[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Oxidation of Oxalate Ion by Peroxydisulfate[1]

BY THOMAS L. ALLEN

The silver-catalyzed oxidation of oxalate ion by peroxydisulfate ion was investigated. Reproducible results were obtained by using standard solutions and distilled water of uniform quality. It was found that a catalyst was present in ordinary distilled water. Purification of the water led to reaction rates comparable to the rates of other silver-catalyzed oxidations of peroxydisulfate. Traces of copper sulfate were found to have a pronounced catalytic effect on the rate of the silver-catalyzed reaction. Copper sulfate itself was also found to be an excellent catalyst for the oxidation. The rate of the copper-catalyzed reaction in the region of very low copper sulfate concentration, 0.004 *M* sodium oxalate and 0.004 *M* potassium peroxydisulfate, was a function of the copper sulfate concentration, but not of the peroxydisulfate or oxalate concentration. The uncatalyzed oxidation also was investigated. The first part of the reaction was autocatalytic, and this was followed by what appeared to be an auto-inhibition. Mechanisms to account for the experimental results are proposed.

Introduction

The oxidation of several reducing agents (Cr^{+++}, VO^{++}, Mn^{++}, hydrazine and Ce^{+++}) by peroxydisulfate ion is catalyzed by silver ion, and all of these oxidations obey the same rate law.[2–5] The value of the specific rate constant is a function of the ionic strength, but is otherwise the same for these various reducing agents.

Oxalate ion is an exception. Its oxidation by peroxydisulfate, which proceeds according to the reaction

$$S_2O_8^{=} + C_2O_4^{=} = 2SO_4^{=} + 2CO_2$$

is catalyzed by silver ion, but the rate is from four hundred to four thousand times as fast as the rate for the aforementioned reducing agents.[6–8] Furthermore, King was unable to obtain reproducible results. The rate for duplicate experiments varied by as much as tenfold, despite careful work to eliminate the cause of this variation. (Bledsoe did not perform duplicate experiments, so it is not possible to determine the reproducibility of that work.)

Not all of the reagents in King's experiments were added from standard solutions. The salts were sometimes weighed directly for each experiment. It seemed possible that a variation in impurities from one portion of a solid salt to another might account for the lack of reproducibility. Impurities in the distilled water used in making up the solution might also have varied from one sample to another. Therefore this study was undertaken with the hope that the use of standard solutions and distilled water of uniform quality might lead to more reproducible results.

Experimental Procedure

Standard solutions of the various reagents were prepared by dissolving weighed amounts of either C.P. or reagent-grade reagents in measured volumes of water. Ordinary distilled water was used for the first twelve experiments. Subsequently redistilled water was used.

A sample of National Bureau of Standards sodium oxalate No. 40d was very low in copper impurity, and standard solutions prepared from it were used in all experiments subsequent to those summarized in Table II.

The desired volumes of water and standard solutions, except for the peroxydisulfate, were placed in a glass-stoppered flask. The flask was placed in the thermostat and allowed to reach thermal equilibrium with it. Then the proper volume of potassium peroxydisulfate was transferred to the flask by means of a pipet. The resulting solution was usually 500 ml. in volume. It was thoroughly mixed by repeated inversion and shaking and replaced in the thermostat.

The peroxydisulfate was not usually preheated to thermostat temperature before addition. However, in a typical experiment at 69.7°, the solution reached a temperature of 69.5° 15 minutes after addition of a 25 ml. volume of potassium peroxydisulfate solution.

Aliquot portions of the solution, usually 50 ml., were withdrawn at intervals with a pipet, and analyzed for peroxydisulfate by a modification of Bartlett and Cotman's modification[9] of the method recommended by Rosin.[10] One gram of sodium bicarbonate and 10 g. of potassium iodide were placed in a 300-ml. erlenmeyer flask and dissolved in about 50 ml. of distilled water. Five ml. of 1 *N* sulfuric acid was added, and the solution was swirled. An aliquot portion of the reacting solution was added, iodine being liberated by the peroxydisulfate. The walls of the flask were rinsed with distilled water, the flask was stoppered and placed in the dark for at least ten minutes before titration with sodium thiosulfate solution. No starch was used, as it was found that the disappearance of the color of the triiodide ion gave a sharper end-point. The sodium thiosulfate solution was standardized with primary-standard grade arsenious oxide.[11]

Experiment showed that the presence of oxalate caused no error in this method of analysis.

