The Oxidation of Oxalate Ion by Peroxodisulfate. IV. The Kinetics and Mechanism of the Uncatalyzed Reaction[1]

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Abstract: The oxidation of oxalate ion by peroxodisulfate has been studied at 60.2° in oxygen-free solutions. A small amount of ethylenediaminetetraacetic acid (EDTA) is used to prevent trace-metal ion catalysis. The rate law for this reaction is $-d[S_2O_8^{2-}]/dt = k_I[S_2O_8^{2-}]$, with an activation energy of 32.7 kcal/mole. A chain mechanism (reactions 1–6), invoking participation by sulfate, carboxyl, and hydroxyl radicals, accounts for the observed rate law. In the pH range 0.55–10.25 the rate is a maximum at pH 4.5. The reduction in rate at lower pH is explained by protonation of the carboxyl radical ions. The pK of the ionization reaction of the COOH radical is found to be 2.8. Counterion effects have been observed; potassium ion enhances the rate more strongly than sodium ion. The observed rate law for the reaction inhibited by oxygen at partial pressures (P) from 1.67×10^{-4} to 8.00×10^{-4} atm is $-d[S_2O_8^{2-}]/dt = k_I[S_2O_8^{2-}]/\sqrt{1 + (k_I/k_{O_2})^2P}$. The inhibition by oxygen is explained by a chain-terminating reaction with carboxyl radical ions.

In the first part of this series[2] it was observed that the oxidation of oxalate by peroxodisulfate was catalyzed by trace copper ions in the solution. Many reactions involving peroxodisulfate have been reported to be sensitive to trace-metal ion catalysis.[3] Ball, Crutchfield, and Edwards[4] have used a small amount of a strong chelating agent, ethylenediaminetetraacetic acid (EDTA) at a concentration of about 10^{-5} *M*, to suppress the trace-metal ion catalysis in the oxidation of 2-propanol by peroxodisulfate. This technique was employed recently in the study of salt effects in the oxidation of thiosulfate by peroxodisulfate.[5] It has been used in the present kinetic investigations to elucidate the mechanism of the uncatalyzed oxalate–peroxodisulfate reaction in oxygen-free solutions. The inhibitory nature of oxygen in the oxidation of oxalate ion has been confirmed in recent studies.[6,7]

Experimental Section

Materials. Distilled water was purified by passing through an ion-exchange apparatus (Model 306-4, Caw Engineering Co., Palo Alto, Calif.).

Mallinckrodt reagent grade potassium peroxodisulfate, potassium sulfate, potassium oxalate monohydrate, and anhydrous sodium sulfate were purified by recrystallizing from deionized water and vacuum dried at room temperature. Baker and Adamson reagent grade concentrated sulfuric acid was redistilled and stored in a ground-glass stoppered bottle. National Bureau of Standards sodium oxalate (sample No. 40g), Sigma Chemical Co. sodium peroxodisulfate, J. T. Baker reagent grade disodium ethylenedinitrilotetraacetate, Fisher purified grade sodium binoxalate, Mallinckrodt sodium dibasic phosphate, Baker and Adamson hydrochloric acid, and Eastman Kodak allyl acetate were used without further purification. Gases were Matheson Pre-purified nitrogen and Liquid Carbonic Industrial oxygen.

For spectrographic analyses, Johnson, Mattey and Co., Ltd (73/83, Hatton Garden, London) Catalogue No. J. M. 176 "Specpure" cadmium sulfate was used.

Deionized water was used to prepare the standard stock solutions which were stored in polyethylene bottles. All Pyrex glassware was washed with hydrochloric acid and rinsed thoroughly with deionized water as a precaution against contamination.

Apparatus. The reaction vessel was a Pyrex gas-washing bottle with a fritted disk to allow deaeration of the reaction mixtures by flushing with nitrogen. The cover of the reaction vessel was equipped with a port for withdrawal of samples. A calibrated 20.4-ml pipet was flushed with nitrogen prior to withdrawal of a sample. A second reaction vessel was used for thermal equilibration of a reactant before mixing. An RGI, Inc., F-1200 flowmeter was used to measure the flow rate of the nitrogen. The flow rate was normally regulated to approximately 350 ml/min. To study the inhibitory effect of oxygen quantitatively, oxygen was introduced into the nitrogen stream through a calibrated capillary inlet. Tygon tubing was used for all connections.

