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THE PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE. II

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Introduction

This paper presents the results of a continuation of the investigation of the photochemical decomposition and properties of potassium persulfate in aqueous solutions, a preliminary discussion of which is given in the first paper of this series.¹ In the present paper are presented the results for the absorption spectra of aqueous solutions of potassium persulfate and of such substances as may be produced by the decomposition of it or have an effect upon it, the effect of wave length and intensity of radiation upon the decomposition and, finally, the temperature coefficients of the photochemical decomposition.

Preparation of Materials

All the materials used were prepared and purified as described in the first paper of this series. In addition to those whose preparation has been described, potassium hydroxide was used in some quantity. The commercial product was not suitable for our work, as solutions of the purest obtainable compound became discolored on exposure in quartz to the mercury lamp. We therefore purified the substance as follows.

Potassium Hydroxide.—Water was saturated at 60° with the commercial c. p. by alcohol potassium hydroxide, and the solution was filtered at this temperature through asbestos into non-sol bottles, the sides of which were wrapped with felt. Then at a temperature below 0°, the crystals (the rhombohedral dihydrate existing below 32.5°) grew from the exposed bottom of the bottle and the mother liquor was easily removed. This liquor could not be concentrated since colored products, formed at the higher temperature, adhered to the crystals. This crystallization was repeated thrice and the crystals were stored; less silica is dissolved by the crystals than by the solution.

To determine the efficiency of the method, a solution was prepared from commercial, "pure" electrolytic sticks of which the maker's analysis was: silica, 0.04%; chlorine, 0.364%; other impurities, less than 0.01%; this solution had a cherry-red color after being heated. Three rapid recrystallizations were made and the final crop of crystals washed with water saturated with purified potassium hydroxide. The solution of these crystals contained only a trace of alumina and silica, and there was no perceptible color. The chlorine was determined as silver chloride. The chloride:hydroxide ratios in the original and in the purified solutions were, respectively, 0.0028 and 0.00019.

Apparatus and Procedure

The analytical method and the general method of exposure used have already been described.

¹ Morgan and Crist, *THIS JOURNAL*, **49**, 16 (1927).

Temperature Control.—A modification (Fig. 1) of the stirrer previously used was necessary for the temperature coefficient work; however, where the cooling coil was also in the exposing flask the stirring device C was placed in the flask and fixed in position by the cooling tube A. A fine capillary B extended from the gas connection at the top to the bottom of the "stirrer." The stirring action has already been described.

For the exposures at different temperatures the air was kept constant as before and the temperature of the solution was controlled further by circulating water from the external thermostat above the exposing chamber through the glass tube A within the exposure flask. The water was returned to the reservoir by a pump.² Between the pump and the cooling tube was a safety bottle fitted with a 3-holed stopper carrying the inlet tube connected to the cooling tube, an outlet tube extending to within an inch of the bottom of the bottle and connected to the pump, and an open tube long enough to extend above the reservoir. In the event that for any reason the pump failed, the water stopped flowing from above as soon as the level in the tube was the same as that in the reservoir. The troublesome taping of the rubber connections was avoided by making the connection to the cooling tube with the copper-tin joint described in the first

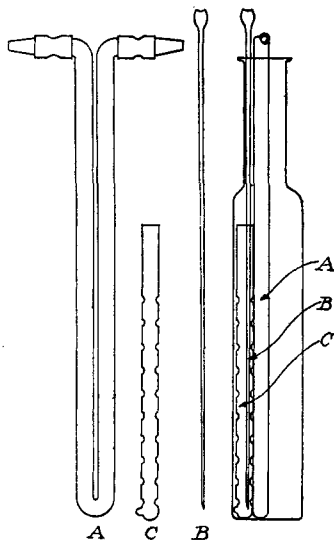


Fig. 1.

paper. By this method the precision at the temperature of the exposing chamber was $\pm 0.1^\circ$, and 20° above or below, it was within $\pm 0.15^\circ$.

