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Chain Lengths in the Decomposition of Peroxomonosulfate Catalyzed by Cobalt and Vanadium. Rate Law for Catalysis by Vanadium

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The loss of active oxygen from peroxomonosulfate ion $HOOSO_3^-$ in the presence of cobalt and vanadium (separately) has been followed. The rate law for the cobalt-catalyzed decomposition $-d[HOOSO_3^-]/dt = k_{Co}\{[HOOSO_3^-][Co^{2+}]/[H^+]\}$ has been extended up to pH 6. For the vanadium-catalyzed decomposition the rate law $-d[HOOSO_3^-]/dt = k_V\{[HOOSO_3^-][VO_2^+][H^+]\}$ has been determined. Concurrent with the decrease in $HOOSO_3^-$ is formation of small amounts of peroxodisulfate $S_2O_8^{2-}$, presumably a termination product. From the ratio of $HOOSO_3^-$ lost to $S_2O_8^{2-}$ formed, chain lengths for the two decompositions were calculated; the values obtained are similar to those found for other $HOOSO_3^-$ decompositions. Related mechanisms are postulated, and the rate constant ratio of one propagation step (k_4) to the termination step (k_5) is found to be near 8.5 for decomposition sequences under a variety of conditions.

Introduction

In the decomposition of peroxomonosulfate $HOOSO_3^-$

$$2HOOSO_3^- \rightarrow 2HSO_4^- + O_2$$

induced by Ce(IV) and by the $Ag^+/S_2O_8^{2-}$ pair, it was found that mechanisms involved chains and peroxo radicals.[1,2] It has been suggested that there might be similar chains for other decompositions.[2,3] The identification of peroxodisulfate $S_2O_8^{2-}$ as a chain termination product in the Ce(IV) induced decomposition[4] indicated that this disubstituted peroxide could be used to measure chain length (defined as the ratio of $HOOSO_3^-$ decomposed to $S_2O_8^{2-}$ formed) in other $HOOSO_3^-$ decompositions. Application of this new technique to the cobalt- and vanadium-catalyzed decompositions is described here. The rate law for the decomposition catalyzed by vanadium is also reported.

Catalysis by Cobalt

Background. The fact that cobalt(II) ion[5] is a good catalyst for $HOOSO_3^-$ decomposition has been known for some time,[6] and it has been found to involve the peroxo radical[2,7] and the sulfate radical anion $SO_4^{\bullet-}$.[8] Thompson[2] found the rate law near pH 0 to be

$$\frac{-d[HOOSO_3^-]}{dt} = k_{Co}\left\{\frac{[HOOSO_3^-][Co^{2+}]}{[H^+]}\right\}$$

and proposed a chain mechanism. Marsh[3] found that $S_2O_8^{2-}$ was formed in small quantities during the decomposition.

Rate Law Extension. In order to see if the same rate law held up to pH 7.2, we checked the orders in Co^{2+} and H^+ over wide ranges. The results are graphically summarized in Figure 1 which shows how the amount of cobalt needed for catalysis decreases as pH increases; data therein (listed elsewhere[9]) include runs in aqueous perchloric acid, in phosphate buffer, and in phthalate buffer. The slopes of the lines range from 0.94 to 1.18 indicating first order in cobalt. The rate law extends up to pH 5.9 and down to $[Co^{2+}] = 5 \times 10^{-8}$ M.

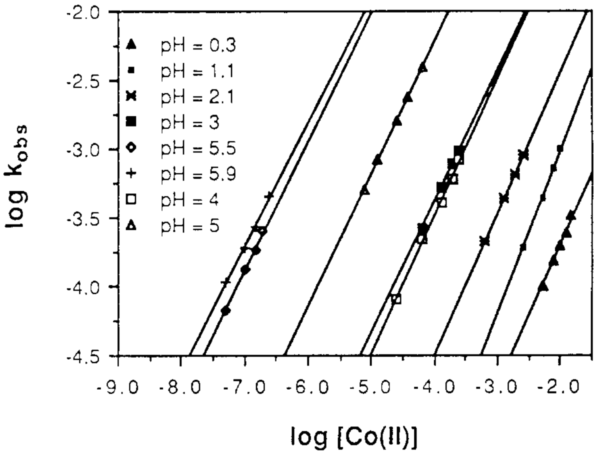

Figure 1. Summary plot to show that order in cobalt(II)—indicated by individual slopes—and order in hydrogen ion—as marked by horizontal displacement—extends up to pH 5.9. Temperature = 23 °C and $\mu \simeq$ 1.0 M.

