

at 0° and ionic strength 0.084 *F*. The data of Wagner and Preiss²² lead to the result $k_{26}/k_{15} = 0.19$ at 0° and ionic strength ~ 1.1 *F* (chloride medium). Since these four parameters were not measured under the same conditions, the calculation indicated in eq. 24 can be only approximate. The value calculated is $1.4 \times 10^{-6} M^2$, compared with the experimental 15×10^{-6}

M^2 . Considering the variation in temperature and medium, these results appear not inconsistent. Especially gratifying is the observation that the concentration dependences of these four measured parameters are in not only apparent internal agreement, but that they combine to the correct form for the equilibrium quotient of reaction 23.

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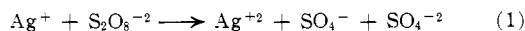
The Oxidation of Oxalate Ion by Peroxodisulfate. III. The Kinetics and Mechanism of the Catalysis by Silver(I)¹

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The silver(I)-catalyzed oxidation of oxalate ion by peroxodisulfate has been studied. The rate law for this reaction in deaerated solution, at concentrations of peroxodisulfate greater than about 0.004 *M*, is $-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}]^{3/2}[AgNO_3]^{1/2}$, with an activation energy of 16.4 kcal./mole. At peroxodisulfate concentrations of 0.004 *M* or less, the rate law is $-d[S_2O_8^{2-}]/dt = k_{11}[S_2O_8^{2-}]^2$. In this concentration region a black precipitate forms during the reaction. It was identified by its X-ray diffraction pattern as metallic silver with traces of silver oxalate. A chain mechanism in which radical-ion chain carriers participate in one-electron-transfer reactions accounts for both rate laws (reactions 1-6). If the catalyst is present as the complex ion $AgC_2O_4^-$, rate laws of the same form are obtained. The effect of pH indicates that Ag^+ catalyzes the reaction at low pH, $AgC_2O_4^-$ at high pH. Oxygen inhibits the reaction. At partial pressures of oxygen between 2.9×10^{-5} and 1.31×10^{-3} atm., the rate law is $-d[S_2O_8^{2-}]/dt = k_{O_2}[S_2O_8^{2-}]^{3/2}[AgNO_3]^{1/2}/P^{1/2}$, with an activation energy of 22.4 kcal./mole. Inclusion of the additional reactions 19 and 20 in the mechanism leads to the observed rate law. The dissociation energy of $O_2CO_2^-$ is estimated to be approximately 8.2 kcal./mole.

The silver(I)-catalyzed oxidations of various substrates by peroxodisulfate are believed to be initiated by a reaction of silver(I) with peroxodisulfate ion.^{3,4} The exact nature of this reaction is not clear although a one-electron oxidation



is in accord with the experimental evidence.^{3,4}

Reaction 1 appears to be rate-determining in the silver(I)-catalyzed oxidations of most substrates.^{3,4} In this respect, the oxidation of oxalate ion is exceptional. King⁵ found that, in partially deaerated solutions, this reaction was about 4000 times as fast as the oxidations of other substrates under similar conditions. The erratic nature of his results precluded a quantitative kinetic investigation.

Later it was shown that, in solutions of very low copper concentration but not deaerated, the silver(I)-catalyzed oxidation of oxalate is only slightly faster than the oxidations of other substrates.⁶

The catalytic properties of copper and the inhibitory nature of oxygen in the oxidation of oxalate ion have been confirmed in a recent study.⁷ For the copper(II)-catalyzed reaction the experimental rate law

$$-d[S_2O_8^{2-}]/dt = k[S_2O_8^{2-}][Cu^{II}(C_2O_4)_2^{-2}]^{1/2}$$

is consistent with a chain mechanism involving the radical ions CO_2^- and SO_4^- and oxidation of copper to

the tervalent state. Inhibition by oxygen occurs through reaction with CO_2^- radicals followed by chain termination.

As silver(I) is susceptible to one-electron oxidation to the unstable silver(II), it can play a role similar to that of copper(II) in catalyzing propagation. It can also initiate chains by reaction 1. Therefore, silver(I) should be at least as effective a catalyst as copper(II).

The present kinetic investigation was undertaken to uncover the mechanism of the silver(I)-catalyzed oxidation of oxalate ion by peroxodisulfate.

Experimental

Materials.—Water was purified by distillation through a 36-in. Vigreux column equipped with an electric heating tape at the takeoff to prevent diffusion of impurities into the distillate.⁸ The distillate was collected and stored in polyethylene bottles.

National Bureau of Standards standard sodium oxalate (batch No. 40g), Mallinckrodt analytical reagent grade potassium peroxodisulfate, silver nitrate, and cupric sulfate, and Baker and Adamson reagent grade anhydrous sodium sulfate were used without further purification. Gases used were Matheson helium and Liquid Carbonic Industrial oxygen.

Baker and Adamson reagent grade concentrated sulfuric acid was redistilled in an all-Pyrex apparatus and stored in a ground-glass-stoppered Pyrex flask. Eastman Kodak (White Label) allyl acetate was fractionally distilled through a 15-cm. column packed with glass helices shortly before use. A fraction boiling at 103° was used.

