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Comparative Kinetic Study of Oxygen Atom Transfer Reactions of Diperoxo and Monoperoxo Complexes of Oxovanadium(V) in Aqueous Solution

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The oxygen atom transfer reactions of peroxo and diperoxo complexes of oxovanadium(V) with $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ have been studied. At 25 °C and $I = 0.10$ M the second-order rate constants ($M^{-1}\ s^{-1}$) are as follows: $VO(O_2)(O_2H)(C_2H_4NCO_2)^-$, 87 ± 3; $VO(O_2)_2(C_5H_4NCO_2)^{2-}$, 13 ± 2; $VO(O_2)_2(C_2O_4)^{3-}$, 12 (pH 5.1 and 20.6 °C); $VO(O_2)_2(H_2O)_2^-$, 11; $VO(O_2)\{C_5H_3N(CO_2)_2\}(H_2O)^-$, $\leq(1-3) \times 10^{-3}$. The observed rates for $VO(O_2)(H_2O)_4^+$ were very low, but a rate constant could not be assigned. A value $pK_a = 4.41 \pm 0.02$ for $VO(O_2)(O_2H)(C_5H_4NCO_2)^-$ was determined by potentiometric titration. The much greater reactivity of the oxo diperoxo complexes relative to the oxo peroxo species confirms an earlier prediction based on studies with peroxo complexes of other d^0 transition-metal ions. A survey of available crystal structures reveals that a significant lengthening of the $(O-O)_{peroxo}$ and one of the asymmetric $M-O_{peroxo}$ bonds occurs in the oxo diperoxo complexes. Both of these features are consistent with their greater reactivity as oxygen atom transfer and inner-sphere, one-electron oxidizing reagents. However, it is unclear why Mo(VI) and W(VI) are so much more effective than V(V) at activating peroxide in the oxo diperoxo complexes.

Introduction

The oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) are remarkable oxygen atom transfer and one-electron oxidizing reagents.[1,2] They are effective at least over the pH range 0–7 in aqueous solution, and in the presence of excess hydrogen peroxide the reactions are strictly catalytic with respect to the metal ion. The complexes have been formulated as $MO(O_2)_2(H_2O)_2$ and $MO(O_2)_2(OH)(H_2O)^-$, with pK_a's of 1.85 [M = Mo(VI)][3] and 0.12 [M = W(VI)].[1] We have demonstrated that atom transfer from the peroxo ligand to the coordinated sulfur acceptor occurs in the stepwise conversion of the thiolato complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ to the corresponding sulfenato (S=O) and sulfinato (O=S=O) complexes.[1] We have proposed direct attack by the substrate at an η^2-peroxo group.[4]

Activation of hydrogen peroxide by d^0 transition-metal ions is not general. For example, the peroxo complexes of Ti(IV)[5,6] and Zr(IV)[7] are orders of magnitude *less* reactive than is hydrogen peroxide in aqueous solution, whereas the oxo diperoxo Mo(VI) and W(VI) complexes are usually 10^2–10^5 times more reactive. The reasons for these enormous reactivity variations are poorly understood. A complicating feature is that a variety of peroxo complexes, mono- and polynuclear, are formed by the d^0 metal ions, with variable peroxide to metal ion ratios, charges, and degrees of hydrolysis (terminal and bridging oxo and hydroxo ligands are not uncommon).[8,9]

We have suggested that the oxo diperoxo configuration may be especially effective at activating peroxide.[2,4] This configuration is often found in V(V), Cr(VI), Mo(VI), and W(VI) peroxo complexes. An interesting test of the suggestion would be a comparison of the reactivity of an oxo peroxo compound versus an oxo diperoxo mononuclear complex. We have chosen V(V) as the metal ion, since the oxo peroxo complexes of the group 6 metal ions are generally unstable in aqueous solution.[10] In this paper, we report the kinetic results of the oxygen atom transfer reactions of $VO(O_2)\{C_5H_3N(CO_2)_2\}^-$ and $VO(O_2)_2(C_5H_4NCO_2)^{2-}$ with $(en)_2CO(SCH_2CH_2NH_2)^{2+}$. In more limited studies $VO(O_2)^+$, $VO(O_2)_2(C_2O_4)^{3-}$, and $VO(O_2)_2^-$ were also used as oxidants.