Above pH 5.9, the plots of ln $[HOOSO_3^-]$ against time were no longer linear; the rate constant decreased with time. An example is presented in Figure 2. A probable explanation for the slowing down of rate with time is the conversion of Co^{2+} to Co^{3+} with the latter precipitating out as either $Co(OH)_3$ ($K_{sp} = 1.6 \times 10^{-44}$) or $CoPO_4$.

Evidence for Radicals. Although the rate law is the same in phthalate buffer as in aqueous perchloric acid and in phosphate buffer (below pH 6), there are several phenomena indicating the presence of radicals other than $^{\bullet}OOSO_3^-$ and $SO_4^{\bullet-}$ in the phthalate medium. The rate constant k_{Co} decreased by a power of 10 suggesting trapping of an active radical (e.g. $SO_4^{\bullet-}$). Further evidence for phthalate oxidation was the appearance of a yellow-brown color in the solution. As is discussed below, an apparently long chain length in phthalate buffer also can be rationalized in

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(1) Billing, W. H. O.; Bridgart, G. J.; Wilson, I. R. *Aust. J. Chem.* **1970,** *23,* 641.

(2) Thompson, R. C. *Inorg. Chem.* **1981,** *20,* 1005.

(3) Marsh, C.; Edwards, J. O. *Prog. React. Kinet.* **1989,** *15,* 35–75.

(4) Marsh, C.; Zhang, Z.; Edwards, J. O. *Aust. J. Chem.* **1990,** *43,* 321.

(5) For simplicity, we use Co^{2+}, Co^{3+}, VO_2^+, etc. for the aqueous species since complete information on hydration state and complexation is not always known.

(6) (a) Ball, D. L.; Edwards, J. O. *J. Am. Chem. Soc.* **1956,** *78,* 1125. (b) Ball, D. L.; Edwards, J. O. *J. Phys. Chem.* **1958,** *62,* 343.

(7) Thompson[2] writes it as HSO_5. We use $^{\bullet}OOSO_3^-$. The correct protonation state is not known. We have seen no rate variation (as pH was changed) that might indicate a change in protonation state.

(8) Lunenok-Burmakina, V. A.; Lezina, G. G.; Emelyanov, V. B.; Microshnichenko, A. G. *Russ. J. Phys. Chem. (Engl. Transl.)* **1977,** *51,* 1650.

(9) The numerical data are stored in the Ph.D. Thesis of Z. Zhang, at Brown University (1990).

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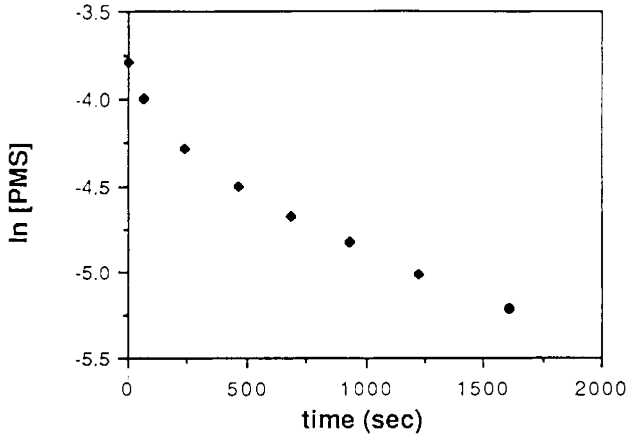

Figure 2. Pseudo-first-order plot in $HOOSO_3^-$ showing the decrease in rate due to conversion of soluble cobalt(II) to insoluble cobalt(III). pH = 6.7 at 23 °C in phosphate buffer at $\mu \simeq 1.0$ M.