The reaction vessels were maintained at constant temperature (±0.04°) in an ethylene glycol thermostat. The pH of the solution was measured with a Beckman Model 76 pH meter.

Procedures. Appropriate volumes of the oxalate and EDTA solutions were pipetted into the reaction vessel which was placed in the thermostat. A second reaction vessel containing the peroxodisulfate solution was placed in the same thermostat. Both solutions were flushed with nitrogen for approximately 0.5 hr to allow temperature equilibration. To avoid excessive loss of water from the reaction vessel, the nitrogen was saturated with water vapor at the same temperature. A kinetic run was started by transferring the appropriate volume of peroxodisulfate to the reaction vessel containing the oxalate solution. The reaction mixture was continuously flushed with nitrogen during the experiment. Aliquots were removed at appropriate times for analyses.

In the allyl acetate experiments, ordinary glass-stoppered erlenmeyer flasks were used. To prevent excessive loss of liquid during the lengthy reaction times, the solutions were not deaerated.

Analyses. Samples were analyzed for peroxodisulfate by an iodometric titration.[6,7] At least four samples were taken during a kinetic run, and reactions were followed to at least 65% completion. Unreacted oxalate was determined by a standard permanganate titration to verify the stoichiometry of the reaction.

Spectrographic analyses were conducted to determine trace elements in the deionized distilled water and the various reagents. A Bausch and Lomb large littrow quartz prism emission spectrograph was used.

The technique used by Liebig, Vanselow, and Chapman[8] was employed to analyze the trace elements in the deionized water. It was found that the deionized water contained about 1.1×10^{-4} mg of Cu/l. and $<1 \times 10^{-5}$ mg of Fe/l.

Results

Stoichiometry. The stoichiometry of the reaction was verified by allowing an oxygen-free solution of

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[1] Abstracted in part from the Ph.D. Dissertation of H. N. Po, University of California, Davis, Calif., 1967.

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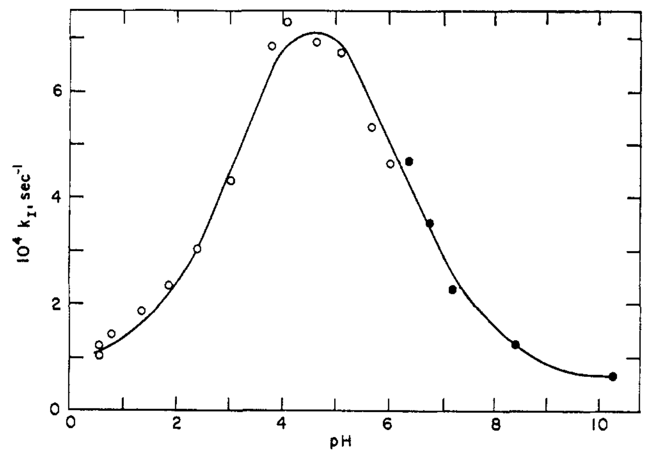

Figure 1. Dependence of the first-order rate constant on pH: 60.2°, 0.008 M $K_2S_2O_8$, (1–2.5) × 10^{-5} M EDTA, and 0.08 M total oxalate concentration ($[H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$): ○, μ = 0.25 M; ●, 0.1 M Na_2HPO_4 added, μ = 0.8 M.

0.0195 M sodium oxalate and 0.0100 M potassium peroxodisulfate to react at 49.8° for about 6 hr. The amounts of peroxodisulfate and oxalate consumed were found to be 0.0085 and 0.0089 M, respectively. The decrease in peroxodisulfate is therefore equal to that in oxalate, within 5%, in agreement with the equation

$$C_2O_4^{2-} + S_2O_8^{2-} \longrightarrow 2CO_2 + 2SO_4^{2-}$$

The same stoichiometry is found in the copper-catalyzed and silver-catalyzed reactions.[6,7]

Peroxodisulfate Dependence. The rate is first order in peroxodisulfate concentration as shown by the linearity of plots of log $[S_2O_8^{2-}]$ *vs.* time. Accordingly

$$-d[S_2O_8^{2-}]/dt = k_I[S_2O_8^{2-}] \qquad (A)$$

The efficacy of EDTA in suppressing the catalytic effect of the trace-metal impurities was demonstrated by varying the concentration of EDTA. The rate constant decreased by one-third as [EDTA] was increased from 0.15 × 10^{-5} to 2.0 × 10^{-5} M. No further decrease in rate was observed as [EDTA] was increased to 2.5 × 10^{-5} M (see Table I).