Reaction mixtures were made from standard stock solutions in most of the experiments. These were prepared with redistilled water and stored in polyethylene bottles. All pipets and other glassware were Pyrex glass and were thoroughly washed with redistilled hydrochloric acid and redistilled water as a precaution against metal contamination.

Apparatus.—Since oxygen is a powerful inhibitor of the silver(I)-catalyzed reaction, the reaction vessel was a Pyrex gas-washing bottle with a fritted disk (flask I) to facilitate deaeration of reaction mixtures by flushing with helium. A 21.0-ml. pipet, equipped with a ground-glass joint fitting snugly into the cover of the reaction vessel, was used for sampling. Aliquots could

(1) Abstracted in part from the Ph.D. Dissertation of A. Joseph Kalb, University of California, Davis, Calif., 1963, presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31-April 5, 1963.

(2) Public Health Service Predoctoral Fellow, 1962-1963.

(3) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms, Conference, Providence, Rhode Island, 1960," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p. 175.

(4) D. A. House, *Chem. Rev.*, **62**, 185 (1962).

(5) C. V. King, *J. Am. Chem. Soc.*, **50**, 2089 (1928).

(6) T. L. Allen, *ibid.*, **73**, 3589 (1951).

(7) E. Ben-Zvi and T. L. Allen, *ibid.*, **83**, 4352 (1961).

(8) R. Ballentine, *Anal. Chem.*, **26**, 549 (1954).

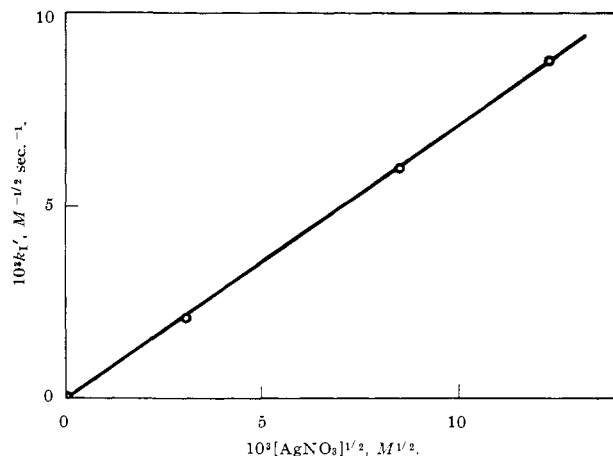


Fig. 1.—Dependence of the three-halves-order rate constant on the square root of silver nitrate concentration.

be forced into the pipet, without seriously slowing the flow of helium, by partly closing the gas outlet of the flask. Except during sampling, when it was open to the atmosphere, the pipet was flushed with helium. A second gas-washing bottle (flask II), with a hole for removal of aliquots, was used for thermal equilibration and deaeration of a reactant before mixing.

Tygon tubing was used for all connections. The flasks were maintained at constant temperature ($\pm 0.02^\circ$) in a water thermostat (except where otherwise stated the temperature was 25.0°). Measurements of pH were made with a Beckman Model G pH meter. Optical density was measured with a Beckman Model DU spectrophotometer.

The apparatus was modified slightly to enable quantitative determination of the inhibitory effect of oxygen. A glass T-joint, equipped with a calibrated capillary inlet for oxygen, was included in the helium line, and a flowmeter (Greiner Model G9144B) was used to measure the helium flow rate. Thus a reaction mixture could be flushed with mixtures of helium and oxygen of known composition.

Procedures.—Appropriate volumes of stock solutions and redistilled water were pipetted into the flasks. Flask I was usually charged with sodium oxalate and flask II with potassium peroxodisulfate. Silver nitrate was sometimes included in flask I, sometimes in flask II. When silver nitrate was added to sodium oxalate, care was taken to avoid local precipitation of silver oxalate. Turbid solutions were discarded. In some experiments, sulfuric acid was added to lower the pH.

The flasks were placed in the thermostat and their contents were flushed with helium (or a mixture of helium and oxygen) for 30 min. A reaction was started by transferring a 25-ml. aliquot from flask II to flask I. The sampling pipet, flushed with the gas, was introduced and aliquot samples were withdrawn at appropriate times. A ground-glass stopper was used to close the sampling port whenever the pipet was removed.

For experiments with allyl acetate, ordinary glass-stoppered erlenmeyer flasks were used. Reaction mixtures were not deaerated and samples were withdrawn with a 25-ml. pipet.

Analyses.—Samples were analyzed for peroxodisulfate by an iodometric titration.⁷ The reaction was quenched by exposure to air and by precipitation of the catalyst as silver iodide. Five samples were usually taken during an experiment and the reactions were followed to at least 65% completion.

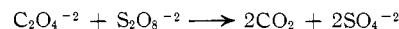
Changes in silver(I) concentration were followed in some experiments by the Fischer dithizone monocolour method.⁹ Samples were passed through a sintered glass filter, acidified with nitric acid, heated for 1 hr. in a boiling water bath to destroy peroxodisulfate (which interferes with the analysis), cooled, and diluted to constant volume with redistilled water. Concentration of silver was evaluated by reference to a standard curve.