Method of Obtaining the Absorption Spectra.—The absorption spectra were obtained by means of a Hilger sector photometer and a Hilger Type A quartz spectrograph. The light source, a condensed spark, was produced by a 0.5kilowatt transformer with a battery of condensers—copper plates in oil—in parallel with the electrodes. The electrodes were a modification of those recommended by Jones,³ which were carbon rods impregnated with oxides of molybdenum and of uranium. In this research, thin carbon plates $1 \times 8 \times 30$ mm. were sawed from such rods and then surfaced with sandpaper. These plates were held in position in two parallel brass jaws by means of a clamp, adjustable in all directions, the carbon plates extending about a millimeter beyond the jaws. Consequently, when the end of the carbon was worn away by the spark it could be ad-

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

³ Jones and Anderson, *Carnegie Inst. Publ.*, No. 110, 8 (1909).

vanced a definite distance and the setting kept the same; furthermore, since the plates were narrow, horizontal wandering of the spark was prevented. The spectrograph stood on a large piece of leveled plate glass. The light train was adjusted visually by observing the spectrum on a ground-glass plate coated with anthracene rubbed in with the fingers. Adjustments were made until the superimposed images of the spectrum were of the same intensity throughout. With proper adjustments when the angle of incidence on the prism was changed by shifting the whole spectrograph, the same distance between the source and the slit being maintained, the superimposed images of the two spectra remained equal, whereas if the prism and slit were not properly adjusted with relation to each other, marked inequalities developed with this changing of the angle of incidence. After a little practice there was no difficulty in getting an adjustment, usually, in which no inequalities could be observed on the photograph taken later. Any stray light was eliminated by strips of black paper at the camera opening.

Wratten and Wainwright panchromatic plates were used for the exposures. The absorption cells used were 20 mm. in depth and the water was collected in quartz with steam escaping.

Results

Absorption Spectra.—Data are presented for aqueous solutions of potassium persulfate, and of sulfuric acid, potassium hydroxide and potassium sulfate. A knowledge of the light properties of these latter substances is necessary for a satisfactory understanding of the mechanism

TABLE I

ABSORPTION-SPECTRA DATA OF SOLUTIONS

Log I_0/I = sector ratio; depth of cell = 2 cm.; values in table are the positions in wave lengths ($m\mu$) of equal intensity in the superimposed spectra.

Log I_0/I	Trans- mission, %	0.001 <i>M</i> K ₂ S ₂ O ₈ , $m\mu$	0.01 <i>M</i> K ₂ S ₂ O ₈ , $m\mu$	0.01 <i>M</i> K ₂ S ₂ O ₈ + 0.02 <i>M</i> H ₂ SO ₄ , $m\mu$	0.1 <i>M</i> K ₂ S ₂ O ₈ , $m\mu$	0.05 <i>M</i> H ₂ SO ₄ , $m\mu$	5.0 <i>M</i> H ₂ SO ₄ , $m\mu$
0.0	100	...	410	390
.1	79	232	315	280	325	201	221
.2	63	227	277	265	315	200	212
.3	50	223	258	260	308	200	207
.4	40	219	251	253	297	199	205
.5	32	216	247	249	291	199	203
.6	25	212	245	247	288	199	202
.7	20	209	244	245	283	199	202
.8	16	208	243	242	282	198	201
.9	13	206	242	240	280	198	200
1.0	10	203	240	239	278	198	200
1.1	8	202	238	237	274	198	200
1.2	6	201	236	236	272	198	200
1.3	5	200	235	235	270	197	200
1.5	3	199	232	232	269	197	200

TABLE I (Concluded)

Log I_0/I	Transmission, %	0.001M KOH, m μ	0.01M KOH, m μ	0.1M KOH, m μ	5.0M KOH, m μ	0.04M K ₂ SO ₄ , m μ
0.0	100
.1	79	235	251	233	330	213
.2	63	214	230	226	320	209
.3	50	207	222	224	290	206
.4	40	207	218	223	282	204
.5	32	205	216	222	263	202
.6	25	204	215	221	257	202
.7	20	204	214	220	249	201
.8	16	202	214	219	241	200
.9	13	202	213	219	238	200
1.0	10	201	213	218	235	200
1.1	8	201	212	218	232	199
1.2	6	199	212	218	230	199
1.3	5	199	212	218	...	199
1.5	3	199	212	218	228	199

of the decomposition. The results are given in Table I for the absorption spectra of solutions of such concentrations as are of interest in this research. In Col. 1 is given the sector setting of the instrument, and in the other columns are given the wave lengths transmitted by the solution that just match in intensity the light which comes through the variable sector,

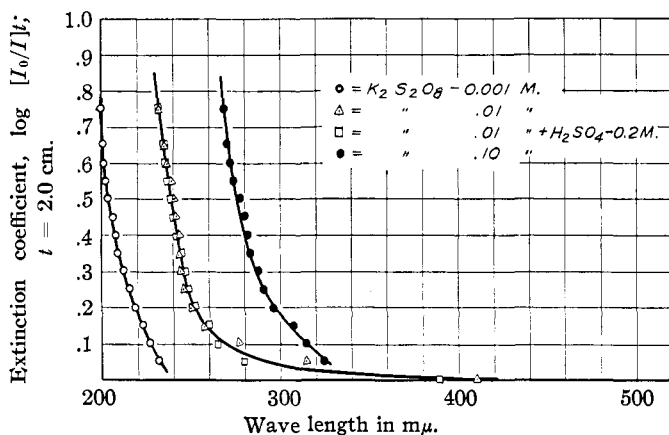


Fig. 2.—Variation of extinction coefficient with wave length for aqueous solutions of K₂S₂O₈.