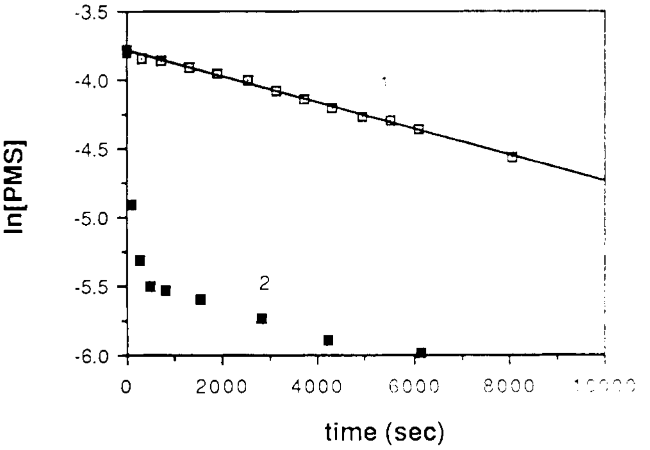

Figure 3. First-order plots where the metal ion for run 1 is cobalt(II) and for run 2 is cobalt(III) at 4 × 10^{-3} M. pH = 5.9 at 23 °C.

terms of a process involving reaction of $SO_4^{\bullet-}$ with buffer to form an organic radical of low reactivity.

Induction by Co^{3+}. Thompson[2] found that the predominant oxidation state of cobalt in $HOOSO_3^-$ solutions near pH 0 is +2. This remains true, as indicated by the constancy of the rate law, at least up to the point (pH ~ 6) where curved rate plots were seen. The dominance of Co^{2+} indicates that any Co^{3+} formed in the mechanism is reduced rapidly back to Co^{2+}. That this indication is correct can be seen in Figure 3 wherein losses of $HOOSO_3^-$ in the presence of the two oxidation states are compared. The rapid drop in $[HOOSO_3^-]$ when the cobalt is initially +3 is accompanied by a change in color from blue to the pink of Co^{2+}.

Chain Length. In order to obtain the chain length L_c as defined by the equation

$$L_c = -\frac{\Delta[HOOSO_3^-]}{\Delta[S_2O_8^{2-}]}$$

the ratio of peroxide concentration changes was evaluated for a number of experiments including those of Figure 1. In aqueous $HClO_4$ the 12 L_c values ranged from 19 to 24, and in phosphate buffers up to pH 5.9 the 17 values ranged from 18 to 21. Between pH 5.9 and 7.2, the range of curved rate plots, the 11 values were either 20 or 21. Finally for four experiments starting with Co^{3+}, the values were 21, 25, 18 and 20. The average of all these measurements is 21 ± 2.

In phthalate buffers, the amount of $S_2O_8^{2-}$ formed is much decreased, apparently even more than the power of 10 decrease for the $HOOSO_3^-$ decomposition rate. The changes in the decomposition when phthalate is present can best be explained by a reaction of $SO_4^{\bullet-}$ with phthalate to form an organic radical which reacts by a very short chain process.

Catalysis by Vanadium

Background. Two previous studies[10,11] have shown that vanadate is a catalyst for the decomposition of $HOOSO_3^-$ in acidic solution. However the peroxide preparations used in both studies had considerable HOOH present along with the $HOOSO_3^-$; we have found that this alters the rate law and mechanism.[12] Using CUROX[13] samples which have no detectable HOOH or $S_2O_8^{2-}$, we have now studied the vanadate-catalyzed decomposition of $HOOSO_3^-$.

The loss of $HOOSO_3^-$ has been followed by iodometric titration. The stoichiometry is again presumed to be

$$2HOOSO_3^- \rightarrow 2HSO_4^- + O_2$$

because peroxide disappears (except for the small amounts of $S_2O_8^{2-}$ formed) and bubbling is observed.

