[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 535]

# THE PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE. III. THE EFFECT OF ADDED ELECTROLYTES

BY J. LIVINGSTON R. MORGAN AND RAY H. CRIST

RECEIVED JANUARY 26, 1927 PUBLISHED APRIL 7, 1927

In our two previous papers[1] published on this investigation, reports have been made on the effect of a change in the concentration of reactants, in the temperature and in the light intensity, on the velocity of the photochemical decomposition of potassium persulfate, as well as on the absorption spectra of aqueous solutions of the various substances concerned in this reaction.

In this paper we are presenting the results of the effect of added electrolytes upon the reaction rate, from which study we hope to obtain a more complete understanding of the chemistry of the reaction, such an understanding being essential in any photochemical study.

The following equilibria are involved in the thermal reaction which was investigated by Palme:[2] $K_2S_2O_8 + H_2O = K_2SO_5 + H_2SO_4$; $K_2SO_5 + H_2O = K_2SO_4 + H_2O_2$; $H_2O_2 \longrightarrow H_2O + {}^1/{}_2O_2$. Palme found approximate constants for the equilibria of the first two reactions, but the third reaction is not reversible. It is our object to determine in the first place whether or not the photochemical reaction involves the same equilibria as the thermal reaction, and secondly, since potassium sulfate and sulfuric acid are products of the reaction, to find the effect of additions of these electrolytes upon the photochemical reaction rate, and also the effect of added potassium hydroxide upon the reaction rate, since it was necessary to add potassium hydroxide to maintain a constant hydrogen-ion concentration during the study of the effect of added potassium sulfate.

We have been unable in the photochemical reaction to detect the presence either of the $SO_5$ ion or of hydrogen peroxide. We have found, however, by making determinations of both hydrogen ion and of persulfate ion simultaneously during the course of a photochemical decomposition that the concentration of hydrogen ion is equal to that calculated from the amount of the persulfate decomposed, taking as the basis of the calculation the equation $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + {}^1/{}_2O_2$. Therefore, we are justified in assuming that a determination of the velocity of decrease in the concentration of potassium persulfate is a determination of the velocity of the primary reaction, probably represented in the first equation of the thermal equilibria, the $K_2SO_5$ in such case being very rapidly decomposed.

## Method of Calculating Results

To avoid the effects of the initial irregularities and of the errors of the

---

[1] Morgan and Crist, THIS JOURNAL, 49, 16, 338 (1927).

[2] Palme, *Z. anorg. Chem.*, 112, 97 (1920).

analytical method, both of which are magnified in the calculation of the unimolecular velocity constant, that is, $K$ in the equation $K = (2.303/t) \log (C_{t_0}/C_{tx})$, these constants were obtained from the slope of the best straight line through the points of the $\log C_{tx}$ against time plot, which best line was found by the method of least squares. The unimolecular equation can be written $Kt = 2.303 (\log C_{t_0} - \log C_{tx})$, or as $\log C_{tx} = \log C_{t_0} - bt$, where $t$ is the time and $b$ is the constant representing the slope of the straight line which this equation represents, and $K$ of the previous equation is 2.303 $b$. From the constants $\log C_{t_0}$ and $b$ of this linear equation, the values of $\log C_{tx}$ and hence of $C_{tx}$ were calculated.

In Table I is presented a typical comparison of the observed and calculated values which shows a justification of the method of calculation described.

TABLE I

TYPICAL RESULTS OBTAINED BY LEAST-SQUARES METHOD

$K$ is calculated from the slope, $b$, of the linear equation $\log C_{tx} = \log C_{t0} - bt$

| No. | Time | $FeSO_4$, cc. obs. | $FeSO_4$, cc. calcd. | $K \times 10^5$ |
|---|---|---|---|---|
| | $H_2SO_4 = 0.01\ M$; $K_2S_2O_8 = 0.00025\ M$ | | | |
| 1 | 100 | 1.75 | 1.74 | |
| 2 | 305 | 1.24 | 1.26 | |
| 3 | 435 | 1.04 | 1.03 | |
| 4 | 620 | 0.77 | 0.77 | |
| | $\log C_t = 0.3091 - 0.0006860 \times t$ | | | 158 |
| | $KOH = 0.02\ M$; $K_2S_2O_8 = 0.001\ M$ | | | |
| 1 | 60 | 3.94 | 3.94 | |
| 2 | 90 | 3.54 | 3.53 | |
| 3 | 120 | 3.22 | 3.16 | |
| 4 | 180 | 2.52 | 2.54 | |
| 5 | 210 | 2.30 | 2.28 | |
| 6 | 235 | 2.03 | 2.08 | |
| | $\log C_t = 0.6906 - 0.001589 \times t$ | | | 366 |

