

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE

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The kinetic study of the photochemical decomposition of potassium persulfate has been reported previously.¹ The reaction $K_2S_2O_8 + H_2O = 2KHSO_4 + 1/2O_2$ is zero order in concentrated solution and pseudo unimolecular in very dilute solution (0.001 *M*), the temperature coefficient is low (1.0–1.15), the absorption starts at 3200 Å. and increases rapidly into the far ultraviolet, and the rate of the reaction is retarded very markedly by additions of sulfuric acid and less so by additions of potassium sulfate and potassium hydroxide. An effort was made to explain these latter results as a kinetic salt effect but with no definite conclusions. The present study gives some further facts for the reëxamination of this problem.

The primary object of this investigation was to determine the quantum efficiency of the reaction under different circumstances of electrolyte concentration and light frequency.

Apparatus and Procedure

The monochromator consisted of a 60° fused quartz prism 11.2 cm. on the side and 7.6 cm. high with fused quartz lenses 7.6 cm. high and 46 cm. focal length. A capillary mercury arc of special construction was used as the source and a Moll surface thermopile with a low resistance galvanometer served to measure the energy.

The lamp was substantially the same as described previously.² The most important change has been to put a transverse magnetic field across the arc and in the direction to displace the arc to the back wall. If the arc runs against the front air-cooled wall the quartz devitrifies very rapidly, if against the back wall the capillary remains clean in front except for a small brown deposit at the anode.³ There is no white deposit as described by Daniels.⁴

Foreign gases were removed by gentle boiling at first and then heating the capillary to redness. A brown deposit formed which decomposed on further heating. The capillaries should be of pure fused crystal quartz instead of machine-blown quartz, which is of somewhat different composition.

The large Moll surface thermopile can be used as a surface instrument only when the energy density is the same throughout the area to be measured. In order to use it with

¹ Morgan and Crist, *THIS JOURNAL*, **49**, 16, 338, 960 (1927).

² Crist, *ibid.*, **52**, 4337 (1930); *J. Opt. Soc. Am.*, **21**, 690 (1931).

³ The cooling was accomplished as before except that the larger stream of water struck the lamp somewhat below the upper end of the luminous arc. This served to reduce the fluctuations of the upper electrode. The copper gauze should cover slightly less than half the capillary, the best arrangement to be determined by experience. The gauze is supported by small wires from the upright part of the lower electrode. The capillary was 5 cm. long with the bore 3–3.4 mm. and the wall 1.8–2.2 mm. The arc burned on 5–5.5 amp. and 90–120 volts.

⁴ Daniels and Heidt, *THIS JOURNAL*, **54**, 2383 (1932).

the divergent beam the whole surface was covered except for a 2.2-mm. slit over the junctions of the middle section, and the light was focused on the slit. The image width was smaller than the slit and a correction was made for the greater sensitivity in the central part of the slit from a plot of the deflections at regular intervals across the middle section. The calibration found was 27.4×10^{-6} watts per sec. or 3.93×10^{-6} cal. per minute.

The transmission of the measuring train, two crystal quartz lenses and the thermopile window was found by direct measurement to be 73%, that of the cell filled with water 91.6%.

Analytical Method.—The method of analysis used in the previous investigation was the ferrous sulfate–permanganate method for the determination of the undecomposed persulfate. The present method was the precipitation of the sulfate formed by the decomposition. Thermal decomposition of the persulfate made precipitation and digestion in a hot solution impossible as well as standing in the presence of the hydrogen-ion concentration usually recommended in barium sulfate precipitations. Consequently the solution to be analyzed was very slowly added to a well-stirred solution of about 50 cc. of 0.005 *M* barium chloride. The crystals obtained were very heavy and were filtered immediately. The method gave quite satisfactory results in the presence of persulfate ions.

Results and Discussion

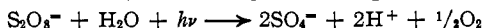
The results of the investigation are given in Table I. The solutions used were 0.05 molar with respect to $K_2S_2O_8$ and the electrolyte concentration was as indicated. For the case of $\lambda 302$ a correction for reflection from the rear wall of the cell was made. The light absorption by the persulfate is given in the third column, corrections having been made for the independent absorption of electrolytes where necessary. In the fourth column is the average intensity (deflections) for the period of the exposure.⁵

TABLE I
QUANTUM EFFICIENCY OF THE DECOMPOSITION OF POTASSIUM PERSULFATE IN THE PRESENCE OF ELECTROLYTES

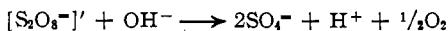
Concn. in moles per liter; $K_2S_2O_8 = 0.05 +$ electrolyte	Wave length in μ	Light absorption	<i>I</i> (def.) incident on solution	Time, min.	Calories incident on soln.	Ab-sorbed	Mole quanta $\times 10^5$	Moles $K_2S_2O_8 \times 10^5$	$\frac{\text{Moles}}{\text{quanta}}$
...	254	1.00	976	981	3.77	3.77	3.35	3.6	1.07
Na_2CO_3 0.005	254	1.00	1168	1905	8.75	8.74	7.78	7.5	0.96
...	265	0.965	5350	387	8.15	7.86	7.31	7.4	1.01
...	265	.965	4660	345	6.32	6.10	5.67	5.6	0.99
Na_2CO_3 0.05	265	.916	7230	320	9.10	8.33	7.75	7.9	1.02
KOH 0.05	265	.930	4750	280	5.23	4.87	4.53	5.1	1.12
H_2SO_4 0.01	265	.965	6430	260	6.55	6.32	5.88	5.0	0.85
...	302	.475	14290	220	12.34	6.00	6.37	6.4	1.01
...	302	.475	11180	242	10.62	5.16	5.48	5.7	1.04
Na_2CO_3 0.05	302	.455	6530	290	7.42	3.47	3.68	3.8	1.03
Na_2CO_3 0.05	302	.455	6440	341	8.63	4.02	4.27	4.4	1.03
H_2SO_4 0.01	302	.475	8630	259	8.78	4.26	4.51	3.8	0.84

⁵ I (incident on solution)/ I (thermopile) = $(1/0.73) \times 0.957 = 1.31$, and one deflection = 3.93×10^{-6} calories per minute.