Vanadium can be added as either $VO(SO_4)$ or $(NH_4)VO_3$. When $VOSO_4$ was used, the blue color characteristic of vanadium(IV) rapidly changed to the yellow of vanadium(V). (This oxidation

$$2VO^{2+} + HOOSO_3^- + H_2O \rightarrow 2VO_2^+ + HSO_4^- + 2H^+$$

which was studied by Thompson,[14] has a second-order rate constant of 12.7 $M^{-1}\,s^{-1}$ at 25 °C.) No difference in the $HOOSO_3^-$ decomposition rate constant was found with the different sources of vanadium.

Rate Law. In all rate runs, linear plots of ln $[HOOSO_3^-]$ against time were obtained, and only a minor variation of slope was observed on change in initial peroxide concentration. Thus the decomposition is first order in $HOOSO_3^-$. The slope of the plot, designated k_{obs}, depended on the concentrations of vanadium and acid as can be seen in Table I. Plots of log k_{obs} against log $[VO_2^+]$ in sulfuric and perchloric acid solutions gave straight lines with slopes of 1.03, 1.07, 1.00, and 1.14 under various conditions. The order in vanadium is considered to be 1. In the table, values of both k_{obs} and k_2, where k_2 is defined by the law

$$\frac{-d[HOOSO_3^-]}{dt} = k_2[HOOSO_3^-][VO_2^+]$$

are given.

In the range of acids with convenient rates, it is appropriate to use the Hammett H_0 function[15] as a measure of acidity. As can be seen in Figure 4, a plot of log k_{obs} against $-H_0$ is linear with a slope of 1. For the 15 runs used to determine the dependence on acid, the average value of log $(k_2 + H_0)$ was calculated to be −2.82 ± 0.04. This gives a third-order constant of 1.5 × 10^{-3} $M^{-2}\,s^{-1}$ at 22.0 °C. The constants in H_2SO_4 and $HClO_4$ match to well within the experimental error.

Activation Parameters. On the basis of measurements from 1.8 to 46 °C (see Table I), the values of $\Delta H^‡$ and $\Delta S^‡$ were calculated to be 66.1 kJ mol^{-1} and −93 J $mol^{-1}\,K^{-1}$, respectively, for the third-order rate constant (using $H_0 = -0.84$ for 2 M H_2SO_4).

Chain Length. As in the studies with cerium and cobalt, $S_2O_8^{2-}$ was found to be formed in the vanadium-catalyzed decomposition. Using the same definition, many L_c values were calculated and are reported in Table I. An average value of 19 ± 6 was obtained.

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(10) Guiraud, H.; Crommelynck, F. *Bull. Chim. Soc. Fr.* **1975**, 521.
(11) Loveitt, M. E. Unpublished study.
(12) Zhang, Z.; Edwards, J. O. Unpublished study.
(13) CUROX is the trademark name for the triple salt form of peroxomonosulfate prepared by Peroxid-Chemie, Munich, Germany.
(14) Thompson, R. C. *Inorg. Chem.* **1981**, *20*, 3745.
(15) (a) Hammett, L. P.; Deyrup, A. J. *J. Am. Chem. Soc.* **1932**, *54*, 2721. (b) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Wiley: New York, 1963; p 272.

Table I. Vanadium-Catalyzed Decomposition Rates[a]

