Table II. Summary of Known Fe(III) Species Water-Exchange Data

	k_1(25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol K)	A/h, MHz
$Fe(H_2O)_6^{3+}$	1.67×10^2	18.5	13.8	
$Fe(TMPyP)H_2O^{5+}$ [a]	7.8×10^5	13.8	14.7	24.9
$Fe(TPPS)H_2O^{3-}$ [a]	1.4×10^7	13.7	20.2	22.6
species 2	$2.6 \times 10^7/n_2$	8.5	$3.9/n_2$	$45.6/n_2$

[a] Reference 9.

as species 2 is disappearing by an additional reaction to form a third species of Fe(III), probably a higher oligomer.

The data in Figure 6 for $10^3/T < 3$ can be fit with the Swift–Connick equations in the form

$$Q_2 = \frac{Q_{2L1M}}{1 + (\Delta\omega_{M2})^2\tau_{M2}^2} \qquad (7)$$

$$T_{2p\bullet 2} = \frac{1}{n_2}\left(\frac{1}{(\Delta\omega_{M2})^2\tau_{M2}} + \tau_{M2}\right) \qquad (8)$$

where $1/T_{2M2} = 0$ and the subscript 2 refers to species 2. The solid lines in Figure 6 were calculated with $\Delta H_2^{\ddagger} = 8.5$ kcal/mol, $n_2(A_2/h) = 45.6$ MHz, $n_2\Delta S^{\ddagger} = 3.9$ eu, and $\tau_{M2}(25\ °C)/n_2 = 3.9 \times 10^{-8}$ s.

Evidently only the $(\Delta\omega_M)^2$ mechanism[5] is effective for broadening and T_{1e2} is so short that T_{2M2} is too long to be effective. The number of rapidly exchanging water molecules per Fe(III), n_2, is not known. Assuming $1 \leq n_2 < 6$, one concludes the water in species 2 exchanges faster than that in $Fe(H_2O)_6^{3+}$ by a factor of $(2-15) \times 10^4$ at 25 °C.

Discussion

Judkins considered $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, and $Fe_3(OH)_4^{5+}$ as possible contributors to the ^{17}O line broadening by Fe(III) in solutions containing 0.019–0.0986 M $HClO_4$. He estimated a water lifetime in the first coordination sphere of less than 1.5×10^{-6} s for $FeOH^{2+}$ and less than 5.8×10^{-7} s for $Fe_3(OH)_4^{5+}$. It is unlikely that any of these species can be identified as species 2 since they should not be stable in 1.5 M H^+ at 25 °C. In addition the shifts observed by Judkins are far too small for species 2 and his solutions showed no hysteresis effects lasting longer than 15 min. This conclusion is also supported by the relatively labile behavior of the μ-oxo iron(III) complexes.[6]

In the case of Cr(III) it has been shown that a dinuclear species is formed by O_2 oxidation of Cr^{2+} in perchloric acid[7,8] and that a mixture of polynuclear species is formed on boiling Cr(III) in $HClO_4$.[7] The μ-oxo or dihydroxo form has been postulated for the dinuclear species in this case.

In view of the above it is difficult to postulate a definite structure for species 2. It seems likely that it is a species formed in the early stages of hydrolysis of Fe(III) at high temperatures in acid, that oxo bridges are involved, that the enhanced water exchange is due to reduction of charge on the Fe(III), and that continued heating leads to higher oligomerization with eventual precipitation of the iron.

Table II summarizes what is known about water exchange on Fe(III) species. The A/h values would give $n_2 = 2$ assuming the hypothesis[3] of constant A/h is valid. The low activation enthalpy and entropy suggest considerable weakening of the iron–water bond.

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Catalytic Decomposition of Peroxymonosulfate in Aqueous Perchloric Acid by the Dual Catalysts Ag^+ and $S_2O_8^{2-}$ and by Co^{2+}

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Aqueous HSO_5^- is catalytically decomposed to O_2 and HSO_4^- by the dual catalysts Ag^+ and $S_2O_8^{2-}$. The rate law in acidic solution is $-d[HSO_5^-]/dt = k'[Ag^+]_0[S_2O_8^{2-}]_0$. Both oxygen atoms in the O_2 product are derived from the terminal peroxide oxygen in HSO_5^-. A chain mechanism of short chain length is proposed in which a HSO_5 intermediate is formed by the reaction of Ag^{2+} and HSO_5^-. HSO_5 rapidly decomposes in parallel, bimolecular paths which produce $O_2 + 2SO_4^-$ and $O_2 + S_2O_8^{2-}$, respectively. The slow step is the well-known reaction between Ag^+ and $S_2O_8^{2-}$. Aqueous Co^{2+} is also a catalyst for the decomposition of HSO_5^-. The rate law, in the presence of dilute Ag^+, is $-d[HSO_5^-]/dt = k_{Co^{2+}}[Co^{2+}]_0[HSO_5^-]$. A redox mechanism similar to that for the Ag^+, $S_2O_8^{2-}$ catalysis is proposed in which Co^{2+} and HSO_5^- replace Ag^+ and $S_2O_8^{2-}$, respectively. The kinetics are considerably more complicated in the absence of added Ag^+. Some probable requirements for efficient, simple catalysis of the decomposition of HSO_5^- are discussed.

Introduction

There have been numerous reports of catalysis of the decomposition of peroxymonosulfate[1] (eq 1). Examples of

$$2HSO_5^- \rightarrow 2HSO_4^- + O_2 \qquad (1)$$

catalysts include metal ions in both acidic and weakly basic solution,[2] traces of nitric acid in concentrated sulfuric acid,[3] and organic substrates such as ketones.[4] Few of these systems

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(1) A more systematic name for HSO_5^-, the predominant species in acidic solution ($pK_a \approx 9.3$), is hydrogen peroxosulfate. However, in this paper we shall yield to common usage.