Although the oxidation of iodide by peroxydisulfate is rather slow, and consequently the analysis is somewhat protracted, no appreciable reduction of peroxydisulfate by oxalate occurred during the analysis. The uncatalyzed reaction is extremely slow except at elevated temperatures. Even at 40° the half-life is about two weeks. When the sample of reacting solution was added to the iodide solution, it was cooled to 45° or less, which effectively stopped the reaction between the oxalate and peroxydisulfate. If a catalyst of silver ion or cupric ion was present, the iodide removed the catalyst as silver iodide or cuprous iodide.

In experiments 11–25, the sodium bicarbonate–sulfuric acid buffer was not used. In some of these experiments a potassium acid phthalate–sodium hydroxide buffer was used, and in others no buffer was used. The error of these titrations was often quite high.

It was necessary to remove the copper impurity in the sodium oxalate and potassium peroxydisulfate. The method used was electrolytic deposition of the copper impurity with platinum electrodes, with a voltage of 1.5 volts. Standard solutions for all experiments subsequent to those summarized in Table II were treated in this manner. The oxalate was electrolyzed at a current of 0.15 milliampere for 90 minutes, and the peroxydisulfate at 0.75 milliampere for 30 minutes.

Spectrographic analyses showed that this method con-

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[1] The first part of this work was carried out at the University of Idaho, Moscow, Idaho.

[2] D. M. Yost, THIS JOURNAL, **48**, 152 (1926).

[3] D. M. Yost and W. H. Claussen, *ibid.*, **53**, 3349 (1931).

[4] A. O. Dekker, H. A. Lévy and D. M. Yost, *ibid.*, **59**, 2129 (1937).

[5] W. H. Cone, *ibid.*, **67**, 78 (1945).

[6] C. V. King, *ibid.*, **49**, 2689 (1927).

[7] C. V. King, *ibid.*, **50**, 2089 (1928).

[8] L. J. Bledsoe, Thesis, University of Idaho, Moscow, Idaho, 1948.

[9] P. D. Bartlett and J. D. Cotman, Jr., THIS JOURNAL, **71**, 1419 (1949).

[10] J. Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., Inc., New York, N. Y., 1946, second edition, p. 349.

[11] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1940, second edition, p. 210.

siderably reduced the copper impurity of both potassium peroxydisulfate and potassium oxalate. No experiments were conducted to determine if the electrolysis had proceeded long enough. Later experiments indicate that some copper remained, but this amounted to only about one part per billion parts of solution.

Results of the Rate Measurements

Figure 1 shows the results of experiments on the rate of oxidation of oxalate by peroxydisulfate in the presence of sulfuric acid, with added silver nitrate as a catalyst. ($S_2O_8^=$) is the concentration of peroxydisulfate at time *t*, and ($S_2O_8^=$)^0 is the concentration at zero time. In each case the rate is first-order with respect to peroxydisulfate.