## The Effect of Sulfuric Acid

Other sources of hydrogen ion were not used in attempting to investigate any specific effect of the hydrogen ion because of the absorption of active light by the negative ion, which would have made it difficult to separate and study any effect of the hydrogen ion alone. Furthermore, the persulfate, under the influence of the light, might have oxidized these sub-

TABLE II

THE EFFECT OF SULFURIC ACID ON THE REACTION RATE

Conditions of exposure: volts = 167; temp., 35°; dist. = 40 cm.; light filtered by (2.5 $M$) KOH; $K_2S_2O_8$, 0.00025 $M$; $K_2SO_4$, 0.0022 $M$

| No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $H_2SO_4$ added, moles | 0.000 | 0.0002 | 0.001 | 0.01 | 0.03 |
| $K \times 10^5$ | 293 | 230 | 197 | 158 | 152 |

stances, and a catalytic effect would have been observed. The results are given in Table II and are plotted in Fig. 1, Curve IV. It is to be recalled here, as reported in the second paper, that at the temperature and the concentration of the hydrogen ion employed, the catalytic effect of the latter on the thermal reaction was found to be inappreciable.

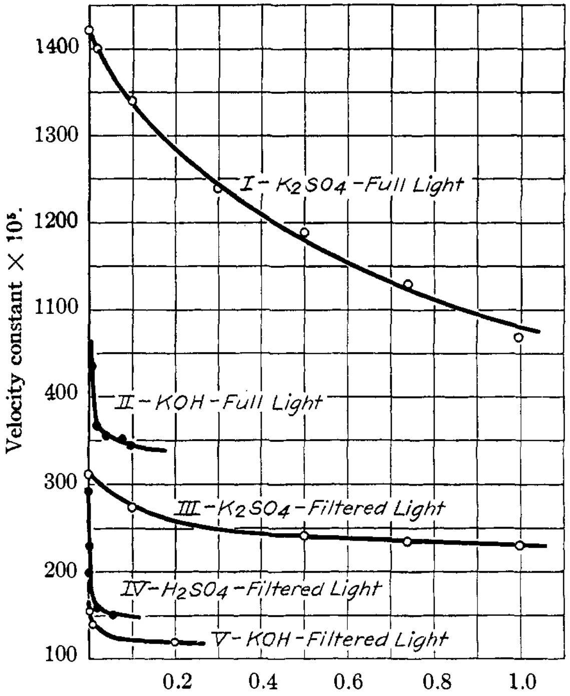

Fig. 1.—The effect of KOH, $K_2SO_4$ and $H_2SO_4$ on the velocity of the photochemical decomposition.

### The Effect of Potassium Sulfate

In the preliminary work it was found that the retarding of the reaction by this salt was of the same character and magnitude in an acid as in an alkaline medium. Alkaline solutions gave more reliable results in full light and were used for the investigation. The results are in Table III and are plotted in Fig. 1, Curves I and III.

### The Effect of Potassium Hydroxide

In the second paper of this series it was shown that whereas the absorption band of potassium sulfate and sulfuric acid is well below the wave length effective in the photochemical decomposition, the absorption band of potassium hydroxide is in the effective ultraviolet region. There is the possibility then in aqueous potassium hydroxide solutions of persulfate

TABLE III

THE EFFECT OF POTASSIUM SULFATE ON THE REACTION RATE

Conditions of exposure: volts = 143; temp., 26°; dist., 40 cm.; full light of lamp; $K_2S_2O_8$, 0.001 *M;* KOH, 0.01 *M*

| No. | $K_2SO_4$ added, moles | $K \times 10^5$ |
|---|---|---|
| 1 | 0.00 | 1420 |
| 2 | .01 | 1400 |
| 3 | .05 | 1340 |
| 4 | .15 | 1240 |
| 5 | .25 | 1190 |
| 6 | .37 | 1130 |
| 7 | .50 | 1070 |