(2) (a) Ball, D. L.; Edwards, J. O. *J. Am. Chem. Soc.* **1956**, *78*, 1125. (b) Goodman, J. F.; Robson, P. *J. Chem. Soc.* **1963**, 2872. (c) Ball, D. L.; Edwards, J. O. *J. Am. Chem. Soc.* **1958**, *80*, 343. (d) Csanyi, L. S.; Solymosi, F.; Szucs, J. *Naturwissenschaften* **1959**, *46*, 353. (e) Csanyi, L. S.; Domonkos, L. *Acta Chim. Acad. Sci. Hung.* **1962**, *34*, 383. (f) Mariano, M. H. *Anal. Chem.* **1968**, *40*, 1662. (g) Billing, W. H. O.; Bridgart, G. J.; Wilson, I. R. *Aust. J. Chem.* **1970**, *23*, 641.

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involve simple catalysis in that some net consumption of the "catalyst" is often observed. Many of these studies have been largely qualitative due in part to the complexity of the reactions. As a result our understanding of the mechanisms by which the catalytic decomposition of peroxymonosulfate occurs is quite limited.

We report in this paper two examples of true catalysis—by the dual catalysts Ag^+ and $S_2O_8^{2-}$ and by Co^{2+} in aqueous perchloric acid solution. A combination of kinetic, stoichiometric, and oxygen-18 tracer results allows us to reach some conclusions about the mechanisms involved.

Experimental Section

Reagents. Solutions of HSO_5^- were prepared from OXONE, kindly supplied by Du Pont. The formula given for this material is $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. We have found that the solid is contaminated with small amounts of $K_2S_2O_8$. Otherwise, OXONE has desirable properties. The solid is very stable, especially when stored in a refrigerator. Aqueous solutions are free of H_2O_2, a troublesome impurity present if HSO_5^- is prepared from concentrated sulfuric acid and hydrogen peroxide,[2g,3] concentrated hydrogen peroxide and chlorosulfonic acid,[2a] or the decomposition of peroxydisulfate in strongly acidic solution.[5] The potassium ion is largely removed through precipitation of $KClO_4$ if concentrated solutions are prepared in cold, aqueous perchloric acid.

Solutions of specifically labeled $O_3SOO^*H^-$ were prepared by the decomposition of $CsSO_4F$ in H_2O^* containing 1 M $HClO_4$. Under these conditions increased yields of $O_3SOO^*H^-$ and substantially less HOO^*H are obtained over those formed in dilute acid or in water.[6] In a typical preparation, 0.3 g of $CsSO_4F$ (1.2 mmol) were dissolved in 3.0 mL of 1 M $HClO_4$ in H_2O^*. After decomposition of the SO_4F^-, the solution contained 0.178 M HSO_5^- and 0.017 M H_2O_2. H_2O_2 was destroyed by addition of a slight excess of Ce(IV).

$CsSO_4F$ was prepared as described previously[6,7a] and contained 99.2% $CsSO_4F$ and 0.60% $Cs_2S_2O_8^{2-}$.[7b]

Cobaltous perchlorate was prepared from reagent grade cobaltous carbonate and perchloric acid and was recrystallized three times. Solutions of cobalt(III) perchlorate were prepared by electrolytic oxidation.

Lithium perchlorate was prepared from reagent grade lithium carbonate and perchloric acid and recrystallized three times. Sodium azide was recrystallized twice according to the procedure of Browne.[8]

Solutions of $VO(ClO_4)_2$ were prepared from commercial vanadyl sulfate by ion exchange.

All other chemicals were of reagent grade and were used without further purification. Deionized water was distilled before use, first from acid dichromate and then from alkaline permanganate.

Analytical Procedures. Solutions of HSO_5^- were analyzed iodometrically by reaction with iodide followed by titration with thiosulfate. The $[S_2O_8^{2-}]$ of these solutions was determined by difference after measuring $[HSO_5^-] + [S_2O_8^{2-}]$ by first allowing the reaction with 1 M I^- to proceed for 15 min at room temperature with oxygen excluded. Solutions of HSO_5^- containing appreciable $S_2O_8^{2-}$ were assayed for HSO_5^- by conducting the titration in dilute I^- promptly and at 0 °C; under these conditions the $S_2O_8^{2-}$ does not interfere.

Very dilute solutions of HSO_5^- were assayed by spectrophotometrically measuring I_3^- formed by adding aliquots to NaI solutions such that the final $[I^-]$ was 0.1 M. Under these conditions the $[I_2]$ is less than 1% that of the $[I_3^-]$. The average extinction coefficient determined at 353 mm was 2.52×10^4 M^{-1} cm^{-1}; the reported[9] $\epsilon_{I_3^-}$ is 2.64×10^4 M^{-1} cm^{-1}. Measurements were made promptly to minimize the slow additional growth of absorbance due to the $S_2O_8^{2-}$–I^- reaction. Co^{2+} present in the solutions analyzed by this procedure did not interfere.