Experimental Section

Reagents. The compounds $K[VO(O_2)(dipic)]\cdot 2H_2O$,[11] $K_2[VO(O_2)_2(pic)]\cdot H_2O$,[12] $K_3[VO(O_2)_2(ox)]\cdot 2H_2O$,[13] and $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$[14] were synthesized as described in the literature. In this paper "dipic" refers to pyridine-2,6-dicarboxylate, $C_5H_3N(CO_2)_2^{2-}$, "pic" is pyridine-2-carboxylate, $C_5H_4NCO_2^-$, and "ox" is oxalate ion. The preparation and analysis of solutions of vanadium(V), H_2O_2, and $LiClO_4$ have been reported previously.[15]

All other chemicals were of reagent grade and were used as supplied. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

Determination of the Protonation Constant, K_p, for $[VO(O_2)_2(pic)]^{2-}$. A solution containing 2.69×10^{-3} M $K_2[VO(O_2)_2(pic)]\cdot H_2O$, 0.030 M H_2O_2, and 0.10 M KNO_3 at 25.0 °C was titrated potentiometrically with 0.273 M HNO_3. The change in pH was monitored throughout the titration with an Orion Research Model 601A digital ion analyzer fitted with a Ross 8103 combination electrode. Values of K_p were calculated for 25 points between 20 and 80% of the equivalence point by means of eq 5, which can be derived from eqs 1–4; log $\gamma\pm$ was calculated by means of the Davies equation.

$$VO(O_2)_2(pic)^{2-} + H^+ = HVO(O_2)_2(pic)^- \qquad K_p = 1/K_a \tag{1}$$

$$[H^+]_{added} = [H^+] + [HVO(O_2)_2(pic)^-] \tag{2}$$

$$[VO(O_2)_2(pic)^{2-}] + [HVO(O_2)_2(pic)^-] = [2:1]_{tot} \tag{3}$$

$$\log [H^+] = -pH - \log \gamma\pm \tag{4}$$

$$K_a = 1/K_p = [H^+]\{[2:1]_{tot}/([H^+]_{added} - [H^+]) - 1\} \tag{5}$$

Kinetic Studies. A Zeiss PMQ-11 spectrophotometer equipped with a rapid-mixing (ca. 1 s) thermostated sample compartment was used for the kinetic experiments. The reactions were usually monitored at 365 nm, an absorption maximum[16] for the sulfenato complex, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$. In most cases duplicate experiments were performed for each set of experimental conditions. Acetate buffers and the biological buffers MOPS and MES were used to control pH from 4 to 7; spectral studies indicate that complexation of the peroxo complexes of d^0 metal ions by these buffer systems is negligible.

Stability Studies of the Heteroligand Peroxo Complexes. Spectral studies showed that solutions of $VO(O_2)(dipic)^-$ were stable for long

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Table I. Kinetic Results for the Oxidation of (Thiolato)cobalt(III) to (Sulfenato)cobalt(III) by Oxodiperoxo(picolinato)vanadium(V) at 25 °C[a]

$10^4[VO(O_2)_2(pic)^{2-}]_0$, M	$10^2[H_2O_2]_0$, M	k_{obs},[b] s^{-1}	k_{pic},[c] $M^{-1}\ s^{-1}$
	$[HNO_3]$ = 0.0010 M		
2.21	0.80	0.0271	81
3.19	0.80	0.0381	94
2.35	1.00	0.0297	78
3.29	1.00	0.0433	97
4.23	1.00	0.0524	97
			89 ± 8 (⟨av⟩)
	pH 4.1 Acetate Buffer		
2.04	1.70	0.0298	49
2.37	2.00	0.0356	54
2.37	2.50	0.0404	50
3.08	2.50	0.0461	57
			53 ± 3 (⟨av⟩)
	pH 5.1 Acetate Buffer		
2.25	0.125	0.00848	32
2.17	0.30	0.0105	34
2.28	0.30	0.0115	37
3.60	0.30	0.0161	39
3.51	0.45	0.0171	33
3.50	0.80	0.0233	40
4.73	0.80	0.0262	36
3.39	1.00	0.0224	33
3.50	1.15	0.0262	38
3.56	1.50	0.0322	40
			36 ± 3 (⟨av⟩)
	pH 6.1 MES Buffer		
2.09	0.012	0.00259	12
1.19	0.025	0.00158	11
2.09	0.032	0.00287	12
2.09	0.048	0.0030	12
1.43	0.050	0.00205	10
2.37	0.050	0.0032	11
2.39	0.050	0.0036	13
2.71	0.052	0.00394	13
2.37	0.10	0.0037	11
2.39	0.10	0.00432	14
4.77	0.10	0.00633	11
2.26	0.30	0.0065	13
2.71	0.52	0.00393	12
			12 ± 1 (⟨av⟩)
	pH 7.0 MOPS Buffer		
2.44	0.050	0.00229	7.0
3.42	0.050	0.00311	7.5
			7.3 ± 0.3 (⟨av⟩)