set as it is in the position given in Col. 1. In Figs. 2 and 3 these wave lengths are plotted against the extinction coefficient; in this case the sector setting, divided by 2, that is, $\log [I_0/I]/t$ (t is the depth of layer in cm.). The extinction coefficient is K in $I = I_0 e^{-Kt}$, or $K = \log [I_0/I]/t$. It will be observed that the change in the curve for 0.01 M potassium persulfate (Fig. 2) at the lower values of the extinction coefficient is not of great

importance, since the points in this region of the curve are burdened with considerable error due to difficulties in matching the spectra. It is to be noticed further that with the exception of potassium hydroxide, the absorption spectra of the substances examined could not account in any part in the photochemical decomposition of potassium persulfate solutions. This fact will be discussed in a future paper.

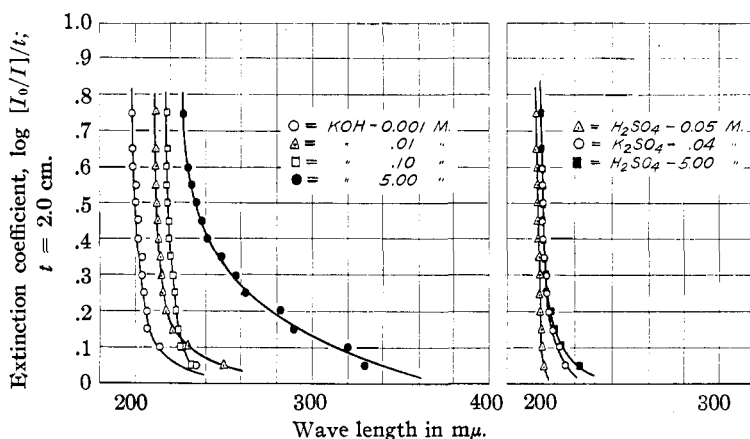


Fig. 3.—Variation of the extinction coefficient with wave length for aqueous solutions of KOH, K_2SO_4 and H_2SO_4 .

The Wave Lengths Effective in the Photochemical Decomposition.—

When solutions were exposed in Pyrex flasks there was no measurable decomposition, while in uviol flasks the reaction rate was very slow, the constant being approximately one one-hundredth of that for solutions exposed to the quartz lamp in quartz flasks. With 4.0 *M* potassium hydroxide solution in a quartz cylinder of 30 mm. diameter placed directly in front of the exposure flask, the unimolecular constant decreased from 0.00685, the value for full light, to 0.00305. The rate decreased very much as the lamp aged.

This behavior of the solutions in Pyrex and in uviol shows the upper limit of the effective radiation to be between the limits of transmission of these glasses (320 $m\mu$ and 275 $m\mu$, respectively), probably about 290 $m\mu$. An examination of the absorption spectra of potassium hydroxide in connection with the above experiments indicates the maximum effect to be in the region of 230 $m\mu$. Corresponding to this is the maximum of absorption of potassium persulfate at 200 $m\mu$.

Inasmuch as a satisfactory correlation of the actions of heat and light energy is not of general value unless the mechanisms of the resulting reactions are completely understood, such correlation in the present instance is of a preliminary nature only. We have, therefore, calculated

E in the equation $d \log K/d t = E/RT^2$ for use in the equation⁴ $E = Nh\nu$, from the data on the thermal decomposition given by Green and Masson⁵ for the decomposition of sodium persulfate. The results for this salt were more complete and were the same as for the potassium persulfate. From these calculations the effective wave length should be 1μ , but there is no measurable decomposition of a solution exposed to sunlight in glass where some of this radiation is undoubtedly present, while the maximum sensitivity is about $230m\mu$. The qualitative nature of this result is to be emphasized, as monochromatic light was not used, nor were the values of E from Green and Masson's data very concordant. However, it seems that a divergence from the far ultraviolet to the infra-red is significant and cannot be ascribed entirely to these experimental errors.

The Effect of the Intensity of the Light.—It can be assumed quite generally that the rate of a photochemical reaction will be proportional to the intensity of the effective wave lengths. The primary photochemical reaction is, without doubt, of that nature, but chemical complications such as chain reactions and secondary chemical reactions may result in other than a direct proportionality. Therefore a determination of the reaction rate-intensity relationship is of interest in connection with the mechanism of the decomposition.