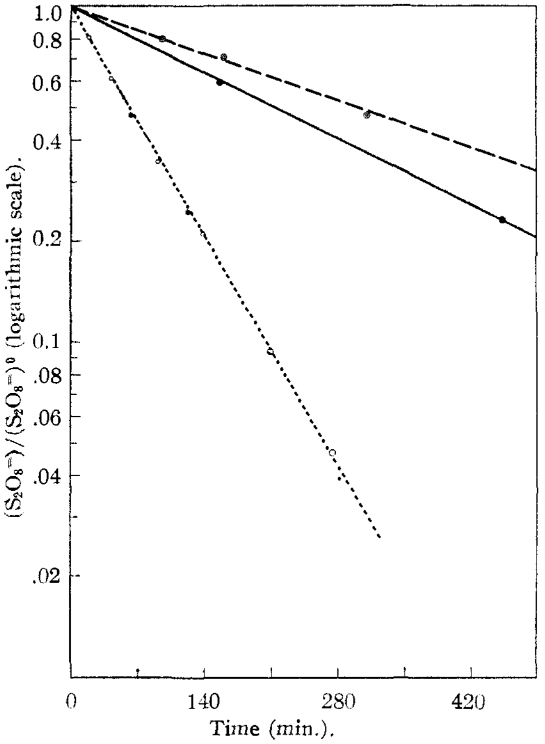

Fig. 1.—Silver-catalyzed oxidation of oxalate by peroxydisulfate at 35.0°: ●, ◎, expts. 1 and 2 (different distilled water): o, ●, O, expts. 3, 4 and 5 (uniform distilled water).

Table I gives the concentrations of the various reagents in moles/liter. It should be noted that the silver nitrate for experiments 3–5 was quintuple that for the first two.

TABLE I

THE OXIDATION OF OXALATE BY PEROXYDISULFATE AT 35.0°

Expts.	$K_2S_2O_8$	$Na_2C_2O_4$	$AgNO_3$ $\times 10^{-5}$	H_2SO_4	50% reaction[a]
1	0.02	0.04	2	1.0	3.5
2	.02	.04	2	1.0	5.0
3, 4, 5	.02	.04	10	1.0	1.03
11, 12	.01	.02	2	None	10
13, 14[b]	.01	.02	2	None	60

[a] Time in hours required for the disappearance of 50% of the peroxydisulfate. [b] Redistilled water was used in experiments 13 and 14.

In preparing experiments 1 and 2 ordinary distilled water was used as drawn from the faucet. The disagreement is marked. Distilled water was taken from the same bottle for experiments 3–5, and the agreement is good. This indicates that, at least in the presence of sulfuric acid, lack of reproducibility is due to variation of impurities from one experiment to another.

The effect of purification of the water is shown by experiments 11–14 (see Table I). Distilled water was used for experiments 11 and 12, and redistilled water for experiments 13 and 14. (No sulfuric acid was used in these experiments.) Since redistillation decreased the rate, either a catalyst in the ordinary distilled water had been eliminated or an inhibitor had been accidentally introduced. During the course of experiments 13 and 14, samples were withdrawn and added to equal volumes of distilled water in three cases, and to redistilled water in another case. They were then replaced in the thermostat. The samples with distilled water reacted very rapidly, whereas the sample with redistilled water continued at the same rate. These experiments prove that the redistillation removed a catalyst in the distilled water.

Qualitative experiments showed that the addition of copper sulfate greatly accelerated the silver-catalyzed reaction, whereas the addition of zinc sulfate gave no noticeable change. The effect of a trace of copper sulfate is shown quantitatively in Table II. It is seen that the addition of 4 × 10^{-6} *M* $CuSO_4$ changed the rate by a factor of ten.

TABLE II

THE OXIDATION OF OXALATE BY PEROXYDISULFATE AT 40.0°[a]

$Na_2C_2O_4$	$AgNO_3$ $\times 10^{-5}$	$CuSO_4$	50% reaction[b]
0.04	4	None	80 hours[c]
.04	4	4 × 10^{-6}	8 hours
.04	None	4 × 10^{-5}	5.4 hours
.04	None	2 × 10^{-5}	9.3 hours
None	None	None	20 days
0.04	None	None	14 days

[a] The concentration of $K_2S_2O_8$ in these experiments was 0.01 *M*. [b] Time required for the disappearance of 50% of the peroxydisulfate. [c] Result of duplicate experiments.

From these experiments it is found that the rate constant for the silver-catalyzed oxidation, calculated on the basis of

$$-d(S_2O_8^=)/dt = k(S_2O_8^=)(Ag^+)$$

is 3.6 moles^{-1} liter min.$^{-1}$. Extrapolation to 40° of the rate constants for the silver-catalyzed oxidations which obey this rate law[2–5] leads to a maximum value of 1.89. It seems possible that removal of the copper impurity in the sodium oxalate and potassium peroxydisulfate will lead to rate constants in better agreement with those of references 2–5.