[a] Ionic strength maintained at 0.10 M by use of KNO_3; buffer concentrations were 0.010 M; $[(thiolato)cobalt(III)]_0 = (1.79-3.30) \times 10^{-5}$ M. Reactions were monitored at 365 nm. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Values calculated by use of eq 7, where $k_{H_2O_2} = 1.18[H_2O_2]$ at pH 3 and $1.14[H_2O_2]$ at higher pH values.

Table II. Kinetic Results for the Oxidation of (Thiolato)cobalt(III) to (Sulfenato)cobalt(III) by Oxodiperoxo(oxalato)vanadium(V) at pH 5.1 and 20.6 °C[a]

$10^4[VO(O_2)_2(ox)^{3-}]_0$, M	$10^3[H_2O_2]_0$, M	k_{obs},[b] s^{-1}	k_{ox},[c] $M^{-1}\ s^{-1}$
2.25	1.25	0.003 79	12
3.60	2.00	0.006 27	12
2.25	3.25	0.005 83	13

[a] Conditions: ionic strength maintained at 0.10 M by use of KNO_3; [acetate buffer] = 0.010 M; $[(thiolato)cobalt(III)]_0 = (1.88-3.78) \times 10^{-5}$ M. Reactions were monitored at 365 nm. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Values calculated by use of the equation $k_{ox} = \{k_{obs} - k_{H_2O_2}\}/[VO(O_2)_2(ox)^{3-}]_0$.

periods at pH 4 and 5 and in water. Solutions of $VO(O_2)_2(pic)^{2-}$ and $VO(O_2)_2(C_2O_4)^{3-}$, on the other hand, were somewhat unstable with respect to loss of a peroxo ligand depending on the acidity. We therefore determined the added $[H_2O_2]$ required to maintain the complexes in the diperoxo form at each pH examined in the kinetic studies. The spectral studies demonstrated that the heteroligand remained bound under all the conditions we examined; the charge-transfer peaks of the aquo mono- and diperoxo V(V) complexes are red shifted relative to the corresponding heteroligand species.

Results

Oxidation of (Thiolato)cobalt(III) by Oxodiperoxo(picolinato)vanadium(V). The net chemical reaction in all the kinetic studies is given in eq 6; the subsequent conversion of the sulfenato

$$(en)_2Co(SCH_2CH_2CH_2NH_2)^{2+} + H_2O_2 \rightarrow (en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+} + H_2O \qquad (6)$$

product to the sulfinato ($S\{O\}_2$) complex is extremely slow under most of our experimental conditions. The rate law for eq 6 has been thoroughly determined;[16–18] we are interested here in determining the corresponding expression for $VO(O_2)_2(pic)^{2-}$. A substantial excess of the oxidant relative to the (thiolato)cobalt(III) complex was used, but in addition added hydrogen peroxide was present to maintain the V(V) complex in the diperoxo form. The kinetic results and the experimental conditions are summarized in Table I. The values of k_{obs} are the slopes of plots of $-\ln (A_\infty - A)$ vs t, which were linear for at least 3 half-lives. Values of k_{pic}, the rate constant for the reaction of oxodiperoxo(picolinato)vanadium(V) with the (thiolato)cobalt(III) complex, were calculated by means of eq 7. Values of $k_{H_2O_2}$, the pseudo-first-order rate constant for the reaction of H_2O_2 with the thiolato complex, were $\leq 0.4k_{obs}$ under our experimental conditions except for a few experiments at pH 4.1.