A black powder, which appears at low peroxodisulfate concentration, was collected by centrifugation, washed, dried, and identified by its X-ray diffraction pattern. The sample, mounted on a glass filament, was exposed in an X-ray powder camera to Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Exposure time was 5 hr. in one experiment and 10 hr. in another. Interplanar

spacings were calculated by the Bragg equation from the measured diameters of the diffraction circles and compared with spacings listed in the ASTM file of X-ray powder patterns.¹⁰

Results

Stoichiometry.—The stoichiometry of the reaction was verified by allowing a solution containing 0.0540 M Na₂C₂O₄, 0.0450 M K₂S₂O₈, and 1.8×10^{-5} M AgNO₃ to react for 4.5 hr., at which time virtually all of the peroxodisulfate had been consumed. The decrease in peroxodisulfate concentration was found to be equal to that in oxalate concentration, within 0.3%, in accordance with the equation



The Reaction at High Peroxodisulfate Concentration. Peroxodisulfate Dependence.—At peroxodisulfate concentrations greater than approximately 0.004 M, the rate is proportional to $[\text{S}_2\text{O}_8^{-2}]^{3/2}$ as shown by the linearity, up to at least 70% reaction, of plots of $[\text{S}_2\text{O}_8^{-2}]^{-1/2}$ vs. time. Accordingly, $-d[\text{S}_2\text{O}_8^{-2}]/dt = k_1'[\text{S}_2\text{O}_8^{-2}]^{3/2}$.

Silver Nitrate Dependence.—As shown in Fig. 1, k_1' is proportional to the square root of the silver nitrate concentration.¹¹ Accordingly

$$-d[\text{S}_2\text{O}_8^{-2}]/dt = k_1[\text{S}_2\text{O}_8^{-2}]^{3/2}[\text{AgNO}_3]^{1/2} \quad (\text{A})$$

where $k_1 = k_1'/[\text{AgNO}_3]^{1/2}$. Analysis of reaction mixtures in the high range of peroxodisulfate concentration showed no change in catalyst concentration during at least 75% of the reaction.

The dependence on silver nitrate concentration at low pH is discussed below in the section on pH dependence.

Oxalate Dependence.—The data in Table I show that k_1 is practically constant over a 50-fold range of

TABLE I
SECOND-ORDER RATE CONSTANTS

$[\text{S}_2\text{O}_8^{-2}]_0, M$	$[\text{C}_2\text{O}_4^{-2}]_0, M$	$10^2[\text{AgNO}_3], M$	μ, M	$k_1, M^{-1} \text{ sec.}^{-1}$
0.0080	0.080	7.5	0.26	0.628
0.0160	0.080	7.5	0.29	0.664
0.0160 ^a	0.080	7.5	0.34	0.650
0.0560	0.080	7.5	0.41	0.724
0.0160	0.200	7.5	0.65	0.650
0.0160 ^b	0.020	7.5	0.35	0.638
0.0200 ^b	0.004	1.1	0.31	0.682
0.0160	0.080	1.1	0.29	0.658
0.0960	0.120	1.1	0.65	0.596
0.0960	0.200	1.1	0.89	0.622
0.0160	0.080	15.5	0.29	0.690
0.0200	0.004	1.1	0.07	0.840

^a 0.016 M Na₂SO₄ also present. ^b 0.080 M Na₂SO₄ also present.

initial oxalate concentrations, and therefore, the rate law is zero order in oxalate concentration in this range. The constancy of k_1 over a 12-fold range of initial peroxodisulfate concentrations and a 14-fold range of catalyst concentrations confirms the correctness of the rate law. Excluding the last experiment (in which the ionic strength was much lower than in the others), the average rate constant is $0.655 \pm 0.026 M^{-1} \text{ sec.}^{-1}$.

(10) "X-Ray Powder Data File, Sets 1-5 (Revised)," J. V. Smith, Ed., American Society for Testing Materials, Philadelphia, Pa., 1960.

(11) In these solutions the catalyst is probably present as Ag⁺, AgC₂O₄⁻, and Ag⁺, a point which will be considered in more detail in the Discussion. To avoid ambiguity, experimental results are expressed in terms of the concentration of silver nitrate used to prepare the solutions.

(9) F. J. Welcher, "Organic Analytical Reagents," Vol. III, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 517.

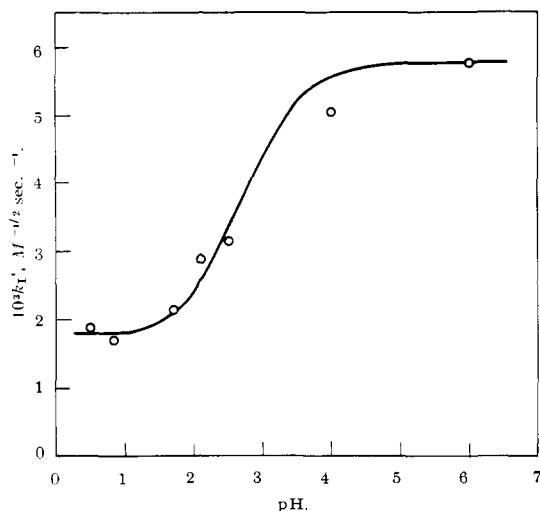


Fig. 2.—Dependence of the three-halves-order rate constant on pH at $0.016 M S_2O_8^{2-}$, $8.0 \times 10^{-5} M AgNO_3$, and $0.080 M$ total oxalate concentration ($[C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$); the curve was calculated by means of eq. 18.

