 0.001 M potassium permanganate solution used was obtained best by observing the colors at the high light, the reflection of the lamp by the wall of the flask, and the adjacent darker part. The end-point correction, namely 0.02 cc., for each 15 cc. of the final volume was read from a plot of cc. of permanganate used for 5 cc. of ferrous solution in different final volumes.

In the procedure adopted, the solutions were made 0.2 M in sulfuric acid to retard oxidation by atmospheric oxygen.[10] During the heating and cooling a beaker was inverted over the iodine flask to prevent convection currents bringing laboratory contaminations. In addition, it was found that the alkaline persulfate solutions had to be acidified before being added to the ferrous solution even though this latter contained a large excess of acid. It appears that the non-homogeneous mixing during the addition of an alkaline solution results in ferrous ion being momentarily in the presence of alkali, whence it is quickly oxidized by any dissolved oxygen.

The results of a large number of combinations of the variables, ferrous, persulfate and hydrogen ions demonstrated conclusively that the reduction of the persulfate was independent of the concentration of hydrogen ion.

To determine the effect of an excess concentration of ferrous ion upon the reaction, solutions of potassium persulfate 0.1000, 0.01 and 0.001 M, respectively, were prepared (the two latter by dilution) with a constant concentration of 0.2 M sulfuric acid. These were titrated, *twice* the cal-

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[10] Ref. 10. Banerjee, *Z. anorg. chem.*, **128**, 343 (1923).

culated equivalent of ferrous sulfate being used, and gave as the results for the concentration of persulfate 0.0998, 0.00994 and 0.000975 *M*, respectively; with the same persulfate solutions and *ten* times the calculated concentration of ferrous sulfate the results were erratic, an explanation of which phenomenon might be found in the publication of Le Blanc and Eckardt on the effect of ferrous ion on the reaction.[11] Accordingly the potassium persulfate was determined over this range of concentrations with an initial concentration of ferrous ion equal to twice the calculated equivalent.

Apparatus and Procedure

Apparatus.—The light source, the exposing chamber, the thermostats and their regulation have already been described.[2] To insure a constant light intensity a definite voltage was maintained across the lamp by the mechanical adjustment of a large resistance that was placed in parallel with the series starting resistance and the temperature of the lamp was kept constant by a method to be described later. Any change in the intensity was discovered by repeating one of the first of a set of determinations at the end of the series. Thus the reaction itself served as an actinometer specific for this region.[12]

Apparatus of the clearest quartz, designed similarly to that used by Morgan, Lammert and Crist, was used for the exposure flask and filter flask. This latter was found to give duplicable results when placed immediately in front of the exposure flask.

Temperature Control.—The factors that vary with the temperature are the emission of the lamp, the transmission of the light-filter solution and the velocity of the reaction. The control of all of these was obtained by keeping the temperature of the air in the exposure chamber constant. This was accomplished in the following way. A fan placed in the center of the exposing chamber, in a vertical position, kept the air in the chamber well stirred. A sirocco fan to remove the heated air and another fan to blow in the cooler air from the outside, connected in parallel in place of the heating element in the thermostatic control described by Beaver and Beaver,[13] were automatically started and stopped as the temperature rose and fell. An asbestos chute directed the cold air from the second fan to the top of the chamber to the end that it was thoroughly mixed by the stirring fan before coming in contact with the lamp or the regulator. Any change in the rate of cooling of the lamp affected the resistance of the mercury vapor appreciably. The best control was obtained with the room temperature 8° to 10° below that of the exposure chamber and with room temperature fluctuations within ±1.5°.

[11] Le Blanc and Eckardt, *Z. Electrochem.*, **5**, 355 (1899).

[12] See Reeve, *J. Phys. Chem.*, **29**, 39 (1925).

[13] Beaver and Beaver, *Ind. Eng. Chem.*, **15**, 359 (1923).

The variations of temperature in the exposing chamber were recorded with a Taylor Instrument Company recording thermometer. The temperatures of the solutions are those obtained by a thermometer in the exposed solution. Under the working conditions due to the high specific heat of water and the low heat conductivity of air and quartz, the exposed liquid did not follow the thermal inhomogeneity and fluctuations of the air, and so with efficient stirring could be maintained at a definite temperature with a variation of less than ±0.1°.