Table I. Effect of EDTA Concentration[a]

10^5[EDTA], M	10^4k_I, sec^{-1}
0.15	6.77
0.50	6.00
1.0	5.63
1.0	5.91
2.0	4.53
2.5	4.54

[a] 60.2°, 8 × 10^{-3} M $K_2S_2O_8$, and 0.08 M $Na_2C_2O_4$.

Oxalate Dependence. The effect of oxalate on rate was studied over a sevenfold range of initial oxalate concentration. The data in Table II show that within the precision of the results k_I is essentially constant, and therefore the rate law is zero order in oxalate concentration in this range. Duplicate kinetic runs were performed for each oxalate concentration and sodium sulfate was used to maintain constant ionic strength and sodium ion concentration.

Specific Ion Effects. Alkali metal ion effects have been observed and examined carefully using recrystallized salts of peroxodisulfate, oxalate, and sulfate. Table III shows that, over a threefold increase in the alkali metal ion concentration, the rate constant doubles in the potassium ion case and increases by two-thirds in the sodium ion case. The increase in rate cannot be due to copper impurities in K_2SO_4 and Na_2SO_4. For instance, the highest copper concentration (in the third experiment of Table III), calculated from the spectrographic analyses of the various reagents, is 5 × 10^{-7} M. Using the stability constants of the EDTA and oxalate complexes of copper, the concentration of the dioxalatocupric complex (the form of the catalyst in the copper-catalyzed reaction[6]) is estimated at about 5 × 10^{-14} M, a very small quantity indeed. Therefore the present results are not due to catalysis by copper impurities but are due to the effect of counterions.

Table II. Oxalate Dependence[a]

$[Na_2C_2O_4]$, M	$[Na_2SO_4]$, M	10^4k_I, sec^{-1}
0.02	0.14	4.65, 4.35
0.04	0.12	4.80, 4.72
0.08	0.08	5.00, 4.65
0.12	0.04	5.52, 5.29
0.14	0.02	5.25, 5.20
	Average	4.94 ± 0.31

[a] 60.2°, 0.008 M $K_2S_2O_8$, 2.5 × 10^{-5} M EDTA, 0.32 M Na^+, and μ = 0.50 M.

Table III. Specific Ion Effects[a]

10^3 $[M_2S_2O_8]$, M	$[M_2C_2O_4]$, M	$[M_2SO_4]$, M	$[M^+]$, M	10^4k_I, sec^{-1}
8.0	0.078	...	0.172	5.54, 6.05
8.0	0.080	0.10	0.376	9.20
8.0	0.080	0.20	0.576	12.0
7.5	0.078	...	0.171	4.36, 3.90
7.5	0.078	0.12	0.411	4.81
8.0	0.080	0.20	0.576	6.86

[a] 60.2° and (2.0–2.9) × 10^{-5} M EDTA. In the first three entries, M represents K; in the last three entries, M represents Na.

pH Dependence. The effect of pH of the solution on the rate of reaction was studied over a wide range, from pH 0.55 to 10.25. In most of this range oxalic acid and its ions served as a buffer, and throughout a kinetic run the pH of the solution remained constant. Sodium biphosphate was used as a buffer in the basic region. Redistilled sulfuric acid was used to adjust the reacting solutions to the desired pH. The ionic strength of the solution was about 0.25 M at low pH. In the basic range where 0.1 M Na_2HPO_4 was used to maintain constant pH the ionic strength was 0.8 M.

The first-order kinetic plots at high and low pH were linear in all cases. As shown in Figure 1, the rate constant increases rapidly from pH 0.55 to a maximum at 4.5 followed by a rapid drop to pH 10.25.

Oxygen Dependence. Inhibition of the reaction by oxygen has been studied at oxygen pressures from 1.67 × 10^{-4} to 8.00 × 10^{-4} atm. The rate is inversely proportional to the square root of the partial pressure of oxygen as shown by the constancy of k_{O_2} in the last column of Table IV.