The photochemical reaction has been established in the previous papers,¹ as proceeding quantitatively according to the equation



The results in Table I show definitely a quantum efficiency of unity for the neutral and alkaline solutions. The absorption of active light is undoubtedly by the peroxide bond in the persulfate group. This would result in a dissociation and immediate reaction of the products with water or in an excited ion which would have an appreciable life period during which it could react with water or hydroxyl ions. It is difficult to explain even qualitatively the effects of neutral salts by the first process, and it has not been possible to account for their effect quantitatively if excited ions are assumed. An excited ion must collide with the reacting molecule during its life period and if this reaction were with water molecules the efficiency should be maintained unless the negative ions were readily able to take up the energy of excitation. This type of energy transfer has been investigated in the case of excited uranyl ions.⁶ The ratio of the original fluorescence efficiency to that in the presence of the salt is proportional to the concentration of the salt. Persulfate solutions do not fluoresce as each excited ion results in reaction, but since the quantum efficiency is equivalent to fluorescence efficiency, the ratio of unity to the yield in the presence of electrolytes should be proportional to the concentration of electrolyte. The values used were calculated from the rate measurements in the previous papers⁷ by assuming a value of unity for the lowest salt concentration and then obtaining the yield from the velocity constants. Plots were then made to see if $\gamma_0/\gamma_{(\text{electrolyte})}$ was proportional to the concentration of electrolyte. The points for potassium sulfate and potassium hydroxide fell on a somewhat curved line but those for sulfuric acid were widely off, which would suggest the operation of important additional factors. If the reaction were



then at sufficiently low concentrations of hydroxyl ion, the efficiency should decrease. Such an effect was analyzed kinetically but the equations did not approximate the observed rate. Some further information is available in the data. From Table I 0.05 *M* $\text{K}_2\text{S}_2\text{O}_8$ + 0.01 *M* H_2SO_4 gives a yield of 0.85 and from the rate study⁷ the solution 0.00025 *M* $\text{K}_2\text{S}_2\text{O}_8$ + 0.01 *M* H_2SO_4 gave a calculated yield of 0.55. This would indicate that since the ratio of persulfuric acid to persulfate ion is very much larger in the second case the persulfuric acid is more stable than the persulfate ion, it being found in the previous papers that 0.01 *M* sulfuric acid did not change the absorption characteristics of the persulfate solution.

⁶ West, Müller and Jette, *Proc. Roy. Soc. (London)*, [A] **121**, 294 (1928); Jette and West, *ibid.*, [A] **121**, 299 (1928); Wawilow, *Z. Physik*, **53**, 665 (1929).

⁷ Morgan and Crist, *THIS JOURNAL*, **49**, 960 (1927).

It was thought that the efficiency of the reaction in the presence of sulfuric acid could be raised again by introducing relatively high concentrations of other "receptor" ions. Experiments showed that chloride ions are oxidized by persulfate when exposed, the dark reaction being very slow and autocatalytic. The chlorine produced was removed by a stream of oxygen, then absorbed in a potassium hydroxide solution and determined. In unstirred solutions the oxygen produced was very much less than before and the chlorine determined in the stirred samples was perhaps a third of the sulfate produced.⁸ The results for various chlorides are given in Table II. The reduced yields for potassium chloride and hydrochloric acid are about the same and this would indicate that hydrogen ion has a much less effect than chloride, a result which could be attributed to the very high deactivating efficiency of chlorides.⁶ Unfortunately the effect of potassium chloride in alkaline solutions could not be investigated for comparison with potassium sulfate and potassium hydroxide, since the oxidized chlorine would be retained as hypochlorites, etc., which are photosensitive with the wave lengths employed.

TABLE II
QUANTUM EFFICIENCY FOR PERSULFATE IN PRESENCE OF ELECTROLYTES

Concn. of electrolytes in moles per liter	Wave length in $m\mu$	γ
KCl ^a 0.05	302	0.73
KCl 0.05	302	.67
HCl 0.05	302	.74
KCl 0.20 + H ₂ SO ₄ 0.001	302	.67
HgCl ₂ 0.1 + H ₂ SO ₄ 0.001	302	.72

^a This solution was unstirred and the absorption of light increased during the exposure, due to the chlorine for which a correction was made. The stirred solutions did not change in absorption when exposed.

Summary

The quantum efficiency of the persulfate decomposition has been found to be unity for neutral and alkaline solutions.

The effect of electrolytes and the mechanism of the reaction have been discussed.

The capillary mercury arc as a source of light has been further improved by deflecting the arc with a magnet.

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⁸ It was not possible to remove completely the chlorine from the exposed solution as several hours aeration did not remove the odor and some of the chlorine was probably retained in the solution by photochemical change to higher states of oxidation.