Table I. Kinetic Results for the Ag^+–$S_2O_8^{2-}$-Catalyzed Decomposition of HSO_5^- [a]

$10^2 \times [HSO_5^-]_0$, M	$10^2 \times [Ag^+]_0$, M	$10^6 k$, M/s	$10^3 \times [S_2O_8^{2-}]_0$ (added), M	$10^2 k'$,[b] M^{-1} s^{-1}
3.30[c]	3.18	4.22		5.04
3.30	4.23	5.72		5.11
1.63	4.23	3.02		5.48
1.58	0.317	1.00	4.88	5.13
1.65	0.799	2.62	4.92	5.26
1.65[d]	0.788	2.28	4.43	5.03
3.07	0.391	2.31	9.43	4.97
			av	5.15 ± 0.13
3.47[e]	4.23	6.00		
1.66[f]	0.788	3.63	4.43	8.01
1.59[g]	0.788	1.36	4.43	3.00
1.63[h]	6.88	2.59		2.90
1.71[i]	1.63	2.41		10.8

[a] $[HClO_4] = 0.50$ M, $T = 17.0$ °C, $I = 0.63 \pm 0.03$ M unless otherwise indicated. [b] $k' = k/\{[Ag^+]_0(0.08[HSO_5^-]_0 + [S_2O_8^{2-}](\text{added}))\}$. [c] $AgNO_3$ used instead of $AgClO_4$. [d] 0.10 M $HClO_4$, $I = 0.60$ M ($LiClO_4$). [e] New sample of OXONE used. [f] 0.10 M $HClO_4$, $I = 0.20$ M. [g] 1.91 M $HClO_4$, $I = 2.01$ M. [h] $T = 10.0$ °C. [i] $T = 25.0$ °C.

Spectrophotometric assays were made for Co^{2+} ($\epsilon = 4.79$ M^{-1} cm^{-1} at 510 nm), Co^{3+} ($\epsilon = 34.5$ M^{-1} cm^{-1} at 602 nm, 265 M^{-1} cm^{-1} at 280 nm), VO^{2+} ($\epsilon = 17.1$ M^{-1} cm^{-1} at 762.5 nm), and VO_2^+ ($\epsilon = 145$ M^{-1} cm^{-1} at 350 nm).

Kinetic Procedures. The Ag^+–$S_2O_8^{2-}$- and Co^{2+}-catalyzed decompositions of HSO_5^- were monitored by measuring the $[HSO_5^-]$ at appropriate times. The reactions were carried out in a thermostated glass vessel wrapped with aluminum foil to exclude light. The possible influence of light on the reaction rates were not investigated.

The Ag^+-catalyzed oxidation of VO^{2+} by $S_2O_8^{2-}$ was monitored spectrophotometrically by measuring the formation of VO_2^+. A Zeiss PMQ 11 spectrophotometer equipped with a rapid mixing, thermostated sample compartment was used.

All glassware was thoroughly cleaned, copiously rinsed with deionized water, and baked at 150 °C before use.

Oxygen-18 Tracer Experiments. The experiments were carried out by placing the reagents in separate legs of a vessel shaped like an inverted Y, evacuating the vessel, outgassing the solutions, and mixing. After the reaction had proceeded nearly to completion, the evolved gas was removed, and its molecular and isotopic compositions were determined by mass spectrometry, using a Consolidated Model 21-260 mass spectrometer. These experiments were performed by Dr. Evan H. Appelman, Chemistry Division, Argonne National Laboratory.

Results

Catalytic Decomposition of HSO_5^- by the Dual Catalysts Ag^+ and $S_2O_8^{2-}$. The rate of decomposition of HSO_5^- in 0.50 M perchloric acid is very slow at room temperature. The decomposition rate is markedly enhanced by the presence of moderate concentrations of silver(I). Plots of $[HSO_5^-]$ vs. time were strictly linear for at least 90% of the total reaction, in accordance with rate expression 2. However, the value of the

$$-d[HSO_5^-]/dt = k \qquad (2)$$

pseudo-zero-order rate constant was found to decrease with a decrease in the initial peroxymonosulfate concentration. This behavior is suggestive of the action of a second catalyst present in the peroxymonosulfate stock solutions. Analysis of the OXONE used as the source of HSO_5^- showed the presence of 9 ± 2% $S_2O_8^{-2}$ (% ≡ $10^2[S_2O_8^{2-}]/[HSO_5^-]$). Titrations of the spent reaction mixtures of HSO_5^- and Ag^+ revealed that the $[S_2O_8^{2-}]$ initially introduced with HSO_5^- was unchanged within experimental uncertainty. Additional kinetic experiments were performed with varying concentrations of Ag^+ and added $S_2O_8^{2-}$. Each of these experiments again obeyed pseudo-zero-order kinetics. Values of the rate parameter k obtained in this study over a range of experimental data are summarized in Table I.

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Table II. Kinetic Results for the Ag^+-Catalyzed Oxidation of VO^{2+} by $S_2O_8^{2-}$ [a]

T, °C	I, M	10^3k_1,[b] $M^{-1}\ s^{-1}$	k_4/k_5[c]
25.0	0.65	5.04	9.7
17.0	0.65	2.63	8.8
17.0	2.05	1.80	7.3
10.0	0.65	1.51	8.6

[a] Conditions: $[VO^{2+}]_0 = 1.14 \times 10^{-2}$ M, $[S_2O_8^{2-}]_0 = 1.82 \times 10^{-3}$ M, $[Ag^+]_0 = 0.0948$–0.181 M, and $[HClO_4] = 0.402$–1.88 M. [b] Reaction monitored by following appearance of VO_2^+ at 350 mm. Values of $k_1 = k_{obsd}/[Ag^+]_0$, where k_{obsd} was obtained from the slope of plots of $\ln (A_\infty - A_t)$ vs. time. [c] Values obtained from the expression $k' = k_1[(2k_4 + 2k_5)/k_5]$, with use of the appropriate values of k' from Table I.

The data were analyzed in terms of the postulated rate expression (3). The fraction of $S_2O_8^{2-}$ initially present in the

$$-d[HSO_5^-]/dt = k'[Ag^+]_0[S_2O_8^{-2}]_0 \qquad (3)$$

HSO_5^- stock solutions was left as an unknown ($f \equiv [S_2O_8^{2-}]_0/[HSO_5^-]_0$). The best value of f was determined to be 0.080 by solving expression 4 by an iterative procedure.

$$k = k'[Ag^+]_0(f[HSO_5^-]_0 + [S_2O_8^{2-}]_{added}) \qquad (4)$$

This value is in satisfactory agreement with the titrimetric result. Values of k' are listed in the last column of Table I. The constancy of these values for the first seven experiments indicates that the rate expression (3) adequately correlates the kinetic results.