Copper itself is a much better catalyst for this oxidation than silver, as shown in Table II. The rate is approximately first order with respect to both peroxydisulfate and copper sulfate.

The uncatalyzed oxidation was compared with the rate of decomposition of peroxydisulfate, which proceeds according to the equation

$$S_2O_8^= + H_2O = 2SO_4^= + 2H^+ + {}^1/_2O_2$$

in experiments summarized in the last part of

Table II. The oxidation did not go much faster than the decomposition. It seemed possible that removal of the copper impurity in the peroxydisulfate and oxalate might lead to the agreement of the rates of these reactions. The copper impurity was removed as described under Experimental procedure, and the temperature was increased to 69.7° for more convenient reaction times.

Figure 2 shows the results of experiments on the uncatalyzed reaction. Although three of the experiments are duplicates, the agreement is not good. However, in each case there is an autocatalysis, followed by what appears to be an autoinhibition, and then the curve is approximately linear.

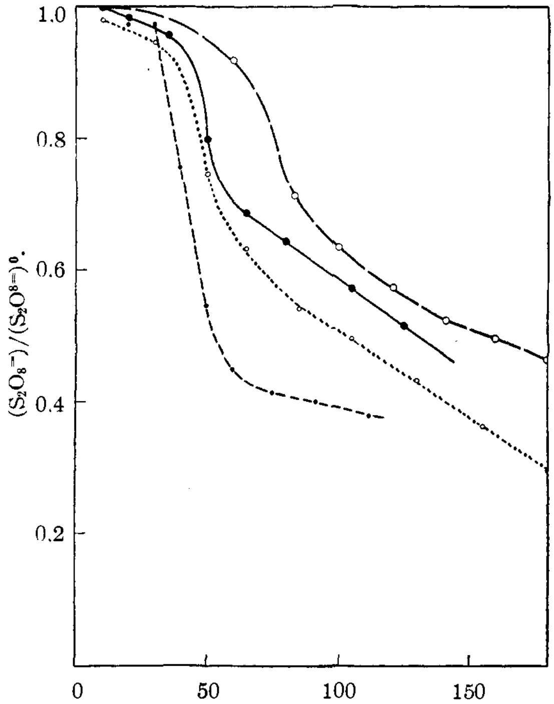

Fig. 2.—Uncatalyzed oxidation at 69.7° with 0.004 M $K_2S_2O_8$: ●, o, O, expts. with 0.004 M $Na_2C_2O_4$; •, expt. with 0.008 M $Na_2C_2O_4$.

Doubling the oxalate concentration accentuates this behavior, as shown in Fig. 2. In this case there is an induction period of about 30 minutes. A rapid reaction ensues, followed by a sharp decrease in rate.

It was possible to study the copper catalysis at this temperature, using very low copper concentrations. Figure 3 shows the results of experiments with 1, 2 and 4 × 10^{-7} M $CuSO_4$. The rate curves are quite linear to about 50% reaction. The rate law is therefore

$$-d(S_2O_8^=)/dt = k \qquad (1)$$

where k is a function of the copper sulfate concentration. Table III summarizes the results of the experiments on the copper catalysis.

TABLE III

THE COPPER-CATALYZED OXIDATION OF OXALATE BY PEROXYDISULFATE AT 69.7°[a]

$CuSO_4$, × 10^{-7} M	$k \times 10^5$[b]			
1	2.49	2.16	2.15	
2	3.19	3.30	3.36	3.28
4	5.40			

[a] Both the $K_2S_2O_8$ and the $Na_2C_2O_4$ concentrations were 0.004 M. [b] k is given in moles liter^{-1} min.$^{-1}$.