Table IV. Oxygen Dependence[a]

10^4P, atm	10^4k_{app}, sec^{-1}	$10^6k_{O_2}$, atm$^{1/2}$ sec^{-1}
1.67	3.60	4.65
1.67	3.70	4.77
2.54	3.13	4.97
3.57	2.46	4.65
8.00	1.55	4.40

[a] 60.2°, 0.008 *M* $K_2S_2O_8$, 0.08 *M* $Na_2C_2O_4$, and 2.9×10^{-5} *M* EDTA.

However, this represents only an extreme case since the rate does not increase without limit as the oxygen pressure decreases. Thus a suitable rate law is

$$-d[S_2O_8^{2-}]/dt = k_I[S_2O_8^{2-}]/\sqrt{1 + (k_I/k_{O_2})^2P} \tag{B}$$

where *P* is the partial pressure of oxygen. As *P* approaches zero, (B) reduces to (A), the rate law in oxygen-free solutions. Under oxygen pressures greater than 1.67×10^{-4} atm, (B) becomes

$$-d[S_2O_8^{2-}]/dt = k_{O_2}[S_2O_8^{2-}]/\sqrt{P} = k_{app}[S_2O_8^{2-}] \tag{C}$$

Only the two extreme cases represented by eq A and C have been studied.

Allyl Acetate Inhibition. Allyl acetate, an efficient scavenger of sulfate radical ions,[9] inhibits the reaction. A reaction mixture composed of 0.008 *M* $K_2S_2O_8$, 0.08 *M* $Na_2C_2O_4$, and 0.047 *M* allyl acetate reacted very slowly at 60.2°. The observed half-life was 35.9 hr, which agreed reasonably well with the half-life of 38.6 hr calculated for the thermal decomposition of peroxodisulfate at this temperature.[10]

Temperature Dependence. The temperature effect has been studied at five temperatures covering a range of 18°; the data are presented in Table V. An Arrhenius plot of the data is linear. The results are expressed by the equation

$$k_I = 1.61 \times 10^{18} \exp(-32{,}700/RT) \text{ sec}^{-1}$$

The estimated uncertainty of the Arrhenius activation energy is ±0.8 kcal/mole.

Table V. Temperature Dependence[a]

Temp, °C	10^4k_I, sec^{-1}
63.8	7.28
60.2	4.54, 4.53
55.8	2.35, 2.05, 2.34
50.4	1.05, 1.03
45.4	0.43

[a] 0.008 *M* $K_2S_2O_8$, 0.08 *M* $Na_2C_2O_4$, and $(2.5\text{–}2.9) \times 10^{-5}$ *M* EDTA.

Discussion

The uncatalyzed oxidation of oxalate by peroxodisulfate is believed to be a free-radical chain mechanism for several reasons.

(1) In the presence of allyl acetate, an efficient scavenger of sulfate radical ions,[9] the reaction is strongly inhibited. In addition, the half-life of the inhibited reaction is essentially the same as that of the thermal decomposition of peroxodisulfate[10] at the same temperature. Therefore the rate-determining step in that reaction, $S_2O_8^{2-} \rightarrow 2SO_4^-$, is very probably the chain-initiating step in the oxidation of oxalate.

(2) The strong inhibition by oxygen indicates that this is a chain reaction in which CO_2^- (or $C_2O_4^-$) radicals participate. Oxygen is known to inhibit certain chain reactions involving CO_2^-, such as the oxidation of oxalate by permanganate,[11-14] by mercuric chloride,[15-17] and by peroxodisulfate in the presence of copper(II)[6] and silver(I).[7] Evidence for the existence of CO_2^- radical ions has been obtained in studies of γ-irradiated crystals of sodium formate[18] and carbon dioxide adsorbed on ultraviolet-irradiated magnesium oxide.[19]

A reasonable mechanism is postulated conforming to the observed kinetics.