The results of this determination are given in Table II. The lamp was at constant intensity and in a vertical position, and its distance was varied so as to make the intensity incident on the flask a definite fraction of the intensity at 10 cm. as indicated in the table. If the reaction rate is directly proportional to the intensity, then the product of K_1 , the unimolecular velocity constant and the reciprocal of this relative intensity, should in each case give the value of the velocity constant (K_2) at the unit intensity ($x = 10$ cm.). It is to be remarked that this method is burdened with some error, the inverse-square law holding strictly for a point source. With the lamp used in the vertical position this condition might have

TABLE II
THE EFFECT OF LIGHT INTENSITY ON THE REACTION VELOCITY

K_1 = monomolecular velocity constant; $K_2 = (1/\text{Intensity})K_1$; x = distance to lamp; voltage = 145 v.; $t = 40^\circ$; $K_2S_2O_8 = 0.001M$; $KOH = 0.01M$; $I = \text{Intensity}$.

No.	x , cm.	I	K_1	K_2
1	63.3	1/40	0.0060	0.24
2	44.7	1/20	.0093	.19
3	31.6	1/10	.020	.20
4	22.3	1/5	.038	.19

⁴ These equations are of Arrhenius and Perrin, respectively. K is the velocity constant of the thermal reaction, E the "critical increment," N is Avogadro's constant, h Planck's constant, and ν the frequency of the activating radiant energy.

⁵ Green and Masson, *J. Chem. Soc.*, 97, 2083 (1910).

been approached by isolating segments of the arc with parallel mica disks, as used by Luther and Forbes⁶ to get parallel radiation.

The constancy of the results in Col. 5 would indicate that the deviation from the inverse-square law is small relative to the other errors and, therefore, that the reaction is proportional to the light intensity and consequently more likely to be truly photochemical and free from intermediate or side reactions. It follows, also, that it is possible in cases where the intensity of the light changes by reason of intervening filters or of a change

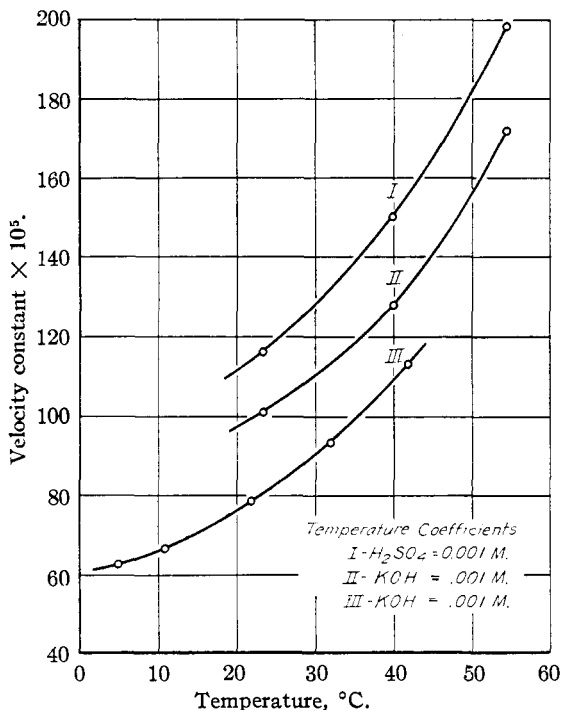


Fig. 4.—The variation of the velocity of the photochemical decomposition of potassium persulfate with the temperature. Curve I, 0.001 M H_2SO_4 ; Curve II, 0.001 M KOH ; Curve III, 0.001 M KOH .

in the distance between the lamp and the flask, that the respective series obtained under the changed conditions are related by a direct proportionality factor. It is to be noted that since the order of the reaction is unchanged by a change in the frequency, the difference between the frequency bands is an efficiency factor which gives a direct proportionality between the results produced by two different frequencies.

Temperature Coefficients of the Photochemical Decomposition.—The temperature coefficient of a reaction is expressed as a ratio of the

⁶ Luther and Forbes, *THIS JOURNAL*, 31, 770 (1909).

velocity constants taken at 10° intervals of temperature. The relationship between temperature and rate of chemical reaction is of particular interest in photochemical reactions, for, so far as is known, they are low in contrast to the higher coefficients for thermal reactions. This difference affords a basis for distinction between a true photochemical reaction and a photochemical reaction accompanied by thermal "after-effects." Accordingly, the data for a calculation of the temperature coefficients under varying conditions of acidity and with exposures to full and filtered light are given in Table III, and the plot of the temperatures against the velocity constants, calculated on the assumption that the reaction is unimolecular, in Fig. 4. All of the runs of each series were made without interruption, a check run being made at the end of each series. The samples were taken from the same original solution and duplicates were made for each time value.