Ionic Strength Dependence.—Except at the lowest salt concentration ($\mu = 0.07$), the rate is insensitive to changes in ionic strength (Table I). No quantitative evaluation was made of the negative salt effect at low ionic strength.

Sulfate Dependence.—As sulfate ion is a reaction product, its concentration increases during an experiment. However, the second and third experiments listed in Table I show that the addition of sodium sulfate had no effect on the rate.

Surface Effect.—The reaction is not markedly sensitive to changes in surface area. Addition of 1 g. of diatomaceous earth (Celite analytical filter aid) depressed the rate by 25%. This may have been caused by traces of some inhibitor. Furthermore, it is not necessary to condition the walls of the reaction vessels in order to obtain reproducible results. (In the copper-(II)-catalyzed reaction, the reaction vessel must be conditioned and a special washing technique is needed to obtain reproducibility.⁷)

pH Dependence.—The rate is somewhat depressed by increasing hydrogen ion concentration (Fig. 2). The reaction is three-halves order in peroxodisulfate concentration at every pH studied.

Table II presents the results of a series of experiments at low pH, where oxalic acid is the principal oxalate species. Although the rate is independent of

TABLE II
OXIDATION OF OXALIC ACID BY PEROXODISULFATE^a

$[S_2O_8^{2-}]_0, M$	$[Na_2C_2O_4]_0, M$	$10^3 [AgNO_3], M$	$10^3 k_1', M^{-1/2} sec^{-1}$
0.016 ^b	0.004	1.6	0.38
0.016	0.080	8.0	1.88
0.040	0.080	8.0	1.40
0.020	0.080	24.0	4.64
0.020	0.020	24.0	4.98
0.020	0.080	40.0	7.10
0.020	0.080	80.0	10.72

^a pH adjusted to 0.49 by addition of H_2SO_4 . ^b pH 1.10, 0.08 $M Na_2SO_4$.

the concentration of reducing agent and three-halves order in peroxodisulfate concentration as at higher pH, the order with respect to silver nitrate concentra-

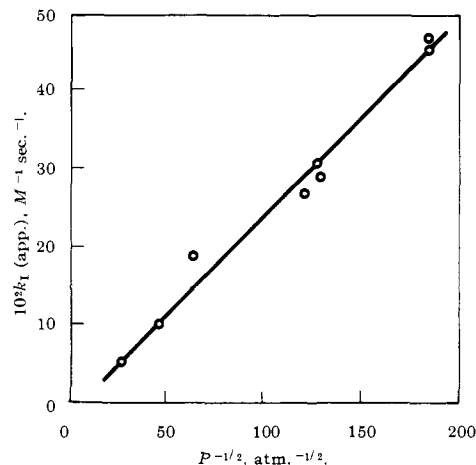


Fig. 3.—Dependence of the apparent second-order rate constant on the reciprocal of the square root of oxygen pressure.

tion changes from first order at low catalyst concentration to half order at higher concentration.

Copper Sulfate Dependence.—In these oxygen-free solutions, the rate was unaffected by the presence of $CuSO_4$ at concentrations of 8.0×10^{-5} and $64.0 \times 10^{-5} M$. These results contrast sharply with the extreme sensitivity of the rate to traces of copper sulfate when oxygen is not excluded.⁸

Allyl Acetate Inhibition.—Allyl acetate, an effective captor of sulfate radical ions,¹² inhibits the reaction. However, the very slow silver-catalyzed decomposition of peroxodisulfate in the presence of allyl acetate is about two and one-half times faster when oxalate is also present than when it is absent. The rate of the inhibited reaction depends only slightly on oxalate concentration from 0.004 to 0.080 M (Table III).

TABLE III
ALLYL ACETATE INHIBITION^a

$[C_2O_4^{2-}]_0, M$	$t_{1/2}, hr.$
0.080	90
0.010 ^b	102
0.004 ^b	106
... ^b	248
0.080 ^c	0.5

^a 0.01 $M K_2S_2O_8$, $8 \times 10^{-5} M AgNO_3$, and 0.02 M allyl acetate. ^b Ionic strength adjusted to that of the first experiment by addition of Na_2SO_4 . ^c No allyl acetate, oxygen-free solution.

Oxygen Dependence.—The fact that oxygen is a powerful inhibitor of the reaction was demonstrated by conducting an experiment without flushing with helium. Although the temperature was 39.7° , it took 90 hr. for half of the peroxodisulfate to react. In oxygen-free solutions, the half-life for a comparable reaction mixture is about 1 hr. at 25.0° .

At low oxygen pressures, the rate is inversely proportional to the square root of the partial pressure of oxygen (Fig. 3). Dependence on peroxodisulfate, oxalate, and silver nitrate concentrations is the same as in the absence of oxygen (Table IV). The rate does not increase without limit as oxygen pressure decreases. Thus, a suitable rate law is

$$-d[S_2O_8^{2-}]/dt = k_1[S_2O_8^{2-}]^{1/2}[AgNO_3]^{1/2}/\{1 + P(k_1/k_{O_2})^2\}^{1/2} \quad (B)$$

(12) I. M. Kolthoff, E. J. Meehan, and E. M. Carr, *J. Am. Chem. Soc.*, **75**, 1439 (1953).