Initiation

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^- \tag{1}$$

Propagation

$$SO_4^- + H_2O \xrightarrow{k_2} SO_4^{2-} + H^+ + OH \tag{2}$$

$$OH + C_2O_4^{2-} \xrightarrow{k_3} OH^- + CO_2^- + CO_2 \tag{3}$$

$$OH^- + H^+ \xrightarrow{k_4} H_2O \tag{4}$$

$$CO_2^- + S_2O_8^{2-} \xrightarrow{k_5} CO_2 + SO_4^- + SO_4^{2-} \tag{5}$$

Termination

$$CO_2^- + SO_4^- \xrightarrow{k_6} CO_2 + SO_4^{2-} \tag{6}$$

Using the usual steady-state approximation for the free-radical species SO_4^-, CO_2^-, and OH, and assuming that $(4k_1k_2/k_5k_6) >> (k_1/k_5)^2$, it may be shown that

$$-d[S_2O_8^{2-}]/dt = (k_1k_2k_5/k_6)^{1/2}[S_2O_8^{2-}] \tag{7}$$

The derived rate law conforms to the experimental rate law A and the experimental rate constant $k_I = (k_1k_2k_5/k_6)^{1/2}$. At 60.2° k_1 is 5×10^{-6} sec^{-1}, the rate constant of the thermal decomposition of peroxodisulfate as determined by Kolthoff and Miller.[10] At this temperature and under various conditions, k_I varied from about 25 to 250 times as large as k_1 suggesting that the average chain length varied in this range. Therefore, it follows that

$$(2k_I/k_1)^2 = \frac{4k_1k_2/k_5k_6}{(k_1/k_5)^2} \geq 2.5 \times 10^3$$

showing that the results are consistent with the inequality assumed in the derivation.

The sulfate radical ions could react with solvent water as postulated in reaction 2 and also with oxalate.

$$SO_4^- + C_2O_4^{2-} \xrightarrow{k_8} SO_4^{2-} + CO_2 + CO_2^- \tag{8}$$

Inclusion of reaction 8 in the postulated mechanism (reactions 1-6) yields a rate law of the same form as the

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experimental rate law only if it is assumed that $k_2 >> k_8[C_2O_4^{2-}]$, implying therefore that reaction 2 is more important than reaction 8.

The Arrhenius activation energy of the oxidation of oxalate by peroxodisulfate in oxygen-free solutions is 32.7 ± 0.8 kcal/mole. From the relationship between the experimental rate constant, k_I, and the individual rate constants appearing in rate law 7, it follows that $E_I = {}^1/_2(E_1 + E_2 + E_5 - E_6)$. The activation energy E_6 for the reaction involving two free radicals is estimated to be very small, $E_1 = 33.5$ kcal/mole,[10] and $E_5 = 7.4$ kcal/mole,[7] so that $E_2 = 24.5$ kcal/mole. Accordingly, reaction 2 should be fairly slow. This would lead to a relatively high steady-state concentration of sulfate radical ions, accounting for the importance of termination reaction 6.

In an earlier investigation[7] it was found that the activation energy for reaction 9 was 28.6 kcal/mole.

$$SO_4^- + Cu^{II}(C_2O_4)_2^{2-} \longrightarrow SO_4^{2-} + Cu^{III}(C_2O_4)_2^- \quad (9)$$

It was surprising to find that reaction 9 has a higher activation than reaction 2, for one would expect the contrary to be the case. A recalculation showed an error in the previous calculation; the corrected value is $E_9 = 23.5$ kcal/mole. This value is slightly less than E_2 and is thus more reasonable.[20] This is tantamount to saying that the oxidation of oxalate by sulfate radical ions (reaction 8) has a high activation energy requirement; in the presence of copper(II) there must be a reduction in the activation energy since copper(II) facilitates the electron-transfer process. Therefore, in the present studies, the oxidation of water by SO_4^- to generate OH radicals which propagate the chain is consistent with the fact that $E_8 >> E_2$.