run no.	$[PMS]_0$ (M)	[HX][b] (M)	[V(V)][c] (M)	T (°C)	L_c	10^4k_{obs} (s^{-1})	10^3k_2 ($M^{-1}\,s^{-1}$)
V1	0.153	2.6 (S)	0.020 (A)	22.0	17	5.28	26.4
V2	0.153	1.0 (S)	0.020 (A)	23.0		0.580	2.9
V3	0.153	2.3 (S)	0.020 (A)	22.0	16	3.53	17.6
V4	0.153	1.5 (S)	0.020 (A)	22.0	26	1.12	5.6
V5	0.101	2.0 (C)	0.010 (A)	22.0	13	0.903	9.0
V6	0.101	2.0 (C)	0.015 (A)	22.0	10	1.28	8.5
V7	0.101	2.0 (C)	0.020 (A)	22.0	34	1.72	8.6
V8	0.101	2.0 (C)	0.025 (A)	22.0	33	2.23	8.9
V9	0.101	2.0 (C)	0.030 (A)	22.0	13	2.82	9.4
V10	0.101	1.0 (C)	0.020 (A)	22.0	14	0.488	2.4
V11	0.101	1.5 (C)	0.020 (A)	22.0	15	0.999	5.0
V12	0.101	2.3 (C)	0.020 (A)	22.0	10	2.52	12.6
V13	0.101	2.6 (C)	0.020 (A)	22.0	12	3.60	18.0
V14	0.136	2.0 (S)	0.020 (B)	22.8	13	2.13	10.7
V15	0.136	2.0 (S)	0.010 (B)	22.8	13	1.04	10.4
V16	0.136	2.0 (S)	0.015 (B)	22.8	18	1.64	11.0
V17	0.136	2.0 (S)	0.025 (B)	22.8	29	2.67	10.7
V18	0.136	2.0 (S)	0.030 (B)	22.8	16	3.55	10.8
V19	0.136	1.0 (S)	0.020 (B)	22.0	29	0.450	2.8
V20	0.136	1.5 (S)	0.020 (B)	22.0	25	0.953	4.8
V21	0.136	2.5 (S)	0.020 (B)	22.0	18	3.79	20.0
V22	0.136	3.0 (S)	0.020 (B)	22.0	16	6.29	31.4
V23	0.136	2.0 (S)	0.010 (A)	22.8	13	0.905	9.1
V24	0.136	2.0 (S)	0.015 (A)	22.5	19, 18	1.37	9.1
V25	0.136	2.0 (S)	0.020 (A)	22.0	27, 20	1.96	9.8
V26	0.136	2.0 (S)	0.025 (A)	22.0	15, 30	2.71	10.8
V27	0.136	2.0 (S)	0.030 (A)	22.8	18, 25	3.16	10.5
V28	0.112	2.0 (S)	0.010 (A)	28.0	11	1.40	14.0
V29	0.112	2.0 (S)	0.010 (A)	32.0	19	2.02	20.2
V30	0.112	2.0 (S)	0.010 (A)	38.0		3.59	35.9
V31	0.112	2.0 (S)	0.010 (A)	46.0	18	7.20	71.9
V32	0.112	2.0 (S)	0.010 (A)	1.8		0.11	1.11
V33	0.112	1.0 (S)	0.015 (A)	22.0	11	0.335	2.24
V34	0.112	1.0 (S)	0.025 (A)	22.0	10	0.576	2.30
V35	0.112	1.0 (S)	0.030 (A)	22.0	12	0.681	2.27
V36	0.112	1.0 (S)	0.035 (A)	22.0	20	0.772	2.21
V37	0.112	4.05 (S)	0.005 (A)	22.0		4.78	95.6
V38	0.112	4.05 (S)	0.007 (A)	22.0	18	6.87	98.2
V39	0.112	4.05 (S)	0.001 (A)	22.0		7.40	74.0
V40	0.112	4.05 (S)	0.003 (A)	22.0		2.70	90.0
V41	0.112	4.05 (S)	0.009 (A)	22.0		8.93	99.3

[a] Because of the necessity of using H_0 values, ionic strength was not held constant. [b] S indicates H_2SO_4 and C indicates $HClO_4$. [c] A indicates $VOSO_4$ and B indicates NH_4VO_3.