TABLE IV
 OXYGEN DEPENDENCE^a

[C ₂ O ₄ ⁻²], <i>M</i>	10 ⁴ <i>P</i> , atm.	<i>k</i> ₁ (apparent), <i>M</i> ⁻¹ sec. ⁻¹	10 ³ <i>k</i> _{O₂} , <i>M</i> ⁻¹ atm. ^{1/2} sec. ⁻¹
0.10	13.1	0.051	1.85
0.10	4.5	0.097	2.05
0.10	2.4	0.187	2.90
0.10	0.67	0.268	2.19
0.10	0.60	0.303	2.35
0.15 ^b	0.60	0.288	2.23
0.25	0.29	0.451	2.43
0.10	0.29	0.464	2.50

^a 0.02 *M* K₂S₂O₈ and 7.5 × 10⁻⁵ *M* AgNO₃. ^b 15.5 × 10⁻⁵ *M* AgNO₃.

where *P* is the partial pressure of oxygen. As *P* approaches zero, B reduces to A, the rate law in oxygen-free solutions. At values of *P* greater than about 3 × 10⁻⁵ atm., B becomes

$$-d[S_2O_8^{-2}]/dt = k_{O_2}[S_2O_8^{-2}]^{1/2}[AgNO_3]^{1/2}/P^{1/2} \quad (C)$$

Since no experiments were conducted at partial pressures of oxygen between zero and 3 × 10⁻⁵ atm., only the extreme cases represented by A and C were observed.

Temperature Dependence.—The effect of temperature on *k*₁ over a range of 25° and *k*_{O₂} over a range of 20° is given in Table V. Arrhenius plots of these

 TABLE V
 TEMPERATURE DEPENDENCE^a

Temp., °K	<i>k</i> ₁ , <i>M</i> ⁻¹ sec. ⁻¹	10 ³ <i>k</i> _{O₂} , <i>M</i> ⁻¹ atm. ^{1/2} sec. ⁻¹
283.4	0.148	...
288.3	...	0.68 ^b
288.6	0.296	...
293.3	0.384	...
298.2	0.655 ± 0.026 ^c	2.31 ± 0.23 ^d
303.0	1.04	...
308.2	1.61 ^e	8.56 ^b

^a 0.020 *M* K₂S₂O₈, 0.080 *M* Na₂C₂O₄, and 7.5 × 10⁻⁵ *M* AgNO₃. ^b 6.0 × 10⁻⁵ atm. oxygen pressure. ^c Average of eleven experiments with various initial concentrations. ^d Average of eight experiments with various initial concentrations, and oxygen pressures from 2.9 × 10⁻⁵ to 131 × 10⁻⁵ atm. ^e 3.5 × 10⁻⁵ *M* AgNO₃.

data are linear and give

$$k_1 = 5.90 \times 10^{11} \exp(-16,400/RT) M^{-1} \text{ sec.}^{-1}$$

$$k_{O_2} = 5.05 \times 10^{13} \exp(-22,400/RT) M^{-1} \text{ atm.}^{1/2} \text{ sec.}^{-1}$$

The Reaction at Low Peroxodisulfate Concentrations.—At peroxodisulfate concentrations of about 0.004 *M* or less, there is considerable deviation from linearity in plots of [S₂O₈⁻²]^{-1/2} vs. time. Under these conditions, it is the reciprocal of peroxodisulfate concentration which is linear with time showing second-order dependence of the rate on peroxodisulfate concentration.

In this range, the rate is independent of oxalate, sulfate, and silver nitrate concentrations. Except at the lowest salt concentration (*μ* = 0.016), it is insensitive to changes in ionic strength (Table VI).

Accordingly, the rate law at peroxodisulfate concentrations of 0.004 *M* or less is

$$-d[S_2O_8^{-2}]/dt = k_{II}[S_2O_8^{-2}]^2 \quad (D)$$

TABLE VI

EXPERIMENTS AT LOW PEROXODISULFATE CONCENTRATION

10 ³ × [S ₂ O ₈ ⁻²] ₀ , <i>M</i>	[C ₂ O ₄ ⁻²] ₀ , <i>M</i>	10 ³ × [AgNO ₃], <i>M</i>	<i>μ</i> , <i>M</i>	10 ³ <i>k</i> ₁₁ , <i>M</i> ⁻¹ sec. ⁻¹
4.0	0.080	8.0	0.25	1.15
2.4	0.080	8.0	0.25	1.18
2.4	0.080	16.0	0.25	0.92
2.4	0.080	1.6	0.25	0.97
2.4	0.003	8.0	0.50 ^a	1.19
2.4	0.003	8.0	0.016	3.40

^a 0.16 *M* Na₂SO₄ also present.