$$k_{pic} = (k_{obs} - k_{H_2O_2})/[VO(O_2)_2(pic)^{2-}]_0 \qquad (7)$$

The values of k_{pic} are reasonably contant at a given pH over a modest range of initial concentrations of the vanadium complex and free hydrogen peroxide. The rate constants diminish with a rise in pH over the range 3.0–7.0. Quilitzsch and Wieghardt[12] have proposed that $VO(O_2)_2(pic)^{2-}$ and analogous complexes with different heteroligands are completely protonated as $VO(O_2)(OOH)(pic)^-$ at $[H^+] \geq 0.01$ M. We have determined the value of log K_p for protonation for the picolinato complex (eq 1) to be 4.41 ± 0.02 at 25 °C and $I = 0.10$ M by potentiometry (Experimental Section). The assigned uncertainty is the average deviation, but the true uncertainty would be larger if systematic errors were included. It is important to have sufficient free hydrogen peroxide present during the titration to prevent some of the diperoxo complex from converting to the monoperoxo form.

Additional evidence for protonation was obtained from visual observation and spectrophotometry. The protonated form has an orange hue and and extinction coefficient 690 ± 10 $M^{-1}\ cm^{-1}$ at 330 nm, whereas at the same wavelength $\epsilon = 610\ M^{-1}$ for the yellow $VO(O_2)_2(pic)^{2-}$. The titration curve could be reversed by addition of 1 equiv of base, but unusual effects were observed. For example, when approximately 1 equiv of base was added to a solution containing 2.69×10^{-3} M oxodiperoxo(picolinato)vanadium(V) and 0.03 M hyrogen peroxide at pH 3.5, the pH immediately became 6.8 but then slowly drifted toward a final value of 5.3 over nearly 2 h. During this time the color slowly changed from orange to yellow, and the spectrum became that usually observed for $VO(O_2)_2(pic)^{2-}$ at pH 6.

Oxidation of (Thiolato)cobalt(III) by Oxodiperoxo(oxalato)vanadium(V). It is important for the purposes of this paper that the kinetic results obtained for the picolinato complex are representative of oxodiperoxovanadium(V) complexes and not highly dependent on the nature of the heteroligand. We therefore performed a very limited kinetic study using $VO(O_2)_2(ox)^{3-}$ at pH 5.1. The results listed in Table II show that the second-order rate constant k_{ox} is comparable to k_{pic}. The protonation constant is not known for the oxalato complex.

Oxidation of (Thiolato)cobalt(III) by Oxoperoxo(dipicolinato)vanadium(V). This monoperoxo complex is much less reactive than hydrogen peroxide. Accordingly, higher concen-

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Table III. Kinetic Results for the Oxidation of (Thiolato)cobalt(III) to (Sulfenato)cobalt(III) by Oxoperoxo(dipicolinato)vanadium(V) at 25 °C[a]

$10^3[VO(O_2)(dipic)^-]_0$, M	$10^4[H_2O_2]$, M	$10^9 k_{obs}$,[b] M/s	$10^3 k_{dipic}$,[c] $M^{-1}\ s^{-1}$
	$[HNO_3] = 8.9 \times 10^{-3}$ M		
9.52		4.0	0.8_3
	pH 4.1 Acetate Buffer		
9.05		4.8 ± 0.9	$1._1$
8.95	1.28	3.9 ± 0.2	$1._1$
	pH 5.1 Acetate Buffer		
5.05		5.7	$2._3$
8.85		9.5	$2._3$
8.85	1.28	7.3 ± 0.8	$2._6$
	pH 6.1 MES Buffer		
9.05		7.0 ± 1.5	$3._4$