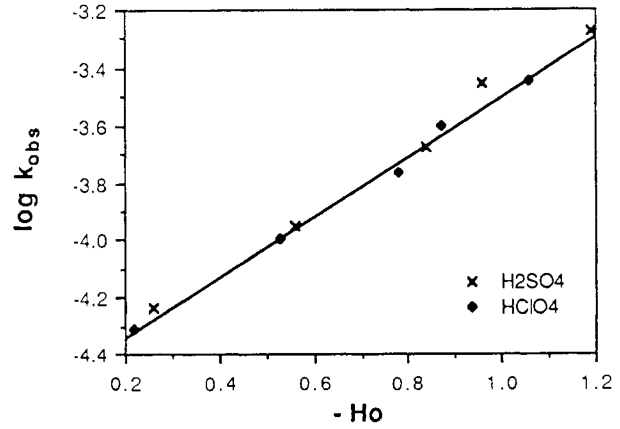

Figure 4. Order plot for acid strength in the vanadium(V)-catalyzed decomposition in $HClO_4$ and in H_2SO_4 at 22 °C.

There was no evidence for an L_c dependence on temperature, on vanadium concentration, or on acid.

Discussion

Chain Lengths. It is important to point out initially that a number of decompositions of $HOOSO_3^-$ have similar chain lengths, suggesting that the termination step and a related propagation step are common to the several reactions. A summary of these reactions with the values of L_c is given in Table II.

Table II. Chain Lengths for $HOOSO_3^-$ Decomposition

inductor	medium	L_c[a]	k_4/k_5	ref
Ce(IV)	aq H_2SO_4	17.4[b]	8.7	1
Ce(IV)	aq $HClO_4$	15.0 ± 0.4[c]	7.5	4
Ag^+ and $S_2O_8^{2-}$	aq $HClO_4$		8.6	2
Co^{2+}	aq $HClO_4$	22 ± 2	9.5	*d*
Co^{2+}	aq phosphate	20 ± 1	8.5	*d*
Co^{2+}	pH >6	20.5	9.3	*d*
Co^{3+}	varied	21	9.0	*d*
VO_2^+	aq H_2SO_4	19 ± 6	8.5	*d*
VO_2^+	aq $HClO_4$	17 ± 8	7.5	*d*

[a] All L_c values here except where indicated are recorded as $-\Delta[HOOSO_3^-]/\Delta[S_2O_8^{2-}]$. [b] Initially measured as $\Delta[HOOSO_3^-]$-Δ[Ce(IV)]; here multiplied by two to make comparable to others. [c] Some measurements of $-\Delta[HOOSO_3^-]/\Delta[S_2O_8^{2-}]$ and some $\Delta[HOOSO_3^-]$-Δ[Ce(IV)]. [d] Present Study.

As pointed out earlier,[3] when the termination step and one propagation step for a chain reaction have the same species and molecularity, the rate law orders reflect the initiation step only; when several reactions are related by the termination and propagation steps, the chain lengths will be almost the same even though the initiation steps differ. This situation is well established for the decomposition of *tert*-butyl hydroperoxide induced by a variety of initiators.[16] In this organic peroxide decomposition, the yields of products including termination product di-*tert*-butyl peroxide are insensitive to the nature of the inductor so chain lengths are constant.[17] In fact the chain length (near 9) for this hydroperoxide decomposition is quite similar to that for $HOOSO_3^-$. A number of articles[18] and reviews[19] spell out the details of organic peroxy radical and polyoxide chemistry.

Mechanism. Following the scheme set up earlier[3] and that presently accepted for the organic hydroperoxide,[16,18,19] the steps common to these $HOOSO_3^-$ decompositions are postulated to be

$$2\cdot OOSO_3^- \overset{K_3}{\rightleftharpoons} {}^-O_3SOOOOSO_3^-$$

$${}^-O_3SOOOOSO_3^- \xrightarrow{k_3} \{SO_4^{\bullet-}\ O_2\ SO_4^{\bullet-}\}$$

$$\{SO_4^{\bullet-}\ O_2\ SO_4^{\bullet-}\} \xrightarrow{k_4} O_2 + 2SO_4^{\bullet-}$$

$$\{SO_4^{\bullet-}\ O_2\ SO_4^{\bullet-}\} \xrightarrow{k_5} O_2 + S_2O_8^{2-}$$

where ${}^-O_3SOOOOSO_3^-$ represents a tetroxide intermediate and the wavy brackets with inclusions represent a cage complex. There is evidence for both types of species in organic peroxide decompositions.[18,19]