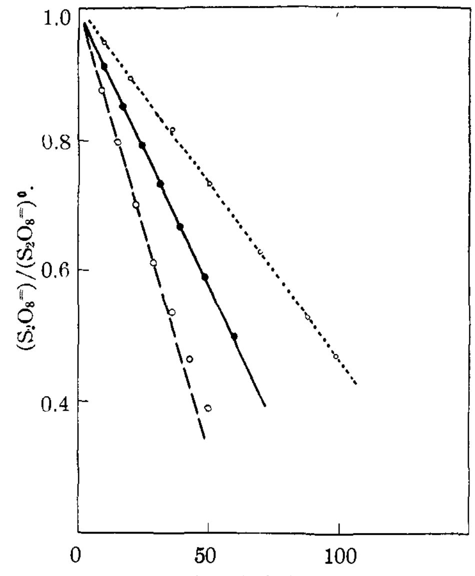

Fig. 3.—Copper-catalyzed oxidation at 69.7° with 0.004 M $K_2S_2O_8$ and 0.004 M $Na_2C_2O_4$: o, 1 × 10^{-7} M $CuSO_4$; ●, 2 × 10^{-7} M $CuSO_4$; O, 4 × 10^{-7} M $CuSO_4$.

If k is plotted *versus* the copper sulfate concentration, the points lie on or near a straight line of equation

$$k = 1.08 \times 10^{-5} + 108(CuSO_4) \qquad (2)$$

where $(CuSO_4)$ is in moles/liter.

Extrapolation of this line to zero copper sulfate concentration leads to a k of 1.08 × 10^{-5}. With no added copper ions the rate curves are not linear, as was seen in Fig. 2. However, the curves are linear near the end of the reaction, with k values of 1.16 × 10^{-5}, 1.04 × 10^{-5} and 0.60 × 10^{-5} for the reactions with 0.004 M peroxydisulfate and oxalate.

These results lead one to suspect that there is a copper impurity of about 1 × 10^{-7} M in all of these solutions. Spectrographic analyses were made on those portions of several reaction mixtures which had not been withdrawn for titration, and relative copper concentrations were determined. The analyses obeyed the equation

$$\text{relative concentration} = 1 + 5 \times 10^7 (CuSO_4)$$

This shows that the impurity of copper was only about 2 × 10^{-8} M, or about one part of copper per billion parts of solution.

The fact that the peroxydisulfate concentration in the copper-catalyzed experiments is a linear function of the time indicates that the rate is zero order with respect to peroxydisulfate. However, the oxalate concentration is equal to the peroxydisulfate, and should continue to remain so as the reaction proceeds. Therefore a more general expression for the rate law is

$$-\mathrm{d}(S_2O_8^{=})/\mathrm{d}t = k(S_2O_8^{=}/C_2O_4^{=})^n \qquad (3)$$

where *n* is a constant.

Experiments were conducted to determine the effect of varying the initial peroxydisulfate and oxalate concentrations, with the copper sulfate concentration kept at 2 × 10^{-7} *M*. Figure 4 shows the results of increasing the oxalate concentration by 40% and 100%. The line of long dashes represents the average rate for the experiments with 0.004 *M* oxalate and 2 × 10^{-7} *M* copper sulfate. It is seen that increasing the oxalate concentration decreases the rate slightly.

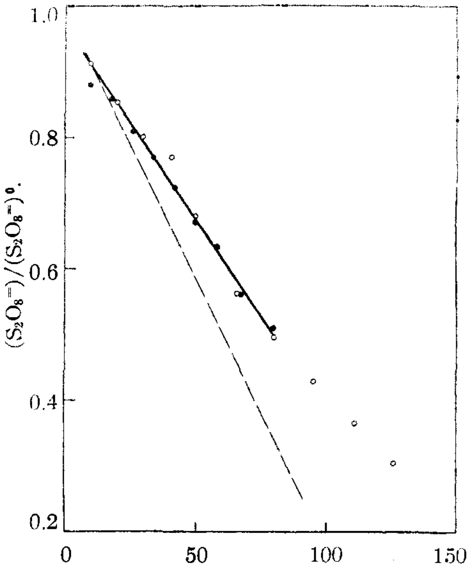

Fig. 4.—Copper-catalyzed oxidation at 69.7° with 0.004 *M* $K_2S_2O_8$ and 2 × 10^{-7} *M* $CuSO_4$: ●, 0.0056 *M* $Na_2C_2O_4$; O, 0.008 *M* $Na_2C_2O_4$.