At low temperatures with high acid concentration, and at high temperatures with the solution slightly acid, the rate of the dark decomposition is appreciable. It was necessary, therefore, to determine the relative rate of this dark reaction and, further, to find if it were independent of the light reaction, that is, additive with respect to it. By a determination of the titer for the light reaction and for the dark reaction on consecutive days, the reactions were found to be independent and therefore additive, but the data are omitted in the interests of economy of space. It was found that there was no measurable decomposition at 40° with 0.001 *M*

TABLE III
DATA TO SHOW THE EFFECT OF TEMPERATURE ON THE VELOCITY OF THE PHOTOCHEMICAL
DECOMPOSITION OF POTASSIUM PERSULFATE

Temp., °C.	$K \times 10^4$	Temp. coeff., $K(t^\circ + 10^\circ)/Kt^\circ$ at $(t^\circ - 10^\circ)$	Temp., °C.	$K \times 10^4$	Temp. coeff., $K(t^\circ + 10^\circ)/Kt^\circ$ at $(t^\circ - 10^\circ)$
Alkaline soln. in light filtered by 2.5 <i>M</i> KOH. $K_2S_2O_8 = 0.001 M$, KOH = 0.001 <i>M</i> .			Acid soln. in filtered light. $H_2SO_4 = 0.001 M$, $K_2S_2O_8 = 0.002 M$.		
42	11.3		54.5	19.8	
32	9.31	1.21 (42—32)	40	15.0	1.22 (54.5—40)
22	7.86	1.19 (32—22)	23.4	11.6	1.18 (40—23.4)
12	6.68	1.16 (22—12)			
5	6.28	1.09 (12—5)			
Alkaline soln. in full light. KOH = 0.001 <i>M</i> , $K_2S_2O_8 = 0.001 M$.			Alkaline soln. in filtered (2.5 <i>M</i> KOH) light. KOH = 0.001 <i>M</i> , $K_2S_2O_8 = 0.002 M$.		
32	92.9		54.5	17.2	
22	80.5	1.15 (32—22)	40	12.8	1.24 (54.5—40)
12	69.7	1.15 (22—12)	23.4	10.1	1.16 (40—23.4)
Alkaline soln. in full light. KOH = 0.01 <i>M</i> , $K_2S_2O_8 = 0.001 M$, $K_2SO_4 = 0.02 M$.					
32	87.4				
22	73.0	1.20 (32—22)			

potassium hydroxide or sulfuric acid, but when the concentration of sulfuric acid was increased to 0.15 *M* the rate of the thermal reaction was considerable.

In the first three series in Table III, the temperatures recorded in Col. 1 are such that the dark reaction is inappreciable but in the last two series the temperatures were selected to include the two types of reaction. In Fig. 4, Curve III is plotted from the first series, Curve II from the last and Curve I from the fourth series data.

In general it is to be observed that the temperature coefficient of the photochemical decomposition is low, having an average value of 1.18, as compared to the approximate value of 3 (calculated from Green and Masson's data) for the thermal reaction. A comparison of the temperature coefficients for full and filtered light shows no significant differences between those rather limited regions of the spectrum. Large effects are to be predicted only when a comparison is made between larger variations of effective frequencies. From the data in the last sections of Table III, it is evident that the coefficient is unaffected by potassium sulfate, by an excess of hydrogen ion or of hydroxyl ion, when these are present in rather low concentration. This independence would indicate that there is no chemical mechanism affecting the activation of the reacting substances.

Summary

This paper continues an investigation of the photochemical properties of aqueous solutions of potassium persulfate, with the following results.

1. The absorption spectra of solutions of potassium persulfate, potassium sulfate, potassium hydroxide and sulfuric acid in varying concentrations have been determined. The regions absorbed by the substances used, except potassium hydroxide, do not overlap to any extent with the regions absorbed by potassium persulfate solutions.

2. The wave length effective in producing the reaction, as well as the region of maximum absorption, is in the lower ultraviolet, at about 22 $m\mu$. The value predicted from the equations of Arrhenius and of Perrin is 1μ .

3. The velocity of the reaction is proportional to the intensity of the light, which fact is evidence that the reaction is purely photochemical and unaccompanied by side or intermediate reactions.

4. The temperature coefficient of the photochemical decomposition has the average value 1.18, which low value is further evidence of the simplicity of the reaction. Within the limits of experimental error it is the same for acid, alkaline, and alkaline potassium sulfate solutions in full or in filtered light.