The Stirring of the Exposed Solution.—Stirring of the exposed solution is necessary whenever the radiation density is not the same throughout the reacting system, by reason of the concentration of an absorbing reactant or because of the shape of the flask, and to obtain a homogeneous temperature. If the light absorption is strong the intensity at any position of the flask is given by $I = I_0e^{-kt}$, where I is the emergent and I_0 the incident intensity, k the extinction coefficient and t the depth of the absorbing layer or, if the layer is constant, the concentration of the solution. For a constant intensity throughout, then, I must equal I_0. This is true in very weakly absorbing substances when t is variable, or in very strongly absorbing solutions when t is very small. If I is not equal to I_0, then the rate of reaction is a function of the stirring.

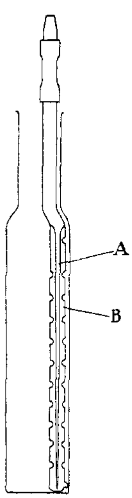

Fig. 1.

As stirring by mechanical means was impracticable, bubbling gases were used for the purpose. The apparatus finally adopted is shown in Fig. 1. The gas coming through the capillary A escapes at the bottom of the tube and rising carries with it much of the liquid above it in the tube B. This liquid flows out through the upper holes and other liquid consequently comes in through the lower holes. This device works very efficiently. There is no spattering and the bubbles do not become uncontrolled refraction centers in the radiated field. A copper-tin joint, to obviate retaping of exposed rubber, made of tapered copper tubing forced into a short piece of block-tin condenser tubing to the upper end of the taper giving a perfect gas-tight union, was used to make the connection to the gas main at the top of the flask. To keep the stirring tube in place a deep groove was blown in one side of a short piece of 5mm. glass tubing and a small section of rubber tubing slipped over this. It was then placed in the neck of the flask, on the lamp side, and held the tube in place without any undue strain on the tube since the latter was against the stretched rubber. The lower part of the tube was kept from turning by pressing its triangular base against the convex flask. With this procedure the results were found to be independent, within fairly wide limits, of the rate and size of the bubbles.

The sample to be exposed was brought to the particular temperature desired for the exposure. The flask was then placed in an upright position 40 cm. from the lamp, which was run in a horizontal position, its vertical plane perpendicular to the line joining the center of the flask and the center of the lamp. This was necessary as it was found that when the removal of successive samples lowered the level of the liquid in the exposure flask, there was less error than when the lamp was vertical. In the vertical position indirect light (non-parallel rays) would be absorbed and refracted by the liquid in the upper part of the flask, but the same amount of indirect light would not pass through the liquid when the level was lowered below the effective length of the arc. For all of the photochemical results obtained, except those on the effect of the concentration of the potassium persulfate, a separate exposure was made for each determination. After the exposure two 25cc. samples were taken and the persulfate was determined as previously described. Two or more determinations of the end-point were made for each sample taken by adding a further 2cc. sample of the ferrous sulfate solution and again running to the end-point. For some of the work two exposures were made and each point was then the mean of eight titer values. The flask was rinsed with water and dried between the exposures, and at the end of a series was cleansed with chromic acid.

Procedure for the Effect of Gases on the Reaction.—After several attempts with pressure above 760 mm. the following procedure was adopted, whereby the persulfate was made up in oxygen-free water, to which was added a quantity of oxygen-saturated water of an amount to make the resulting solutions 0, 25, 50, 75 and 100%. Stirring was found necessary because of the non-homogeneous radiation due to the cylindrical flask, and a mixture of oxygen and nitrogen, containing oxygen of approximately the same partial pressure as that in the solution to be exposed, was used.

Saturated solutions of hydrogen and of nitrogen were prepared in the same way and partial pressures of the particular gas in question used for stirring.

Results

Decomposition of Solutions of Potassium Persulfate Initially Neutral.—It was discovered early in the work that the hydrogen-ion and the salt concentration of the solutions played an important role in a study of this reaction; the results of an investigation of this effect will be presented in another paper. In Table I, however, are given the results of a number of preliminary runs in solutions initially neutral, which were simple aqueous solutions of the potassium persulfate of the concentrations given. In Col. 1 is given the time of exposure in minutes; in Col. 2 the cc. of barium hydroxide solution used, a value proportional to x, the persulfate decomposed in the time t; in Col. 3 is given the value of cc. of barium hydroxide solution proportional to the value of $(a-x)$ in the unimolecular equation $K = (1/t) \log (a/a - x)$. In some cases the value proportional to a was not determined experimentally and in other cases it was not very reliable, consequently the following method of approximation was used

$$\frac{1}{t_1}\log\frac{a}{a-x_1} = \frac{1}{t_2}\log\frac{a}{a-x_2}; \quad \frac{t_2}{t_1} = \frac{\log\dfrac{a}{a-x_2}}{\log\dfrac{a}{a-x_1}} = c$$

Values of a are assumed and the value of the right-hand ratio c is calculated, for which the experimental values proportional to x and x_2 were used for the times t_1 and t_2. The assumed values of a and the calculated values of c are plotted; t_2/t, being the true value of c, the curve of a against c is extended through this value; the intersection gives the best value of a.