An increase of 40% in the peroxydisulfate concentration produced the result shown in Fig. 5. The line of short dashes represents the average value of $-\mathrm{d}(S_2O_8^{=})/\mathrm{d}t$ for the experiments with 0.004 *M* oxalate and peroxydisulfate and 2 × 10^{-7} *M* copper sulfate, on the basis of an initial peroxydisulfate concentration of 0.0056 *M*. Despite the 40% increase, the rate follows the dashed line closely, especially during the first part of the experiment. This shows that the value of *n* in equation (3) is zero, and thus the rate law is that given by equation (1). Unfortunately this rate law seems to apply over a rather limited range of concentrations.

In the experiment with a 100% increase in peroxydisulfate and the experiment with a 100% increase in both the peroxydisulfate and oxalate (see Fig. 5), the autocatalytic curves resemble those for the uncatalyzed reaction.

Discussion

The autocatalytic character of the uncatalyzed reaction may be due to a chain reaction of the type

$$S_2O_8^{=} \longrightarrow 2SO_4^{\dot{-}} \qquad (4)$$

$$SO_4^{\dot{-}} + C_2O_4^{=} \longrightarrow SO_4^{=} + CO_2 + CO_2^{\dot{-}} \qquad (5)$$

$$CO_2^{\dot{-}} + S_2O_8^{=} \longrightarrow SO_4^{=} + CO_2 + SO_4^{\dot{-}} \qquad (6)$$

$$SO_4^{\dot{-}} + CO_2^{\dot{-}} \longrightarrow SO_4^{=} + CO_2 \qquad (7)$$

$$SO_4^{\dot{-}} + H_2O \longrightarrow HSO_4^{-} + OH\cdot \qquad (8)$$

$$2OH\cdot \longrightarrow H_2O + {}^1/_2O_2 \qquad (9)$$

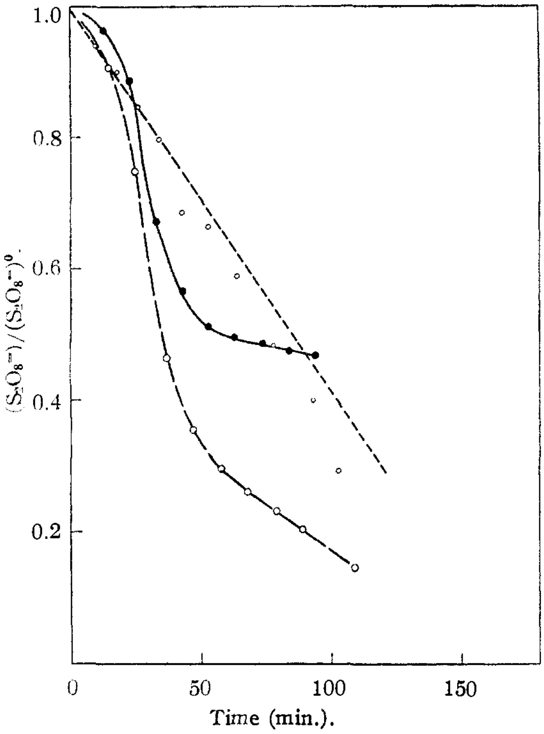

Fig. 5.—Copper-catalyzed oxidation at 69.7° with 2 × 10^{-7} *M* $CuSO_4$: o, 0.0056 *M* $K_2S_2O_8$ and 0.004 *M* $Na_2C_2O_4$; ●, 0.008 *M* $K_2S_2O_8$ and 0.004 *M* $Na_2C_2O_4$; O, 0.008 *M* $K_2S_2O_8$ and 0.008 *M* $Na_2C_2O_4$.