As oxygen does not inhibit other reactions involving sulfate radical ions, such as the thermal decomposition of peroxodisulfate[10] and the thiosulfate–peroxodisulfate reaction,[21] it is probable that oxygen does not react with SO_4^-. It appears then that oxygen inhibition is caused by a species derived from the oxalate. Many reactions involving oxalate as the reducing agent are known to be inhibited by oxygen.[11–17] This is believed to occur through a reaction with CO_2^- with formation of a molecular complex or carbon peroxide

$$O_2 + CO_2^- \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} O_2CO_2^- \quad (10)$$

followed by a chain-terminating reaction

$$O_2CO_2^- + SO_4^- \xrightarrow{k_{11}} O_2 + CO_2 + SO_4^{2-} \quad (11)$$

By including reactions 10 and 11 together with reactions 1–6, assuming $k_{-10}[O_2CO_2^-] >> k_{11}[O_2CO_2^-][SO_4^-]$, long chain lengths, and the steady-state condition, it may be shown that

$$-d[S_2O_8^{2-}]/dt = \left(\frac{k_1k_2k_5}{k_6 + k_{10}k_{11}P/k_{-10}K_H}\right)^{1/2}[S_2O_8^{2-}] \quad (12)$$

where P is the partial pressure of oxygen and K_H is the Henry's law constant for oxygen. Equation 12 has the same form as the experimental rate law B. Other possible chain-terminating reactions involving CO_2^- or OH radicals do not lead to the experimental rate law, suggesting that reaction 11 is the important chain-terminating step. This is consistent with the previous energy calculation indicating that the steady-state concentration of sulfate radical ions in solution is relatively high.

The principal characteristics of the pH dependence shown in Figure 1 are a rapid increase of k_I as the pH increases from 0.55 to 4.5 followed by a rapid decrease of k_I as the pH increases to 10.25. The dependence of rate on pH is not typical of other reactions involving peroxodisulfate. For instance, Sorum and Edwards have reported that the thiosulfate–peroxodisulfate reaction is independent of pH from 4 to 10.5. Since $H_2S_2O_8$ is a strong acid, the species participating in the reaction over the pH range studied must be the peroxodisulfate ion. The acid-catalyzed peroxodisulfate decomposition at pH <2.0 apparently is not important since a reduction in rate at low pH is observed.

The pH dependence has the same general appearance as a curve showing the concentration of $HC_2O_4^-$ as a function of pH when total oxalate ($[H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$) is held constant. Thus one might conclude that $HC_2O_4^-$ is more reactive than either $H_2C_2O_4$ or $C_2O_4^{2-}$. However, there are two indications that this is not the correct explanation.

(1) The maximum rate of reaction occurs at about pH 4.5, but $[HC_2O_4^-]$ reaches its maximum at about pH 2.75. (The dissociation constants of oxalic acid at 25° are $pK_1 = 1.25$ and $pK_2 = 4.28$. The effect of temperature on the dissociation constants is small. At 60° $pK_2 = 4.45$.[22])

(2) The rate is zero order in oxalate, and oxalate is not a reactant in any of the steps (1, 2, 5, and 6) whose rate constants affect k_I.

It appears that the CO_2^- protonation reaction may be an important factor.

$$COOH \longrightarrow H^+ + CO_2^- \quad (13)$$

Husain and Hart[23] have studied the effect of pH on the carbon dioxide yield, $G(CO_2)$, in the chain radiolysis of dilute aqueous formic acid–hydrogen peroxide solutions. They observed a rapid rise of $G(CO_2)$ in the low pH range to a maximum at pH 4.4 and then a rapid drop in $G(CO_2)$ from pH 4.4 to 6.0, followed by a constant yield of CO_2 to pH 10. On the basis of their kinetic evidence, the pK of reaction 13 was estimated to be 2.5 ± 0.5. In an earlier study of the chain radiolysis of formic acid and peroxodisulfate, Hart[24] suggested that reaction 13 was responsible for the rapid decrease in $G(CO_2)$ between pH 5.1 and 7. Buxton and Wilmarth[25] indicated that protonation of CO_2^- occurs at pH <4. Keene, Raef, and Swallow[26] studied the recombination reaction of carboxyl radical as a function of ionic strength and using the Debye–Brønsted treatment showed that at pH 5 the radical was present as the ion with a − 1 charge.

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[20] The closeness of E_2 and E_9 implies that reaction 2 can be a chain-propagating step in the copper(II)-catalyzed reaction. In an alternate mechanism[6] SO_4^- radicals generate OH radicals (reaction 2), which then substitute for SO_4^-. This alternate mechanism also conforms to the rate law of the copper(II)-catalyzed reaction.