[a] Conditions: $[(thiolato)cobalt(III)]_0 = 5.59 \times 10^{-4}$ M; $I = 0.10$ M, maintained by use of KNO_3; buffer concentrations 0.010 M. Reactions were monitored in 1-mm cells at 365 nm. [b] Values were obtained from plots of absorbance vs t and are the slopes (converted to concentration change) to 20% consumption of the (thiolato)cobalt(III) by the slow portion of the overall reaction. [c] Values were calculated by use of eq 8.

trations of both the peroxo complex and the thiolato substrate were used. The kinetic traces obtained at 365 nm always showed an initial rapid reaction followed by a much slower one. Extrapolation of the slower portion to zero time indicated that a reactive impurity equal to about 0.4% of $[VO(O_2)(dipic)^-]_0$ would account for the rapid portion. The "impurity" could be hydrogen peroxide; if H_2O_2 was added to the reaction mixture, the intercept of the slow portion was equivalent to the concentration of the hydrogen peroxide added. Kinetic data for the monoperoxo complex were obtained by measuring initial rates over 20% of the slower reaction. These pseudo-zero-order rate constants and the experimental conditions are summarized in Table III. Values of the rate constant k_{dipic} were calculated by means of eq 8. These values are reasonably constant at a given pH but increase slightly with decreasing acidity.

$$k_{dipic} = k_{obs}/\{[VO(O_2)(dipic)^-]_{av}[\text{thiolato complex}]_{av}\} \quad (8)$$

Studies of the Oxidation of (Thiolato)cobalt(III) by Aquo Peroxo Complexes of Oxovanadium(V). In acidic solution vanadium(V) rapidly forms both a mono- and a diperoxo complex, as shown by the equilibria in eqs 9 and 10.[19-21] The results of

$$VO_2^+ + H_2O_2 \rightleftarrows VO(O_2)^+ + H_2O \quad K_1 \quad (9)$$

$$VO(O_2)^+ + H_2O_2 \rightleftarrows VO(O_2)_2^- + 2H^+ \quad K_2 \quad (10)$$

a series of kinetic experiments with sufficient $[H_2O_2]$ to complex essentially all the vanadium(V) are summarized in Table IV. Under the experimental conditions listed, the $[VO(O_2)_2^-]_0$:$[VO(O_2)^+]_0$ ratio varied from 0.18 to 7.5×10^7 over the pH range 1.0–5.8. The concentrations of the mono- and diperoxo complexes were calculated by using the values $K_1 = 3.7 \times 10^4\ M^{-1}$ and $K_2 = 0.6$ M, which have been determined previously at 25 °C and $I = 0.10$ M.[21] The values of the pseudo-first-order rate constant k_{corr}, corrected for reaction by the free hydrogen peroxide, are listed in the fifth column. They are best consistent with the assumption of reaction only between $VO(O_2)_2^-$ and the (thiolato)cobalt(III) complex, as evidenced by the values of $k_{VO_5^-}$, given in the last column, at a given acidity. A decrease in this rate parameter with increasing pH was observed.

We tried to determine the rate constant for the reaction of $VO(O_2)^+$ with the (thiolato)cobalt(III) complex by use of excess $[VO_2^+]$ relative to $[H_2O_2]$ and $[H^+] = 0.10$–1.00 M, conditions which favor $VO(O_2)^+$ over $VO(O_2)_2^-$. The first problem encountered, aside from very slow reaction rates, was a stoichiometric $[(sulfenato)cobalt(III)]_\infty$:$[(thiolato)cobalt(III)]_0$ ratio substantially less than unity for $[H^+] > 0.20$ M, as determined at 365 nm. We eventually were able to show that the origin of this result was a competitive oxidation of the absorbing sulfenato product to the weakly absorbing (at 365 nm) sulfinato complex. This may be due to protonation of $[(en)_2Co(S\{O\}CH_2CH_2NH_2)]^{2+}$ ($K_p = 1.4\ M^{-1}$ at $I = 4.0$ M and 25 °C),[16] but in any event we found that the net oxidation of the thiolato complex could be successfully monitored at 323 nm, an isobestic for the sulfenato (both protonated and not) and sulfinato complexes. This introduces an experimental problem, in that the absorbance due to both the (thiolato)cobalt(III) and vanadium(V) species is not negligible. Nevertheless, the values of A_∞ corresponded to stoichiometric conversion of the (thiolato)cobalt(III) complex to a mixture of the sulfenato and sulfinato products, and plots of $-\ln (A_\infty - A)$ vs time were linear. The experimental conditions and results are summarized in Table V.