Reaction (4) is the initial step, reactions (5) and (6) are the chain-carrying reactions, and (7), (8) and (9) are chain-terminating steps. Reactions (4), (8) and (9) have been postulated as the mechanism of the decomposition of peroxydisulfate.[9]

If reactions (4), (7) and (8) are slow compared to (5) and (6), this mechanism leads to a rate of reaction during the initial stages which is proportional to the time. This is at least approximately true of the experiments with 0.004 *M* oxalate (see Fig. 2). As the concentration of $SO_4^{\dot{-}}$ radicals increases, reactions (8) and (9) will become important, with the resultant formation of oxygen. The observed autoinhibition may be due to this oxygen, which could stop the chain reaction by forming a complex with either the $SO_4^{\dot{-}}$ or the $CO_2^{\dot{-}}$ radicals.

On this basis an initial induction period, due to the presence of dissolved air in the solution, would be expected. This is observed in the experiment with 0.008 *M* oxalate but not in those with 0.004 *M* oxalate. However, preliminary experiments on the effect of removal of the dissolved oxygen indicate that the reaction proceeds much more rapidly with oxygen absent.

Other examples of the oxygen inhibition of peroxydisulfate reactions are known.[12,13] However, oxygen has been found to have no effect on the rate of decomposition of peroxydisulfate.[14]

Cupric ion in oxalate solutions is known[15] to exist

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[12] I. M. Kolthoff and W. J. Dale, THIS JOURNAL, **67**, 1672 (1945).

[13] C. C. Price and C. E. Adams, *ibid.*, **67**, 1674 (1945).

[14] P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

[15] H. T. S. Britton and M. E. D. Jarrett, *J. Chem. Soc.*, 1489 (1936).

in the form of the complex, $Cu(C_2O_4)_2^{=}$. A mechanism which leads to the rate law of equations (1) and (2) can be obtained by postulating the oxidation of copper in this complex to the tripositive state.

$$Cu^{II}(C_2O_4)_2^{=} + S_2O_8^{=} \longrightarrow Cu^{III}(C_2O_4)_2^{-} + SO_4^{\div} + SO_4^{=} \tag{10}$$

$$Cu^{II}(C_2O_4)_2^{=} + SO_4^{\div} \longrightarrow Cu^{III}(C_2O_4)_2^{-} + SO_4^{=} \tag{11}$$

$$Cu^{III}(C_2O_4)_2^{-} \longrightarrow Cu^{I}(C_2O_4)^{-} + 2CO_2 \tag{12}$$

$$Cu^{I}(C_2O_4)^{-} + C_2O_4^{=} \longrightarrow Cu^{I}(C_2O_4)_2^{\equiv} \tag{13}$$

$$Cu^{I}(C_2O_4)_2^{\equiv} + S_2O_8^{=} \longrightarrow Cu^{III}(C_2O_4)_2^{-} + 2SO_4^{=} \tag{14}$$

$$Cu^{I}(C_2O_4)_2^{\equiv} + SO_4^{\div} \longrightarrow Cu^{II}(C_2O_4)_2^{=} + SO_4^{=} \tag{15}$$

It is postulated that the rate-determining step is reaction (12), and therefore the rate is first-order with respect to the copper catalyst and zero-order with respect to oxalate and peroxydisulfate. This accounts for the second term on the right-hand side of equation (2), but does not account for the first term. Although it would be convenient to ascribe the first term to the residual copper impurity of the solutions, the spectrographic analyses showed that the impurity was too small for this by a factor of five.

One striking effect on the copper catalysis in this region of concentration is inhibition of the uncatalyzed reaction. The curves of Fig. 3 are very straight and show none of the autocatalytic character of the curves of Fig. 2—this despite the fact that the time for 50% reaction is about the same for the uncatalyzed reaction as for the experiment with 1×10^{-7} *M* $CuSO_4$. Apparently the $SO_4^{\div}$ radicals are removed by reactions (11) and (15) before they can initiate the chain-reaction with reaction (5).