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The ionization of COOH radical could certainly explain the rapid increase in rate as pH increases from 0.55 to 4.5. From the midpoint of the left half of the curve in Figure 1, a pK value of 2.8 is determined for reaction 13 with the assumption that other factors are relatively unimportant in this region.

The explanation at high pH invoking the ionization of HO_2 radical to O_2^- radical[23] is not very likely in the uncatalyzed oxalate–peroxodisulfate reaction where there is no evidence that HO_2 is produced. There is no reason to believe that the phosphate buffer complicates the reaction at high pH since it is known to be not susceptible to attack by free radicals. Also, a few experiments at low pH where phosphate buffer was employed gave the same results as those in the absence of phosphate. All attempts to develop a sound explanation failed, and it seems likely that more than one factor contributes to the reduction in rate in the high pH range.

Many reactions exhibit specific salt effects, and in many instances the effects arise under conditions where ion pairing of the oppositely charged ions occurs in the reacting mixtures. The catalytic effect of added salts in the alkali metal ions is found to increase in the order $Li^+ < Na^+ < K^+$. To explain these effects, the concepts of ion pairing and the relative degree of hydration of the counterions are invoked.

In the present work, potassium and sodium ions are found to enhance the rate of oxidation of oxalate by peroxodisulfate with the former cation exerting a stronger effect. Reaction 6 is an electron-transfer process involving two reactive free-radical species, and it should not be affected by the presence of counterions. It is reasonable to assume that reaction 5 is subject to the catalytic effect of the cations. The alkali metal cations may reduce the unfavorable coulombic repulsion in reaction 5 by forming ion pairs with the anions. The stronger enhancement of the rate by K^+ than by Na^+ is likely due to the greater ability of K^+ to form ion pairs with the anions in solution.[27]

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The Crystal and Molecular Structure and the Solution Conformation of Dimethylgold(III) Hydroxide, an Inorganic Intermediate Ring Compound[1]

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Abstract: Dimethylgold(III) hydroxide has been found to be a tetrameric molecule in the crystalline state by three-dimensional X-ray crystal structure analysis and also in benzene solution by vapor pressure osmometry. There are 32 monomeric formula units in the orthorhombic unit cell in space group Pbca with $a = 19.35 \pm 0.03$, $b = 9.65 \pm 0.02$, and $c = 19.59 \pm 0.03$ Å. The gold, carbon, and oxygen atoms were located by Patterson and Fourier methods. The molecule consists of an eight-membered ring unlike that of any other known gold(III) compound. Gold achieves the expected square-planar coordination *via* bridging hydroxo oxygens, and the molecule has the approximate symmetry S_4. The final structure, with gold atoms refined by anisotropic least squares and with light atoms determined from Fourier maps, had a conventional R of 0.091. The mean bond lengths (with average deviations from the mean) are Au–C = 2.05 ± 0.08 Å and Au–O = 2.15 ± 0.12 Å. The rings stack together in columns; the short oxygen–oxygen contacts of 2.74 Å and the infrared spectrum both indicate strong intermolecular hydrogen bonding. These columns, in turn, pack together tightly to give a very compact structure. In solution, the molecule apparently is stereochemically rigid, and pmr measurements on solutions indicate that the two kinds of methyl groups required by the S_4 symmetry are still magnetically nonequivalent up to at least 94°. Strong axial interactions of the predominantly square-planar d^8 gold(III) may be responsible for the rigidity of the molecule in solution. This is supported by the observation that the dimethylgold(III) aquo ion behaves like a triprotic acid.

Recently, we reported the synthesis of dimethylgold(III) hydroxide.[4] The compound is only very slightly soluble in water but dissolves readily in aqueous acids and bases. The fact that it is moderately soluble in many organic solvents indicates a covalent structure. When this compound was first isolated, we assumed that it would have a symmetrical dimeric structure analogous to the dimethylgold(III) halides.[5] The organ ocompounds of gold(III) are similar in many of their reactions to organoplatinum(IV) compounds, and Morgan, Rennick, and Soong have presented evidence recently that $[(CH_3)_3PtCl]_4$ and $[(CH_3)_3Pt(OH)]_4$

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(4) M. G. Miles, G. E. Glass, and R. S. Tobias, *J. Am. Chem. Soc.*, **88**, 5738 (1966).

(5) See, for example, A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 884.