The steps which form ${}^\bullet OOSO_3^-$ and which recycle $SO_4^{\bullet-}$ depend on inductor nature. When cobalt(II) is the catalyst, the steps

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postulated are as follows:

$$\mathrm{Co^{2+} + H_2O \overset{K_1}{\rightleftharpoons} CoOH^+ + H^+}$$

$$\mathrm{CoOH^+ + HOOSO_3^- \xrightarrow{k_{1a}} CoO^+ + H_2O + SO_4^{\bullet-}}$$

$$\mathrm{CoO^+ + 2H^+ \overset{K_2}{\rightleftharpoons} Co^{3+} + H_2O}$$

$$\mathrm{Co^{3+} + HOOSO_3^- \xrightarrow{k_{1b}} Co^{2+} + H^+ + {}^{\bullet}OOSO_3^-}$$

$$\mathrm{SO_4^{\bullet-} + Co^{2+} \xrightarrow{k_2} SO_4^{2-} + Co^{3+}}$$

This decomposition has K_1, k_{1a}, K_2, k_{1b}, k_2, K_3, k_3, k_4, and k_5 as component steps. Using the steady-state approximation, the derived rate law is

$$\frac{-\mathrm{d}[\mathrm{HOOSO_3^-}]}{\mathrm{d}t} = (k_{1a}K_1)\left(3 + \frac{2k_4}{k_5}\right)\left\{\frac{[\mathrm{HOOSO_3^-}][\mathrm{Co^{2+}}]}{[\mathrm{H^+}]}\right\}$$

so that

$$k_{\mathrm{Co}} = (k_{1a}K_1)\left(3 + \frac{2k_4}{k_5}\right)$$

Also the rate law for $\mathrm{S_2O_8^{2-}}$ formation is

$$\frac{+\mathrm{d}[\mathrm{S_2O_8^{2-}}]}{\mathrm{d}t} = (k_{1a}K_1)\left\{\frac{[\mathrm{HOOSO_3^-}][\mathrm{Co^{2+}}]}{[\mathrm{H^+}]}\right\}$$

which leads to the formula for theoretical chain length

$$L_c = \left(3 + \frac{2k_4}{k_5}\right)$$

so

$$\frac{k_4}{k_5} = \frac{L_c - 3}{2}$$

When vanadium is the catalyst, the new steps postulated are as

$$\mathrm{VO_2^+ + H^+ \overset{K_{1'}}{\rightleftharpoons} VO(OH)^{2+}}$$

$$\mathrm{VO(OH)^{2+} + HOOSO_3^- \xrightarrow{k_{1a'}} VO^{2+} + H_2O + {}^{\bullet}OOSO_3^-}$$

$$\mathrm{VO^{2+} + HOOSO_3^- \xrightarrow{k_{1b'}} VO(OH)^{2+} + SO_4^{\bullet-}}$$

$$\mathrm{VO^{2+} + SO_4^{\bullet-} + H_2O \xrightarrow{k_{2'}} SO_4^{2-} + VO(OH)^{2+} + H^+}$$

Combining $k_{1'}$, $k_{1a'}$, k_{1b}, and $k_{2'}$ with K_3, k_3, k_4, and k_5, and using the steady-state approximation, the derived rate law is

$$\frac{-\mathrm{d}[\mathrm{HOOSO_3^-}]}{\mathrm{d}t} = 2(K_{1'}k_{1a'})\left(\frac{k_4 + k_5}{k_5}\right)\{[\mathrm{HOOSO_3^-}][\mathrm{VO_2^+}][\mathrm{H^+}]\}$$

in agreement with the observed law. The rate of formation of $\mathrm{S_2O_8^{2-}}$ is

$$\frac{+\mathrm{d}[\mathrm{S_2O_8^{2-}}]}{\mathrm{d}t} = (k_{1a'}K_{1'})\{[\mathrm{HOOSO_3^-}][\mathrm{VO_2^+}][\mathrm{H^+}]\}$$

so that k_4/k_5 for the vanadate decomposition is equal to $^1/_2(L_c - 2)$. It is to be noted that the step

$$\mathrm{SO_4^{\bullet-} + HOOSO_3^- \rightarrow HSO_4^- + {}^{\bullet}OOSO_3^-}$$