This analysis requires *both* Ag^+ and $S_2O_8^{2-}$ to function as true catalysts in this system. While Ag^{2+} was never detected during the kinetic experiments, its characteristic brown color and ultraviolet absorption developed in the "spent" reaction mixtures after complete decomposition of HSO_5^-.

These observations coupled with the gas analysis (vide infra) demonstrate that the net stoichiometry for the decomposition is

$$2HSO_5^- \xrightarrow[S_2O_8^{2-}]{Ag^+} O_2 + 2HSO_4^- \qquad (5)$$

All the results in Table I except the eighth experiment were obtained by using a 2 year old sample of OXONE that was stored at 5 °C. The ratio mmol of HSO_5^-/g was 2.63. A newly acquired sample with the same ratio equal to 2.85 was used in the eighth experiment. The kinetic result was identical with that obtained with use of the older sample on the assumption that the $S_2O_8^{2-}$ content was 7.9% that of the HSO_5^- (titrimetric value = 8%).

Silver(I) is a catalyst in many oxidations by peroxydisulfate.[10] We have determined the value of k_1 for rate expression 6 for our experimental conditions in a brief reinvestigation of the silver(I)-catalyzed oxidation of oxovanadium(IV) by peroxydisulfate.[11] The results are summarized in Table II.

$$-d[S_2O_8^{2-}]/dt = k_1[Ag^+][S_2O_8^{2-}] \qquad (6)$$

The rate parameter k_1 has been found previously to be independent of the hydrogen ion concentration but to decrease with increasing ionic strength.[10] These features are also observed for k', the rate parameter for the Ag^+, $S_2O_8^{2-}$ catalyzed decomposition of HSO_5^-.

Catalytic Decomposition of HSO_5^- by Co^{2+}. Cobalt(II) is also a catalyst for the decomposition of peroxymonosulfate. Cobalt(III) was not observed spectrophotometrically during the decomposition ($[Co^{3+}]_{max} < 1\%\ [HSO_5^-]_0$). Nevertheless, a redox process is indicated by the general observation that added Co^{3+} markedly enhances the reaction rate. Unlike the Ag^+ system, the rate is not influenced by dilute $S_2O_8^{2-}$.

Table III. Kinetic Results for the Co^{2+}-Catalyzed Decomposition of HSO_5^- in the Presence of Ag^+ [a]

$10^3 \times [HSO_5^-]_0$, M	$[Co^{2+}]$, M	$10^3 \times [Ag^+]$, M	$[HClO_4]$, M	T, °C	$10^4 \times$ (slope),[b] s^{-1}	$10^3k_{Co^{2+}}$,[c] $M^{-1}\ s^{-1}$
0.891	0.197	1.98	1.95	17.0	8.48	4.30
0.891	0.0985	1.98	1.99	17.0	4.56	4.63
0.891	0.0985	0.793	2.01	17.0	4.28	4.34
0.891	0.0394	1.98	2.01	17.0	1.99	5.05
2.06	0.0389	1.96	2.00	17.0	2.00	5.14
9.89	0.0382	1.92	2.03	17.0	1.83	4.79
30.7	0.0382	9.62	2.03	17.0	(2.32)[d]	(6.07)[d]
2.12	0.0390	1.94	1.02	17.0	3.29	8.43
2.12	0.0390	1.94	2.05	9.0	0.706	1.81
2.12	0.0390	1.94	1.02	9.0	1.19	3.06
2.12	0.0390	1.94	0.554	9.0	2.02	5.19
2.12	0.0390	1.94	0.260	9.0	4.07	10.4
2.12	0.0390	1.94	2.05	25.0	4.98	12.8

[a] $I = 2.0$ M ($LiClO_4$). [b] Obtained from plot of $\ln [HSO_5^-]$ vs. t. [c] $k_{Co^{2+}}$ = slope/$[Co^{2+}]$. [d] The rate of the Ag^+–$S_2O_8^{2-}$ reaction is not negligible; kinetic plot curved upward after ca. 60% reaction. Entry is slope of linear portion.

The kinetics of the reaction are simplified if Ag^+ is also present under conditions where its reaction with $S_2O_8^{2-}$ introduced with HSO_5^- is negligible or nearly so. Excellent pseudo-first-order plots of $\ln [HSO_5^-]$ vs. time for at least 85% of total reaction were obtained over a modest range of initial concentrations and temperature. Values of the slopes of these plots are summarized in Table III. Values of $k_{Co^{2+}}$, appropriate to expression 7 are approximately constant. We will argue later that the role of Ag^+ in this reaction is to scavenge sulfate radicals, SO_4^-. At the lowest Ag^+ concentration tested, there is a slight decrease in $k_{Co^{2+}}$; at the highest concentration the Ag^+–$S_2O_8^{2-}$ reaction is no longer negligible, and the value of the rate parameter increases.

$$-d[HSO_5^-]/dt = k_{Co^{2+}}[HSO_5^-][Co^{2+}]_0 \qquad (7)$$

The hydrogen ion dependence of the rate parameter was briefly examined at 9.0 °C. A plot of $k_{Co^{2+}}$ vs. $1/[H^+]$ was linear, with a slope of $2.56 \times 10^{-3}\ s^{-1}$ and an intercept of $5.5 \times 10^{-4}\ M^{-1}\ s^{-1}$. This result indicates that the reaction rate is predominantly inverse first order with respect to the hydrogen ion concentration.

The kinetic behavior of the Co^{2+}-catalyzed decomposition of HSO_5^- is considerably more complicated in the absence of added Ag^+. We do not have a very complete understanding of this system at the present time. Some of the experimental data are summarized in Table IV.