Conditions of exposure: volts = 143; temp., 26°; dist., 25 cm.; light filtered by (2.5 *M*) KOH; $K_2S_2O_8$, 0.001 *M;* KOH, 0.001 *M*

| No. | $K_2SO_4$ added, moles | $K \times 10^5$ |
|---|---|---|
| 1 | 0.00 | 312 |
| 2 | .05 | 274 |
| 3 | .25 | 242 |
| 4 | .37 | 235 |
| 5 | .50 | 228 |

that the potassium hydroxide is effective in two ways. In the first place it may act as a purely physical factor, that is, as an inner filter; in the second place it may act as a chemical factor by increasing the salt content of the solution. To determine whether its behavior was physical or chemical, exposures were made with varying concentrations of potassium hydroxide in the full light and in light filtered through concd. (2.5 *M*) potassium hydroxide solution.

The results for the effect of additions of potassium hydroxide to the exposed solutions are given in Table IV and in Fig. 1, Curves II and V. The small change made in the initial potassium persulfate for analytical precision was found to have no material effect on the rate of reaction.[1] In view of the very slight absorption of the dil. potassium hydroxide solution within the solution, the results in this filtered light are practically independent of any inner filter effect.[2] Therefore, since the potassium hydroxide does not act in this purely physical manner, its effect must be of a chemical nature.

TABLE IV

THE EFFECT OF POTASSIUM HYDROXIDE ON THE REACTION RATE

Conditions of exposure: volts = 143; temp., 40°; dist., 40 cm.; full light of the lamp; $K_2S_2O_8$, 0.001 *M;* $K_2SO_4$, 0.0022 *M*

| No. | KOH added, moles | $K \times 10^5$ |
|---|---|---|
| 1 | 0.01 | 435 |
| 2 | .02 | 366 |
| 3 | .04 | 355 |
| 4 | .08 | 351 |
| 5 | .10 | 346 |

Conditions of exposure: volts = 143; temp., 40°; dist., 40 cm.; light filtered by (2.5 *M*) KOH; $K_2S_2O_8$, 0.00025 *M;* $K_2SO_4$, 0.0022 *M*

| No. | KOH added, moles | $K \times 10^5$ |
|---|---|---|
| 1 | 0.002 | 155 |
| 2 | .01 | 140 |
| 3 | .20 | 120 |

The differences in the effects of the various added electrolytes, as shown in Fig. 1, are those due to a change of temperature, of light intensity, of wave length and of the salt content of the solution, both in the nature of the salt and in its total amount. It has been shown in the second paper of this series[1] that the reaction velocity is directly proportional, with the exception of the last, to all of these factors. The functional relationship between the velocity and the amount of substance added is hyperbolic, since the data for the effect of each specific electrolyte added can be represented fairly well by the equation $y = x/(a + bx)$, where $y$ = velocity constant and $x$ = moles of electrolyte added.

It is evident that a change of physical conditions does not alter the salt effect for, as shown in the second paper of this series, the temperature coefficient is the same in the presence of any one of the electrolytes potassium sulfate, sulfuric acid and potassium hydroxide and, as is shown in the present paper, the salt effect is independent of the changes in wave length and intensity of the light as produced by interposed filters. This change in the physical factors affects only one of the coördinates—the velocity constant (see Fig. 1)—and as a consequence the curves for filtered and full light are not symmetrical. However, if the function between the salt content and the velocity of reaction has not been altered, then, since only direct proportionality factors have affected the velocity constant, the curves can be made to coincide by treating the values of the coördinate with such a factor. By this procedure it was found that the curves for filtered light do coincide satisfactorily with the corresponding ones for full light.

Now, since the salt effect is not a function of the physical conditions, at least within the errors of the experimental methods, the effects of the various electrolytes under different conditions can be more satisfactorily compared when these effects are reduced in this same manner to a definite set of physical conditions. By this same procedure all the curves for the several electrolytes were also found to coincide fairly well, with the exception of the first part of the curve for sulfuric acid.[3] It would appear, therefore, that the similarity of the effects of these entirely different electrolytes indicates a common cause.[4]

## Discussion of Results

It will be of value, first, to consider the essential facts of the experiments outlined in these papers. No qualitative or quantitative evidence of the intermediate equilibria that exist in the thermal decomposition was found in the photochemical decomposition. The regularity of the temperature

---

[3] Because of the meagerness of some of the data, it was thought that a complete presentation of these calculated results with all the necessary details was not justified, as in any case only qualitative conclusions could be reached.