During these experiments a slight black precipitate appeared, which was identified by its X-ray diffraction pattern as metallic silver with traces of silver oxalate (Table VII). Concurrently, the catalyst concentra-

TABLE VII

INTERPLANAR SPACINGS (*d*, Å.) FROM X-RAY DIFFRACTION PATTERNS

Black ppt. washed with H ₂ O ^a	Black ppt. washed with H ₂ SO ₄	Ag ^b
2.98 ^c
2.75 ^c
2.34	2.34	2.359
2.04	2.04	2.044
1.44	1.44	1.445
1.23	1.23	1.231
1.16	1.16	1.1796
1.02	1.02	1.0215
0.93	0.93	0.9375
0.91	0.91	0.9137
0.83	0.83	0.8341
0.79 ^d	0.79 ^d	...

^a Very faint lines corresponding to spacings of 1.91, 1.76, 1.70, 1.54, and 0.86 Å. were also present. Their source was not determined. ^b Reference 10. ^c The most intense reflections for Ag₂C₂O₄ are at 2.97 and 2.74 Å. (ref. 10). ^d This spacing corresponds closely to a third-order overtone of the 2.359-Å. spacing.

tion decreased. With the same initial concentrations as the first experiment listed in Table VI, the silver concentration dropped to 90% of its initial value after 30 min. Subsequent values were 83% at 70 min., 75% at 100 min., 73% at 120 min., and 65% at 160 min.

Discussion

The silver(I)-catalyzed oxidation of oxalate by peroxodisulfate is believed to be a free-radical chain reaction for the following reasons:

1. The reaction is strongly inhibited by allyl acetate, an efficient captor of SO₄⁻¹². Further, the inhibited reaction proceeds at about the same rate as the silver(I)-catalyzed oxidation of water by peroxodisulfate under similar conditions.

2. The marked inhibition by oxygen implicates CO₂⁻ (or C₂O₄⁻) as a reactive intermediate. (Evidence for the existence of CO₂⁻ in γ -irradiated crystals of sodium formate has been reported recently.¹³) Oxygen is known to inhibit certain chain reactions involving CO₂⁻, such as the oxidation of oxalate by permanganate,¹⁴⁻¹⁶ by mercuric chloride,¹⁷⁻¹⁹ and by per-

(13) D. W. Overall and D. H. Whiffen, *Mol. Phys.*, **4**, 135 (1961).

(14) H. F. Launer, *J. Am. Chem. Soc.*, **54**, 2597 (1932); **55**, 865 (1933).

(15) H. F. Launer and D. M. Yost, *ibid.*, **56**, 2571 (1934).

(16) S. J. Adler and R. M. Noyes, *ibid.*, **77**, 2036 (1955).

(17) W. E. Roseveare and A. R. Olson, *ibid.*, **51**, 1716 (1929).

(18) W. E. Roseveare, *ibid.*, **52**, 2612 (1930).

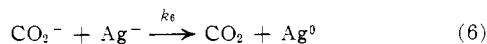
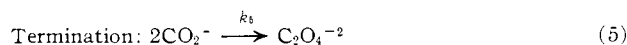
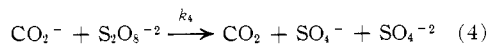
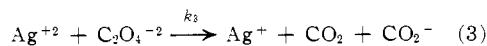
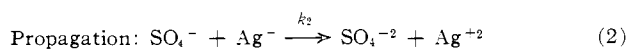
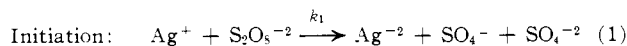
(19) E. A. Hausman and T. W. Davis, *ibid.*, **76**, 5341 (1954).

oxodisulfate in the presence of copper(II).⁷ The lack of reproducibility in a previous study of this reaction was probably caused, to a great extent, by the presence of varying and uncontrolled amounts of oxygen.⁵

3. Fractional orders in silver(I), peroxodisulfate, and oxygen support the hypothesis that this is a chain reaction.

4. This reaction is faster, by several orders of magnitude, than most other silver-catalyzed reactions of peroxodisulfate.^{3,4}

A reasonable mechanism of this sort is



Using the usual steady-state approximation and assuming $k_1[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}] \ll k_4[\text{CO}_2^-][\text{S}_2\text{O}_8^{2-}]$ (as required for long chains), one may show that

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = k_4 k_6 [\text{Ag}^+][\text{S}_2\text{O}_8^{2-}] \left\{ (1 + X)^{1/2} - 1 \right\} / 2k_5 \quad (7)$$

where $X = 8k_1 k_5 [\text{S}_2\text{O}_8^{2-}] / k_6^2 [\text{Ag}^+]$. If the concentration of peroxodisulfate is such that $X \gg 1$, eq. 7 becomes

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = (2k_1 k_4^2 / k_5)^{1/2} [\text{S}_2\text{O}_8^{2-}]^{1/2} [\text{Ag}^+]^{1/2} \quad (8)$$

This equation has the same form as the experimental rate law A for peroxodisulfate concentrations greater than about 0.004 M, provided that practically all of the catalyst is present as Ag^+ . If the peroxodisulfate concentration is so low that $X \ll 1$, eq. 7 may be approximated by means of the relationship $(1 + X)^{1/2} = 1 + 1/2 X$, yielding

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = 2k_1 k_4 [\text{S}_2\text{O}_8^{2-}]^2 / k_6 \quad (9)$$

which has the same form as the experimental rate law D for peroxodisulfate concentrations of 0.004 M or less.