In the first 12 experiments the ratio $[Co^{2+}]_0/[HSO_5^-]_0$ was varied from 0.014–18. Kinetic plots of $\ln [HSO_5^-]$ vs. time usually exhibited what we take as a brief induction period (up to ca. 15% total reaction) followed in all cases by a linear region extending to 90% total reaction. The values of $k'_{Co^{2+}}$ calculated from expression 8 are approximately 40% less than the values of $k_{Co^{2+}}$ obtained under comparable conditions but with added Ag^+. Otherwise, the major features of the reactions are quite similar, including a predominantly inverse first-order hydrogen ion dependence. However, at higher Co^{2+} concentrations than those listed in Table IV, the first-order plots curve upward throughout the reaction. For example, this feature was observed for an experiment with 0.0989 M Co^{2+} but otherwise identical with the third entry.

$$-d[HSO_5^-]/dt = k'_{Co^{2+}}[HSO_5^-][Co^{2+}]_0 \qquad (8)$$

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Table IV. Kinetic Results for the Co^{2+}-Catalyzed Decomposition of HSO_5^-

$[HSO_5^-]_0$, M	$[Co^{2+}]_0$, M	$[HClO_4]$, M	I, M	T, °C	10^4(slope),[a] s^{-1}	$10^2k'_{Co^{2+}}$,[b] $M^{-1}\ s^{-1}$
2.12×10^{-3}	3.90×10^{-2}	0.260	2.0	9.0	2.44	0.627
2.12×10^{-3}	1.95×10^{-2}	0.260	2.0	9.0	1.22	0.625
5.00×10^{-3}	3.98×10^{-2}	1.96	2.0	17.0	1.09	0.274
5.00×10^{-3}	3.98×10^{-2}	0.680	2.0	17.0	3.16	0.794
5.00×10^{-3}	3.90×10^{-2}	0.65	2.0	17.0	(0.67)[c]	(0.17)[c]
5.00×10^{-3}	1.51×10^{-2}	0.393	2.0	17.0	1.65	1.09
5.00×10^{-3}	4.53×10^{-3}	0.106	2.0	17.0	1.92	4.24
1.00×10^{-2}	5.14×10^{-2}	0.521	0.68	17.0	8.48	1.65
5.39×10^{-2}	1.31×10^{-2}	0.506	0.55	17.0	1.76	1.34
2.70×10^{-3}	1.31×10^{-2}	0.506	0.55	17.0	1.58	1.21
1.11×10^{-2}	4.15×10^{-3}	0.503	0.52	17.0	4.19	1.01
4.74×10^{-2}	6.55×10^{-4}	0.500	0.50	39.8	1.04	15.9

$[HSO_5^-]_0$, M	$[Co^{2+}]_0$, M	$[HClO_4]$, M	I, M	T, °C	10^4(slope),[d] s^{-1}	10^2(slope)/ $([HSO_5^-]_0 \times [Co^{2+}]_0)^{1/2}$
4.12×10^{-4}	1.96×10^{-1}	2.0	2.6	17.0	4.0	4.5
4.12×10^{-4}	1.96×10^{-1}	2.0	2.6	17.0	4.0[e]	4.5
8.06×10^{-4}	1.96×10^{-1}	2.0	2.6	17.0	4.8	3.8
4.12×10^{-4}	7.85×10^{-2}	2.0	2.2	17.0	1.8	3.2
1.68×10^{-4}	1.97×10^{-1}	2.0	2.6	17.0	3.4	5.9

[a] Obtained from the plot of ln $[HSO_5^-]$ vs. t. [b] $k'_{Co^{2+}} = \text{slope}/[Co^{+2}]_0$. [c] 2.01×10^{-3} M HN_3 added. [d] From the plot of ln $[(2[X_0(X_0 - X)]^{1/2} - X + 2X_0)/X]$ vs. t, where $X = [HSO_5^-]$. [e] 8.0×10^{-5} M HSO_5^- added to Co^{2+} solution; kinetic experiment listed was initiated ca. 24 h later.

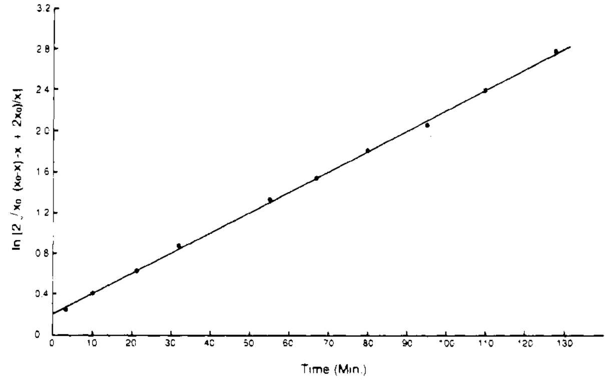

Figure 1. Kinetic plot of ln $[(2[X_0(X_0 - X)]^{1/2} - X + 2X_0)/X]$ vs. time. Conditions: $[HSO_5^-]_0 = 1.68 \times 10^{-4}$ M, $[Co^{2+}]_0 = 0.197$ M, $[HClO_4] = 2.0$ M, $T = 17.0$ °C.

It should be noted that the presence of HN_3 markedly reduces the reaction rate but does not alter the form of the rate law. In the fifth entry of Table IV, HN_3 would competitively reduce traces of Co^{3+} generated during the reaction ($k = 15$ $M^{-1}\ s^{-1}$ under the experimental conditions[12]) and presumably other oxidizing intermediates such as SO_4^- but not significantly reduce the HSO_5^- ($k = 1.6 \times 10^{-5}$ $M^{-1}\ s^{-1}$ under the experimental conditions).[13]

Quite different kinetic profiles are observed at large values of the ratio $[Co^{2+}]_0/[HSO_5^-]_0$. The last five entries summarize results obtained when this ratio was varied from 190–1200. The unusual kinetic behavior does not appear to arise from trace impurities in the Co^{2+} solutions, since the use of such solutions that had been "pretreated" with HSO_5^- yielded identical results. The simplest rate expression we have found that allows a preliminary kinetic analysis is

$$-d[HSO_5^-]/dt \propto [HSO_5^-]([HSO_5^-]_0 - [HSO_5^-])^{1/2} \qquad (9)$$

Integration gives expression 10 where $X = [HSO_5^-]$. The

$$\ln [(2[X_0(X_0 - X)]^{1/2} - X + 2X_0)/X] = t(\text{slope}) \qquad (10)$$

appropriate plots were reasonably linear, as indicated in Figure 1. Values of the slopes of these plots are listed in Table IV.