[4] A possible specific action of potassium sulfate and sulfuric acid in accomplishing a reversal of the reaction is unlikely in view of the inactivity of dissolved oxygen (see Ref. 1). If the effects are not specific but due only to the fact that the substances are electrolytes, then the effects of several electrolytes in solution at the same time would be additive. This would explain the fact that the first part of the curve obtained with potassium sulfate (full light) differs from the curve obtained with sulfuric acid, in that the former solution had a relatively high concentration of potassium hydroxide at the start.

coefficient under varied conditions, and the direct relation found to exist between the intensity of the light and the reaction rate are indirect evidence of the absence of interfering secondary reactions. The inactivity of oxygen indicates an irreversible reaction. The retardations of the reaction rate caused by the addition of potassium hydroxide, sulfuric acid and potassium sulfate show a decided similarity. The absorption spectra of these electrolytes are such that under the conditions of the experiments the retardations cannot be due to an inner filter action. Further, in the case of sulfuric acid, its addition does not change the absorption characteristics of the potassium persulfate solution. Since, therefore, the same quantity of light is absorbed by the reactive component as before the addition of the retarding electrolyte, this latter decreases the quantum yield of the reaction. As yet we have not determined this quantity for the reaction in pure water.

As in most photochemical processes, the above facts do not give very definite information concerning the inner mechanism of the decomposition. If in such systems a molecule that had received the amount of energy necessary for reaction were to react instantly there would be no opportunity for the degradation of this energy, and retardation would consist in preventing the absorption of this critical energy. It is difficult to explain the facts from this view. However, if activated molecules had an appreciable life period, as activated molecules of certain gases are known to have, then collisions of the second kind are possible. These collisions are inelastic and result in a transfer of energy from one to the other. Such an action would be a deactivation and would retard the reaction rate. This is a likely view and might explain the similarity in the effects of the several electrolytes, but it cannot be demonstrated quantitatively.

If we consider the source of the oxygen evolved there are the two possibilities, water and the persulfate. If the oxidation of the oxygen is accomplished in the persulfate molecule then the mechanism is that of a simple decomposition. However, if the oxygen oxidized is that of the water present then the reaction is bimolecular, that is, the activated persulfate reacts either with the water molecule or with the oxide ion of water. The activated persulfate ion can be considered as a sort of new species of matter that has now the property of oxidizing the oxygen of water, the acceptor. According to Brönsted[5] we should expect bimolecular reactions to have salt effects; positive and small if the water molecule is involved and large if the oxide ion is involved. Our experiments, however, show a negative hyperbolic effect. In addition, if we assume the oxide ion to be produced by the equilibrium $H_2O = H^+ + OH^- = 2H^+ + O^=$, then the addition of hydroxyl ion should increase the reaction rate and hydrogen ion should decrease it. The experiments show that both retard it.

[5] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

Two salt effects on photochemical reactions mentioned in recent literature are the displacement of the equilibrium[6] $2Fe^{+++} + 2I^{-} = 2Fe^{++} + I_2$, and the change in the rate of the decomposition of hypochlorous acid.[7] In the former the effect was shown to be that of a change in the thermodynamic concentrations of the reactants on the two sides of the equilibrium. In the latter it was explained as the shifting of an equilibrium which controlled the concentration of the photosensitive component.

It is apparent, therefore, that we are still a long way from a complete understanding of the phenomena here presented; such a comprehension must await a more thorough understanding of similar phenomena in simpler systems. The experiments have, however, brought up for consideration the general phenomenon of the effect of electrolytes on photochemical reactions in solution.

In conclusion, the authors wish to thank Professor O. M. Lammert, of Vassar College, for her assistance in the preparation of these papers for publication.

## Summary

The results of this continuation of the investigation of the photochemical decomposition of aqueous potassium persulfate may be stated as follows.

There is no qualitative nor quantitative evidence of any intermediate equilibria.

The rate of the photochemical decomposition is retarded by the additions of potassium hydroxide, of potassium sulfate and of sulfuric acid.

This retardation is hyperbolic and seems to be of the same general nature for the various electrolytes added.

The phenomena have been discussed from the points of view of deactivation and of a kinetic salt effect.

NEW YORK, N. Y.

---

[8] Rideal and Williams, *J. Chem. Soc.*, **127**, 258 (1925).

[7] Allmand, Cunliffe and Maddison, *ibid.*, **127**, 822 (1925).