(known to have a very low rate constant ($k < 1 \times 10^5$ $\mathrm{M^{-1}\,s^{-1}}$)) need not be postulated in these two decompositions because $\mathrm{SO_4^{\bullet-}}$ can oxidize the metal lower oxidation state to the higher.

Rate Constant Ratio. Along with the collected values of L_c for four decompositions are the related ratios of k_4 to k_5. The range is indeed small (7.5–9.5) confirming the simple relationship (each first order in cage complex) of one propagation step to the termination step.

Acid Dependence. The cobalt(II) rate increases with pH whereas the vanadium(V) rate decreases with pH. The catalysis by manganese(II), like the cobalt(II), increases with pH.[12] The direction of the pH dependence for these three catalyses is determined by the first slow step. If the metal ion is oxidized by $\mathrm{HOOSO_3^-}$, then the rate increase with pH can be ascribed to more facile oxidation of $\mathrm{M(OH)(H_2O)_{x-1}}^y$ than of $\mathrm{M(H_2O)_x}^{y+1}$. On the other hand if the metal ion is reduced, the rate is increased by conversion of an oxo group to a hydroxo group, which has the effect of raising the oxidizing power, in this case that of vanadium(V). This is analogous to the enhancement by acid of some oxoanion and peroxide reduction rates.

Added Note. A thoughtful reviewer posed a question as to why "... the initiation step in the V(V) system is not reversible as in the case with the stronger oxidant Ce(IV)." Relevant facts are that $\mathrm{VO^{2+}}$ is oxidized by both $\mathrm{SO_4^{\bullet-}}$ and $\mathrm{HOOSO_3^-}$ and that Ce(III) builds up in concentration (it is a product) whereas V(IV) does not (it is only an intermediate). The rate constant for the second-order reaction of $\mathrm{HOOSO_3^-}$ with $\mathrm{VO^{2+}}$ is 12.7 $\mathrm{M^{-1}\,s^{-1}}$,[14] but Ce(III) is not oxidized by $\mathrm{HOOSO_3^-}$.[23]

Experimental Section

Chemicals. The triple salt made by Interox (CUROX)[13] was employed as source of $\mathrm{HOOSO_3^-}$. Checks showed no detectable peroxodisulfate. Other chemicals were best grade available (e.g., $\mathrm{HClO_4}$ was Fisher certified ACS grade) and used without further purification. Cobalt(III) perchlorate was prepared in 4 M $\mathrm{HClO_4}$ by electrolytic oxidation at 0 °C as described by Swann[20] and Hargreaves;[21] spectrophotometric measurements were used to determine concentrations of Co(II) and Co(III) ($\epsilon_{509} = 4.84$ $\mathrm{M^{-1}\,cm^{-1}}$ and $\epsilon_{605} = 37.0$ $\mathrm{M^{-1}\,cm^{-1}}$, respectively).[22]

Rate Measurements. Aliquots of reaction solutions were withdrawn at time intervals, analyzed for $\mathrm{HOOSO_3^-}$ at 0 °C using iodometry and for $\mathrm{S_2O_8^{2-}}$ using spectrophotometric determination of Fe(III) formed by reaction of $\mathrm{S_2O_8^{2-}}$ and Fe(II).[4] The pH values were measured with an Orion Research Model 801A meter before and after reaction.

Because of the reaction of vanadium(V) with $\mathrm{I^-}$, it is necessary to subtract the volume of $\mathrm{S_2O_3^{2-}}$ corresponding to the $\mathrm{I_2}$ formed by vanadate oxidation of iodide from the total $\mathrm{S_2O_3^{2-}}$ volume.

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