Table V. Oxygen-18 Tracer Results for the Catalyzed Decomposition of HSO_5^- at 25 °C

	atom % ^{18}O			
reacn solution	solvent enrichment[a]	$O_3SOO^*H^-$ enrichment[b]	O_2 enrichment	n[c]
0.028 M HSO_5^- 0.0145 M $Co(ClO_4)_2$ 0.23 M $HClO_4$	1.566	0.203	0.213	1.97[d]
0.076 M HSO_5^- 0.0008 M $Co(ClO_4)_2$ 0.5 M $HClO_4$	0.770	1.527	1.476	1.92
0.00356 M HSO_5^- 0.20 M $Co(ClO_4)_2$ 0.5 M $HClO_4$	0.299	1.527	1.477	1.92
0.0304 M HSO_5^- 0.012 M $S_2O_8^{2-}$ 0.0042 M $AgClO_4$ 0.5 M $HClO_4$	0.429	1.527	1.485	1.94

[a] Normal oxygen (in HSO_5^-, H_2O, and O_2) is taken as 0.203 atom % ^{18}O. [b] $O_3SOO^*H^-$ was prepared by the decomposition of SO_4F^- in H_2O^* containing 1 M $HClO_4$. The enrichment of the terminal peroxide oxygen of the HSO_5^- product was taken to be that of the H_2O^*.[6] [c] Number of terminal peroxide oxygen atoms per O_2 molecule. [d] By itself, this experiment only shows that 0.015 solvent oxygen atoms are present per O_2 molecule. However, the set of results demonstrates that little, if any, HSO_5^- oxygen atoms other than at the terminal peroxide position are incorporated into the O_2 product.

Oxygen-18 Tracer Experiments. As mentioned earlier, the catalyzed decompositions of peroxymonosulfate investigated in this study yield dioxygen. The isotopic composition of this product was determined in several oxygen-18 tracer experiments. The results are summarized in Table V. The recent availability[6] of $O_3SOO^*H^-$ greatly simplifies the interpretation. The major conclusion that may be drawn is that under all conditions tested the predominant source of both oxygen atoms in the O_2 product is the terminal peroxide oxygen in HSO_5^-, as summarized by reaction 11.

$$2O_3SOO^*H^- \rightarrow O^*O^* + 2HSO_4^- \qquad (11)$$

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(12) Murmann, R. K.; Sullivan, J. C.; Thompson, R. C. *Inorg. Chem.* **1968**, *7*, 1876.

(13) Thompson, R. C.; Wieland, P.; Appelman, E. H. *Inorg. Chem.* **1979**, *18*, 1974.

Discussion

The experimental results obtained for the catalytic decomposition of HSO_5^- by Ag^+ and $S_2O_8^{2-}$ impose severe constraints on the mechanisms that may be proposed. Both Ag^+ and $S_2O_8^{2-}$ are true catalysts in this reaction. The rate law has been determined, and the oxygen product has been found to contain primarily terminal peroxide oxygen from HSO_5^-. We propose the mechanism (12)–(16) to account for these observations. If the steady-state approximation is applied to the concentrations of Ag^{2+}, SO_4^-, and HSO_5, rate law 17 is obtained, in agreement with the experimentally determined expression. The mechanism preserves a constant $[Ag^+]$ and $[S_2O_8^{2-}]$, a required feature if these ions are to function as catalysts.

$$Ag^+ + S_2O_8^{2-} \xrightarrow{k_1} Ag^{2+} + SO_4^- + SO_4^{2-} \qquad (12)$$

$$Ag^+ + SO_4^- \xrightarrow{k_2} Ag^{2+} + SO_4^{2-} \qquad (13)$$

$$Ag^{2+} + HSO_5^- \xrightarrow{k_3} Ag^+ + HSO_5 \qquad (14)$$

$$2HSO_5 \xrightarrow{k_4} O_2 + 2SO_4^- + 2H^+ \qquad (15)$$

$$2HSO_5 \xrightarrow{k_5} O_2 + S_2O_8^{2-} + 2H^+ \qquad (16)$$

$$-d[HSO_5^-]/dt = k_1[(2k_4 + 2k_5)/k_5][Ag^+]_0[S_2O_8^{2-}]_0 \qquad (17)$$

The first two reactions have considerable precedent,[10] and the second is consistent with the observation that silver(I) appears to be an excellent scavenger for sulfate radicals.[14] The third reaction is in harmony with our observation that Ag^{2+} causes immediate formation of O_2 when added to HSO_5^- solutions. HSO_5 (or SO_5^-) has been proposed previously as a product of reactions 18 and 19,[15] as an intermediate in the photolytic decomposition of peroxydisulfate[16] and in the reaction between cerium(IV) and peroxymonosulfate.[2g] The oxygen formed in reactions 15 and 16 of the proposed mechanism is consistent with the oxygen-18 tracer results provided only the terminal oxygen in each HSO_5 molecule is incorporated into the O_2 product. The strength of the S–O bond presumably precludes bond breaking at the sulfur, leading to bimolecular decomposition of HSO_5. This situation is in sharp contrast to hydrogen peroxide chemistry, where oxygen formation invariably incorporates *both* oxygen atoms originally present in the peroxide moiety.[17]

$$OH + HSO_5^- \rightarrow OH^- + HSO_5 \quad (\text{or } SO_5^-) \qquad (18)$$

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad (19)$$

The most unusual feature of the proposed mechanism is the competitive mode of decomposition of HSO_5.[26] The scheme implies that $S_2O_8^{2-}$ is either formed within the cage or the SO_4^- radicals escape and react with Ag^+. Replacement of reaction 16 with eq 20 can be ruled out on the basis of the resulting rate expression. Similarly, reaction 21 cannot be substituted for reaction 15. However, adding reaction 22 to the proposed mechanism does not alter the derived rate law.