In Col. 4 is given the value of the velocity constant K for a unimolecular reaction.

TABLE I

DATA TO SHOW THE RATE OF PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE IN AQUEOUS SOLUTIONS, INITIALLY NEUTRAL

$K_2S_2O_8$ = approx. 0.04 *M;* $Ba(OH)_2$ = approx. 0.001 *M;* voltage across lamp = 190 v.; distance from light = 40 cm.; temperature = 35°.

Time of exposure (t), min.	Cc. of $Ba(OH)_2$ used proportional to x at end of time t	Cc. of $Ba(OH)_2$ proportional to $(a - x)$	K
0	...	42.36	...
75	3.56	38.79	118
150	6.47	35.88	111
300	10.82	31.53	99
600	19.35	23.00	102
840	23.94	18.41	99
1080	27.51	14.84	97
1320	30.58	11.77	97
1563	33.28	9.07	99
1775	34.76	7.59	97
2041	36.78	5.57	99
2224	38.00	4.35	102
		Av.	102

The Effect of Concentration of Potassium Persulfate Upon the Rate of the Reaction.—In Tables II and III are collected some typical results for the reaction rates of potassium persulfate of different concentrations. In these experiments, however, there was added to the solutions enough potassium persulfate and potassium hydroxide to give a normal reaction rate and thus to eliminate any retardation due to the hydrogen ion formed or to the so-called salt effect, both of which will be shown to be of considerable importance. In Table II are given the results for a 0.1 *M* solution of the persulfate which is about as concentrated a solution as possible because of its solubility. In Col. 1 is given the time, in Col. 2 the ferrous sulfate needed to titrate the undecomposed persulfate, and in Col. 3 are given the values for the cubic centimeters of ferrous sulfate calculated on the assumption that the reaction is linear for this concentration according to the equation, $y = 8.95 - 0.001993x$, where y is the cc. of ferrous sulfate and x the time.

TABLE II

DATA TO SHOW THAT THE REACTION RATE OF THE PHOTOCHEMICAL DECOMPOSITION OF $K_2S_2O_8$ IS LINEAR IN CONCENTRATED SOLUTIONS

$K_2S_2O_8$ = 0.1 *M*; K_2SO_4 = 0.1 *M*; KOH = 0.28 *M*; $FeSO_4$ = approx. 0.05 *M*; *t* = 36°; voltage across lamp = 100 v.; distance from lamp = 40 cm.

Time, min.	Cc. of $FeSO_4$ Used	Cc. of $FeSO_4$ Calcd.
0	9.25	..
150	8.75	8.65
360	8.24	8.23
540	7.86	7.87
720	7.51	7.51
940	7.07	7.08
1160	6.64	6.63
1340	6.27	6.28

TABLE III

DATA TO SHOW THE CHANGE IN THE ORDER OF REACTION OF THE PHOTOCHEMICAL DECOMPOSITION OF $K_2S_2O_8$ WITH A CHANGE IN CONCENTRATION OF THE SOLUTIONS

KOH = 0.34 *M*; K_2SO_4 = 0.6 *M*; $FeSO_4$ = 0.05 and 0.005 *M*; *t* = 36°; voltage across lamp = 125 v.; distance from lamp = 20 cm.

Concn. of $K_2S_2O_8$, *M*	Time, min.	$FeSO_4$, used, cc.	*K*
0.08	30	7.23	
	180	5.26	0.00212
.03	30	3.55	
	120	2.48	.00400
.008	30	5.43	
	100	2.95	.00870
.00034	0	5.00	.018
	100	0.92	

From the results in these tables, which are typical of a larger number of results obtained, it is quite obvious that the reaction rate of this photochemical decomposition may be either of unimolecular or of zero order, the former in dilute solutions or when the intensity of the light is increased, the latter in the more concentrated solutions and with a decreased intensity of the light. Between the two extremes we have an obviously changing order.