The relative importance of termination reactions 5 and 6 may be expressed as a function of peroxodisulfate concentration

$$k_5 [\text{CO}_2^-]^2 / k_6 [\text{CO}_2^-][\text{Ag}^-] = (1 + X)^{1/2} - 1 \quad (10)$$

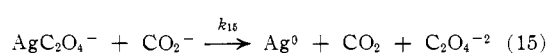
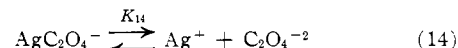
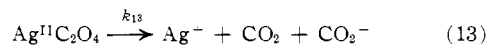
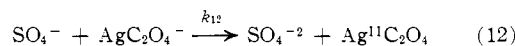
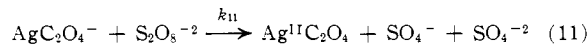
Thus, under conditions which favor rate law 8, reaction 5 predominates. When rate law 9 is observed, reaction 6 predominates. (Tsao and Wilmarth²⁰ have used a similar argument in explaining the concentration dependence of the rate law in the reaction of peroxodisulfate with hydrogen peroxide.) Production of metallic silver at low but not high peroxodisulfate concentrations supports the proposed mechanism.

According to recent evidence on the formation of a mono-oxalato complex of silver(I),²¹ AgC_2O_4^- is the

(20) M.-S. Tsao and W. K. Wilmarth, *Discussions Faraday Soc.*, **29**, 137 (1960).

(21) S. H. Cohen, R. T. Iwamoto, and J. Kleinberg, *J. Am. Chem. Soc.*, **82**, 1844 (1960).

dominant species of silver(I) in the reaction mixtures at higher pH. The mechanism may be modified accordingly, without altering the form of the predicted rate law. The modified mechanism includes reactions 4, 5, and



It leads to the rate law, for high peroxodisulfate concentrations

$$-d[\text{S}_2\text{O}_8^{2-}]/dt = (2k_{11} k_4^2 / k_5)^{1/2} [\text{S}_2\text{O}_8^{2-}]^{1/2} [\text{AgC}_2\text{O}_4^-]^{1/2} \quad (16)$$

which is a satisfactory representation of experimental rate law A provided virtually all silver(I) is complexed, and the concentration of silver(II) is negligible. Calculations based on the dissociation constant of AgC_2O_4^- determined by Cohen, Iwamoto, and Kleinberg²¹ (neglecting deviations of the activity coefficients from unity) show that this is true in most of the experiments listed in Table I. The ratio of $[\text{AgC}_2\text{O}_4^-]$ to $[\text{Ag}^+]$ varies from 50:1 to 1:1. The high solubility of silver nitrate in these solutions (at least 50 times as great as one would predict from the solubility product of $\text{Ag}_2\text{C}_2\text{O}_4$ ²²) is further evidence for the formation of a complex ion.

At low pH practically all of the oxalate is in the form of $\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^- , and very little of the silver(I) is complexed. At intermediate pH, the concentrations of Ag^+ and AgC_2O_4^- are comparable, and therefore one must consider both the Ag^+ mechanism and the AgC_2O_4^- mechanism. On applying the steady-state treatment to a mechanism consisting of reactions 1-5 and 11-14 inclusive (reactions 6 and 15 are not included here as only the region of high peroxodisulfate concentration is being considered), and again assuming long chains, the resulting rate law is

$$\frac{-d[\text{S}_2\text{O}_8^{2-}]}{dt} = \left\{ \frac{2k_1 k_4^2}{k_5} [\text{Ag}^+] + \frac{2k_{11} k_4^2}{k_5} [\text{AgC}_2\text{O}_4^-] \right\}^{1/2} [\text{S}_2\text{O}_8^{2-}]^{3/2} \quad (17)$$

Therefore the three-halves-order rate constant should be of the form

$$k_1' = \{ k_a^2 [\text{Ag}^+] + k_b^2 [\text{AgC}_2\text{O}_4^-] \}^{1/2} \quad (18)$$

At low pH, this reduces to $k_1' = k_a [\text{AgNO}_3]^{1/2}$; at high pH it becomes $k_1' = k_b [\text{AgNO}_3]^{1/2}$. The experimental data at low and high pH shown in Fig. 2 were used to determine k_a and k_b , which were found to be 0.200 and 0.659 $M^{-1} \text{sec}^{-1}$, respectively.

Values of k_1' in the intermediate pH region were calculated from eq. 18, these values of k_a and k_b , the dissociation constant of AgC_2O_4^- , and the dissociation constants of oxalic acid.²² The results are shown

(22) D. T. Ferrell, Jr., I. Blackburn, and W. C. Vosburgh, *ibid.*, **70**, 3812 (1948).

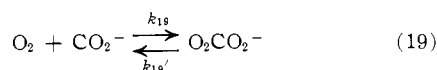
as the curve in Fig. 2, which provides an adequate representation of the experimental data. However, the proposed mechanism does not account for the first-order dependence on catalyst concentration observed at low pH and low catalyst concentration. No mechanism has been found which leads to the experimental rate law for this region.