$$2SO_4^- \rightarrow S_2O_8^{2-} \qquad (20)$$

$$HSO_5 + HSO_5^- \rightarrow O_2 + SO_4^- + HSO_4^- + H^+ \qquad (21)$$

$$SO_4^- + HSO_5^- \rightarrow HSO_5 + SO_4^{2-} \qquad (22)$$

If we accept the mechanism, the ratio k_4/k_5 can be calculated from the values of k' and k_1. The values of k_4/k_5 are listed in the last column of Table II and are approximately constant. This feature is not inconsistent with the assumption that the ratio should be relatively insensitive to temperature and medium effects. The mechanism may be interpreted as a chain reaction of short chain length, in that approximately 20 HSO_5^- ions are decomposed for each reaction of Ag^+ and $S_2O_8^{2-}$.

The cobalt(II)-catalyzed decomposition of peroxymonosulfate is much more complicated, and at present we can only reach some tentative mechanistic conclusions. However, some of the salient features of the Ag^+, $S_2O_8^{2-}$ catalyzed reaction should be operative, but $S_2O_8^{2-}$ inadvertantly introduced with HSO_5^- should play a negligible or at least minor role. Let us first consider the Co^{2+} catalysis under conditions where Ag^+ has been added to minimize any Ag^+–$S_2O_8^{2-}$ reaction.[18] We tentatively propose the reaction scheme (23)–(30). The rapid equilibrium (23) is included to account for the observed predominantly inverse first-order hydrogen ion dependence but is assumed to lie far to the left. Applying the steady-state approximation to the $[Co^{3+}]$, $[Ag^{2+}]$, $[SO_4^-]$, and $[HSO_5]$ leads to the derived rate equation (31). This expression is identical in form with that observed experimentally. The rate law is analogous to that proposed for the Ag^+, $S_2O_8^{2-}$ catalysis, with Co^{2+} and HSO_5^- replacing Ag^+ and $S_2O_8^{2-}$, respectively.

$$Co^{2+} + HSO_5^- \overset{K}{\rightleftharpoons} CoSO_5 + H^+ \qquad (23)$$

$$CoSO_5 \xrightarrow{k_a} CoO^+ + SO_4^- \qquad (24)$$

$$CoO^+ + 2H^+ \rightarrow Co^{3+} + H_2O \qquad (25)$$

$$Co^{3+} + HSO_5^- \xrightarrow{k_b} Co^{2+} + HSO_5 \qquad (26)$$

$$Ag^+ + SO_4^- \xrightarrow{k_2} Ag^{2+} + SO_4^{2-} \qquad (27)$$

$$Ag^{2+} + Co^{2+} \xrightarrow{k_c} Ag^+ + Co^{3+} \qquad (28)$$

$$2HSO_5 \xrightarrow{k_4} O_2 + 2SO_4^- + 2H^+ \qquad (29)$$

$$2HSO_5 \xrightarrow{k_5} O_2 + S_2O_8^{2-} + 2H^+ \qquad (30)$$

$$-d[HSO_5^-]/dt = k_a(K/[H^+])([2k_4 + 2k_5]/k_5)[Co^{2+}]_0[HSO_5^-] \qquad (31)$$

Inclusion of the addition reactions (32) and (33) does not alter eq 31. Reaction 28 is known to be rapid.[19]

$$Ag^{2+} + HSO_5^- \rightarrow Ag^+ + HSO_5 \qquad (32)$$

$$Co^{2+} + SO_4^- \rightarrow Co^{3+} + SO_4^{2-} \qquad (33)$$

The role of Ag^+ in this scheme is primarily to scavenge SO_4^- radicals. Our previous results[14] indicate that Ag^+ is a much more efficient SO_4^- scavenger than Co^{2+}.

The interpretation of the Co^{2+} catalysis without added Ag^+ is more complicated and rather unsatisfactory. We suggest that the major perturbation in most of our experiments is the alternative reaction (eq 34) of the sulfate radical (other than

$$2SO_4^- \rightarrow S_2O_8^{2-} \qquad (34)$$

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(14) (a) Thompson, R. C.; Appelman, E. H., to be submitted for publication. (b) The rate constant for reaction 13 has been estimated to be 3 × 10^9. See: Walling, C.; Camaioni, D. M. *J. Org. Chem.* **1978**, *43*, 3266.

(15) (a) Roebke, W.; Renz, M.; Henglein, A. *Int. J. Radiat. Phys. Chem.* **1969**, *1*, 29. (b) Hayon, E.; Treinen, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47. (c) Maruthamuthu, P.; Neta, P. *J. Phys. Chem.* **1977**, *81*, 937.

(16) Tsao, M.; Wilmarth, W. K. *J. Phys. Chem.* **1959**, *63*, 346.

(17) (a) Cahill, A. E.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 2312. (b) Anbar, M. *J. Am. Chem. Soc.* **1961**, *83*, 2031.

(18) Solutions of HSO_5^- free of $S_2O_8^{2-}$ can be prepared but are contaminated with small amounts of H_2O_2. We have chosen to accept the $S_2O_8^{2-}$ impurity rather than cope with the complications arising from the presence of H_2O_2.