With homogeneous radiation the photochemical reaction should proceed in the same manner as the thermal reaction, namely, according to the first order. On the other hand, if the conditions are such that the radiation is completely absorbed the same total quantity of material will be changed in unit time, the quantity being independent of the concentration of the solution and dependent only upon the intensity of the light. In other words, the reaction proceeds according to the zero order and this is observed in Table II. Thirdly, if the radiation is strongly but not completely absorbed, the molecules in the part of the flask away from the light will not have the same probability of receiving sufficient energy for activation as those in the front. Since this probability approaches a maximum when $I = I_0$ there should be an increase in the monomolecular constant with decreasing concentration of the photochemically active substance. This is the probable explanation of the results of Table III. For a change in the rate of a photochemical reaction due to a change in the thickness of the vessel, see Luther and Forbes.[14]

The Effect of Gases on the Reaction.—One of the final products of the decomposition, thermal or photochemical, is oxygen. In this circumstance, were the reaction reversible, any increase in the concentration of the oxygen would decrease the rate of the decomposition by the formation of the original substance. Solutions of 0.001 *M* potassium persulfate and 0.001 *M* potassium hydroxide were prepared with the oxygen concentrations 25, 50, 75 and 100%, saturated as described earlier, and were exposed to the full light of the mercury lamp. The unimolecular constants were, respectively, 0.0048, 0.0047, 0.0047, 0.0047. With solutions saturated, respectively, with nitrogen and hydrogen the constants were: the former, 0.0050; the latter, 0.0053. With a lamp that had burned but a short time the constants for oxygen and nitrogen were, respectively, 0.0058 and 0.0069. This same lamp after four months' use gave 0.0018 and 0.0018. With a lamp rebuilt by the Company the nitrogen solutions again decomposed more rapidly than those containing oxygen. In addition, it was found that with the light filtered through 4 *M* potassium hydroxide solution there was no difference in the rates with oxygen and nitrogen.

These results indicate that the reaction is irreversible, in that the change in the concentration of the oxygen produces no effect, but that nitrogen and hydrogen under the influence of the extreme ultraviolet radiations increase the rate of the decomposition. Oxygen was used, therefore, for the stirring throughout the work.

Solid potassium persulfate in the dry state has been found to decompose under ultraviolet radiation.

In conclusion the authors wish to express their thanks to Mr. J. K. W. Macalpine for his suggestions in the methods of approximation used.

Summary

1. A variety of inorganic and organic per-compounds have been prepared and found to be photosensitive and of these potassium persulfate

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[14] Luther and Forbes, THIS JOURNAL, 31, 770 (1909).

in aqueous solution has been investigated. The photochemical decomposition has been formulated in a manner similar to the thermal decomposition which takes place above 30°, namely, $K_2S_2O_8 + H_2O = 2KHSO_4 + {}^1/_2 O_2$, but no evidence of any intermediate reaction could be obtained.

2. Analytical methods for following the reaction were studied and a method, capable of yielding precise results in the extremely dilute solutions used, was developed which depended upon the reduction of the remaining persulfate with ferrous sulfate.

3. New methods of photochemical technique were developed including the stirring of the exposed solution and temperature control.

4. The photochemical decomposition was found to proceed according to a zero or linear order in the more concentrated solutions with a limited light intensity and according to a unimolecular order in the very dilute solutions. The order for the intermediate solutions is an accelerated unimolecular one, the value of the constants depending upon the light intensity and upon the concentration. An explanation of this phenomenon is given.

5. The effect of gases and of the aging of the lamp has been studied. Varying the concentration of the oxygen produces no change in the rate of the reaction; consequently, the reaction is not reversible. Hydrogen and nitrogen appear to accelerate the reaction.

6. Solid potassium persulfate has been found to decompose under ultraviolet radiations.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 34]

A REPORT OF ATTEMPTS TO ACTIVATE COPPER FOR CATALYTIC HYDROGENATION BY OXIDATION AND REDUCTION

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In connection with our studies of the activity of copper in catalytic hydrogenation it was desired to devise methods of preparation which would allow control of the nature of the catalyst surface. In particular it was desired to prepare a catalyst which should have a low porosity (and surface area) but a high activity. For this purpose low-temperature oxidation and reduction of a well-sintered sample seemed to be the most promising method. Although we have not been able to prepare a permanently active catalyst by this method, the results are thought to be worthy of record.

The method used was as follows. A bulb containing a sample of copper oxide in wire form was sealed into the usual apparatus consisting of a manometer, gas buret and Töpler pump with suitable leads to gas supplies.