The increase in rate obtained with a large increase in peroxydisulfate concentration can be explained as due to the simultaneous uncatalyzed reaction. This seems especially likely as the curves resemble those for the uncatalyzed reaction.

The slight decrease in rate observed with an increase in oxalate concentration may be due to a competition between the reactions of the catalyzed and uncatalyzed mechanisms. A more exact explanation of this phenomenon is not readily apparent.

Acknowledgments.—I am deeply indebted to Professor Don M. Yost for his aid, encouragement, and for many helpful conversations. I also wish to express my thanks to Professor William H. Cone and Professor Herbert A. Young for their interest and suggestions, and to Mr. John Voth for the spectrographic analyses.

DAVIS, CALIF. RECEIVED SEPTEMBER 5, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF RADIATION BIOLOGY, SCHOOL OF MEDICINE AND DENTISTRY, UNIVERSITY OF ROCHESTER]

The Uranyl:Citrate System. II. Polarographic Studies of the 1:1 Complex[1]

BY W. F. NEUMAN, J. R. HAVILL AND ISAAC FELDMAN

Polarographic studies in acid solution with an excess of citrate showed that the 1:1 uranyl citrate complex was present as a dimer and was reduced according to the reactions: (a) $(U(VI)\text{:citrate})_2 + mH^+ + 2e = 2U(V)\text{:citrate}$; (b) $U(V)\text{:citrate} + nH^+ + e = U(IV)\text{:citrate}$. *m* and *n* were approximately unity at *p*H 4.6 but increased with decreasing *p*H.

Spectrophotometric studies[2] have shown that uranyl and citrate ions combine to form complexes of two combining ratios, represented empirically by UR and U_2R. Both combining ratios are stable over a wide range of *p*H, at least 3.0 to 6.0, and are only slightly dissociated. UR appeared to be the more stable ratio and is the principal ion species present when citrate is in excess.

A polarographic investigation was undertaken to gain additional information. Though considerable interest has been shown in the polarography of uranium,[3-11] no report has appeared which is primarily concerned with the uranyl:citrate system.

Preliminary investigation demonstrated that only a limited application of the polarograph could be made. In the first place, reproducible polarograms (without maxima) were obtained only with acid solutions. Secondly, in the *p*H range of reproducibility, the results were complicated by the presence of several reducible ion-forms: U_2R, UR and uncomplexed uranium. The system was analyzed, therefore, only in acid solutions and in all cases with an excess of citrate to insure that UR was the only combining ratio present in significant concentrations.[2]

Experimental

An automatic recording polarograph (Model XX, E. H. Sargent and Co.)[12] was used throughout these studies. A saturated calomel electrode, connected to the electrolysis cell by means of a saturated potassium chloride–agar bridge, served as an anode.

Stock solutions were prepared from Baker C.P. reagents. Fresh solutions of citric acid were prepared every few days to minimize errors caused by bacterial decomposition. A sample of U_3O_8 (99.95%) obtained from the National Bureau of

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(1) This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

(2) I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951).

(3) G. Tishkoff, Thesis, University of Rochester (in preparation); *cf.* also in C. Voegtlin and H. C. Hodge, "The Pharmacology and Toxicology of Uranium Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 125–146.

(4) R. Strubl, *Coll. Czech. Chem. Comm.*, **10**, 466 (1938).

(5) W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

(6) W. E. Harris and I. M. Kolthoff, *ibid.*, **68**, 1175 (1946).

(7) W. E. Harris and I. M. Kolthoff, *ibid.*, **69**, 446 (1947).

(8) H. G. Heal, *Nature*, **157**, 225 (1946).

(9) E. S. Kritchevsky and J. C. Hindman, THIS JOURNAL, **71**, 2096 (1949).

(10) D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949).

(11) (a) K. A. Kraus, F. Nelson and G. L. Johnson, *ibid.*, **71**, 2510 (1949); (b) K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949).

(12) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).