(19) Huchital, D. H.; Sutin, N.; Warnqvist, B. *Inorg. Chem.* **1967**, *6*, 838.

reaction 33). This reaction cannot have a major stoichiometric significance, as the magnitude of $[S_2O_8^{2-}]_\infty - [S_2O_8^{2-}]_0$ is approximately what would be anticipated as a result of reaction 30. However, a small participation of reaction 34 could have a significant kinetic influence. The brief induction period observed may be due to a buildup of the steady-state concentration of Co^{3+}. A small decrease in this steady-state concentration relative to that maintained in the presence of Ag^+ would account for the lower values of $k'_{Co^{2+}}$ for the first 12 experiments in Table IV compared to $k_{Co^{2+}}$.

Quite different kinetic profiles are exhibited by the last five experiments in Table IV, in which a very large $[Co^{2+}]_0/[HSO_5^-]_0$ ratio was used. We cannot quantitatively account for this behavior, but a crude qualitative interpretation gives some insight. We suggest that, while the $[Co^{3+}]$ is undetectably low during the reaction, it continuously builds up as the reaction proceeds. If we make the obviously nonrigorous approximations of

$$d[Co^{3+}]/dt = k_a[Co^{2+}]_0[HSO_5^-] \qquad (35)$$

$$-d[HSO_5^-]/dt = k_b[Co^{3+}][HSO_5^-] \qquad (36)$$

where k_a and k_b refer to reactions 24 and 26, respectively, expression 37 can be derived. This equation is identical in form

$$-d[HSO_5^-]/dt = (2k_ak_b[Co^{2+}]_0)[HSO_5^-]([HSO_5^-]_0 - [HSO_5^-])^{1/2} \qquad (37)$$

with expression 9, which does correlate the kinetic data for each individual experiment. Integration of eq 37 identifies the slope in eq 10 as $(2k_ak_b[Co^{2+}]_0[HSO_5^-]_0)^{1/2}$. Qualitatively, this treatment lends some support to the suggestion that the unusual kinetic behavior derives in part from a continuous, but very low, buildup of Co^{3+}. Quantitatively, the scheme fails as would be anticipated from the gross approximations made.[20] This failure can be clearly seen by the inconsistent values of the quantity slope/$([HSO_5^-]_0[Co^{2+}]_0)^{1/2}$ listed in the last column of Table IV.

Considerable information is available concerning the uncatalyzed decomposition of peroxymonosulfate. The kinetics are second order over the pH range 6–12, with a maximum rate at a pH of 9.3, the pK_a of HSO_5^-.[2a,b] Predominantly terminal peroxide oxygen is incorporated into the O_2 product.[21] In strongly acidic solution the decomposition instead yields H_2O_2, with both oxygen atoms originating from the peroxide moiety in HSO_5^-.[22] However, we have found that in acidic solutions containing certain metal ion catalysts neither of these modes of decomposition are competitive, and instead a redox process is operative. The metal ion must be oxidized, by either HSO_5^- or a $S_2O_8^{2-}$ impurity. The metal ion must be a weak reducing agent to serve as an effective catalyst, since its oxidized form must be capable of forming HSO_5 from HSO_5^-. The bimolecular decomposition of the HSO_5 intermediate then partially sustains the chain decomposition of HSO_5^-.

Conceivably, catalysis by some metal ions may not involve radical species formed through a redox process. However, this mode of catalysis has not been demonstrated to date.[23]

It will be interesting, when more data are available, to compare the 1-equiv, redox catalysis of the decomposition of peroxymonosulfate and hydrogen peroxide.[24] We anticipate that thermodynamic differences will be important. The standard free energies of the HSO_5^-–HSO_5 and HSO_5–O_2 couples are probably less favorable than for the H_2O_2–HO_2 and HO_2–O_2 couples.[25] Consequently, not only does the oxidized form of the catalyst presumably need to be a more potent oxidant for efficient catalysis of HSO_5^- decomposition but also oxidation of HSO_5 may be a rare event relative to bimolecular decomposition as proposed in this communication.

Acknowledgment. We thank Dr. Evan H. Appelman for carrying out the oxygen-18 tracer experiments and Mrs. A. G. Engelkemeir for mass spectrometric analysis of the O_2 samples.

Registry No. HSO_5^-, 12188-01-1; O_3S–O–O^*–H^-, 76282-18-3; Ag^+, 14701-21-4; $S_2O_8^{2-}$, 15092-81-6; Co^{2+}, 22541-53-3; VO^{2+}, 20644-97-7; $CsSO_4F$, 70806-67-6.

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(20) Even modest refinements in the analysis lead to very cumbersome equations. While the equations can be solved, the extensive number of adjustable parameters that would be required to test our data causes the exercise to be unwarranted.

(21) Koubek, E.; Levey, G.; Edwards, J. O. *Inorg. Chem.* **1964**, *3*, 1331.

(22) Bunton, C. A.; Llewellyn, D. R. *Research* (*London*) **1952**, *5*, 142.

(23) A debate on just this point has arisen over the enhanced rate of decomposition of HSO_5^- in the presence of cerium(IV) in sulfuric acid solution. See ref 2d,e,g. The argument presented by Wilson et al. for a radical process appears to be more persuasive to us.

(24) For a recent review of the Fe^{3+}-catalyzed decomposition of H_2O_2 and of "Fenton's Reagent", see: Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

(25) This prediction is based on available standard electrode potentials. The value of $E°$ for the couple $HSO_4^- + H_2O = HSO_5^- + 2H^+ + 2e^-$ is listed as −1.44 V on the Du Pont data sheet for OXONE. However, a more recent estimate of this potential is −1.75 V. See: Spiro, M. *Electrochim. Acta* **1979**, *24*, 313.

(26) A reviewer pointed out that the self-reaction of tertiary alkylperoxy radicals is quite similar to what we are proposing for HSO_5. See, for example: Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 42.