Allyl acetate suppresses the chain reactions, and the rate in the presence of allyl acetate should be $-d[S_2O_8^{2-}]/dt = k_1[Ag^+][S_2O_8^{2-}]$ where oxalate is absent, and $-d[S_2O_8^{2-}]/dt = k_{11}[AgC_2O_4^-][S_2O_8^{2-}]$ where the silver(I) is in the form of the oxalate complex. From the first and fourth experiments in Table III, k_{11} is $96 M^{-1} hr^{-1}$ and k_1 is $35 M^{-1} hr^{-1}$ (both values at an ionic strength of 0.27). These results lead to $k_b/k_a = (k_{11}/k_1)^{1/2} = 1.66$, whereas the data on pH dependence considered above give $k_b/k_a = 3.30$.

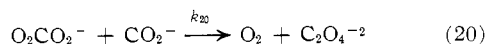
Another point which is difficult to understand is that at the lowest oxalate concentration (0.004 M), where only half of the silver(I) is complexed, the rate should be significantly lower than at higher oxalate concentrations. The data in Tables I and III show that this effect is not observed. A smaller value for the dissociation constant of $AgC_2O_4^-$ would account for this behavior, but it would also shift the curve of Fig. 2 toward lower pH.

The observation that the silver(I)-catalyzed reaction is independent of copper sulfate concentration is in accord with the proposed mechanism. Even if copper(II), as dioxalatoocuprate(II), catalyzes the oxidation of oxalate in reactions analogous to (12-14), the rate should be independent of copper sulfate concentration, since k_{12} , k_{13} , and K_{14} do not appear in the predicted rate law. However, in the absence of silver(I)⁷ or in the presence of oxygen⁸ (which strongly inhibits the silver-catalyzed chain mechanism), copper(II) catalyzes the reaction *via* the mechanism proposed earlier.

Inhibition by oxygen is believed to occur through reaction with CO_2^- to form a molecular complex or peroxide



followed by chain termination



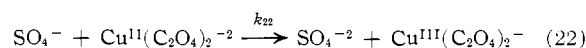
By including these reactions together with reactions 1-6, assuming $k_{19'}[O_2CO_2^-] \gg k_{20}[O_2CO_2^-][CO_2^-]$, $X \gg 1$, long chains, and the steady state, one may show that

$$\frac{-d[S_2O_8^{2-}]}{dt} = \left\{ \frac{2k_1k_4^2[S_2O_8^{2-}]^3[Ag^+]}{k_5 + k_{19}k_{20}P/k_Hk_{19'}} \right\}^{1/2} \quad (21)$$

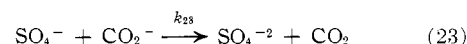
where k_H is the Henry's law constant for oxygen.

Equation 21 has the same form as experimental rate law B.

The Arrhenius activation energy for the reaction at high peroxodisulfate concentrations in oxygen-free solutions, E_1 , is found here to be 16.4 kcal./mole. This is approximately half the activation energy of the copper(II)-catalyzed reaction.⁷ From the relation between the experimental rate constant, k_1 , and the individual rate constants which appear in rate law 8, it follows that $E_1 = E_4 + 1/2(E_1 - E_5)$. If E_5 , the activation energy for combination of two free radicals, is estimated to be very small, then since E_1 is 17.9 kcal./mole,²³ it follows that E_4 is about 7.4 kcal./mole. (The same result is obtained from the alternative mechanism involving $AgC_2O_4^-$, if it is assumed that E_1 and E_{11} are approximately equal.) This value, combined with the mechanism and activation energy for the copper(II)-catalyzed oxidation of oxalate by peroxodisulfate,⁷ leads to an activation energy of 28.6 kcal./mole for the reaction



Accordingly, reaction 22 is probably fairly slow. This would lead to a relatively higher steady-state concentration of SO_4^- during the copper(II)-catalyzed reaction, which accounts for termination reaction



being favored over reaction 5. Conversely it may be argued that, in the silver(I)-catalyzed reaction, step 2 (or 12) is fairly rapid since reaction 5 is preferred to (23).

Comparison of the mechanisms and activation energies of the silver(I)-catalyzed reaction in the presence and absence of oxygen leads to the expression

$$E_{O_2} - E_1 = 1/2(E_{19'} - E_{19} - E_{20} + E_5 - E_s) \quad (24)$$

where E_s is the heat of solution of oxygen, -3.8 kcal./mole.²⁴ The experimental value of E_{O_2} is 22.4 kcal./mole. Both E_{20} and E_5 are probably very small, and they tend to cancel one another. Therefore $E_{19'} - E_{19}$, the dissociation energy of the molecular complex $O_2CO_2^-$ in aqueous solution, is estimated to be approximately 8.2 kcal./mole.

Acknowledgments.—The authors wish to express their appreciation to John L. Voth for technical assistance, and to Clarence Sterling for the use of his X-ray apparatus. The financial assistance of a research grant from the National Science Foundation is gratefully acknowledged.

(23) C. E. H. Bawn and D. Margerison, *Trans. Faraday Soc.*, **51**, 925 (1955).

(24) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, p. 8.