The best fit of the kinetic data again is found by assuming only a reaction of $VO(O_2)_2^-$ with the thiolato complex. However, the values of $k_{VO_5^-}$ determined in 0.10 M $HClO_4$ are substantially greater than those listed in Table IV under quite different experimental conditions. This may indicate some reactivity of $VO(O_2)^+$, albeit very slight, but we were unable to derive a value of the corresponding rate constant from the data in Table V.

Discussion

The kinetic data for the conversion of the (thiolato)cobalt(III) substrate to the sulfenato complex by the oxodiperoxo(picolinato)-, oxodiperoxo(oxalato)-, oxodiperoxo-, and oxoperoxo(dipicolinato)vanadium(V) oxidants are consistent with the general rate law given in eq 11. Where examined, an effect of pH on

$$d[(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}]/dt = k[(en)_2Co(SCH_2CH_2NH_2)^{2+}][\text{peroxo complex}] \quad (11)$$

the second-order rate constant was observed. As in our previous investigations, the $[H^+]$ dependences can be reasonably attributed to chemistry involving the peroxo complex.

The data in Table I can be accommodated by the scheme outlined in eqs 12–14, where RS is the (thiolato)cobalt(III) substrate. The products are the sulfenato complex and dioxo-

$$VO(O_2)(O_2H)(pic)^- \rightleftarrows VO(O_2)_2(pic)^{2-} + H^+ \quad pK_a = 4.41 \quad (12)$$

$$VO(O_2)_2(pic)^{2-} + RS \rightarrow \text{products} \quad k_{13} \quad (13)$$

$$VO(O_2)(O_2H)(pic)^- + RS \rightarrow \text{products} \quad k_{14} \quad (14)$$

peroxo(picolinato)vanadium(V), which would rapidly re-form the diperoxo complex under our experimental conditions. According to this scheme, the observed second-order rate constant $k_{pic} = \{k_{13}K_a + k_{14}[H^+]\}/([H^+] + K_a)$. The nonlinear least-squares fit of the data yields values of $k_{13} = 13 \pm 2\ M^{-1}\ s^{-1}$ and $k_{14} = 87 \pm 3\ M^{-1}\ s^{-1}$. While it was not certain that the peroxo group[22] rather than the oxo ligand is protonated, the greater rate constant for the protonated form is not inconsistent with this proposal.

In contrast, a mild increase in the rate parameter with increasing pH was observed for the oxoperoxo(dipicolinato)vanadium(V) system. This is unusual for reactions of peroxo complexes and hydrogen peroxide itself. The dipicolinato complex is only weakly basic ($K_p = 1.4\ M^{-1}$, with protonation probably at the oxo ligand).[11] The rates were very slow, much slower than those of hydrogen peroxide. It is possible that traces of free hydrogen peroxide are formed during the reaction and contribute to the measured rates, although the complex appears to be quite stable under our experimental conditions. Another possibility is that higher pH's could favor the formation of traces of a more reactive diperoxo complex. While we believe that the rate constants de-

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(22) It is interesting to note that protonation of a peroxo ligand need not convert it to the η^1 form. A crystal structure of a complex containing the $[H\{VO(O_2)_2bpy\}_2]^-$ anion shows protonation at an oxygen of an η^2-bound peroxo group. This does result in a substantial lengthening of that $V–O_{peroxo}$ bond. See: Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1984**, *A38*, 101.

Table IV. Kinetic Results for the Oxidation of (Thiolato)cobalt(III) to (Sulfenato)cobalt(III) by Vanadium(V) in the Presence of Excess Hydrogen Peroxide at 25 °C[a]

$[H^+]$, M	$10^5[VO(O_2)_2^-]_0$,[b] M	$10^5[VO(O_2)^+]_0$,[b] M	$10^3[H_2O_2]_0$,[b] M	10^3k_{corr},[c] s^{-1}	$10^{-2}k_{VO_5}$,[d] M^{-1} s^{-1}
0.10	0.45	2.54	3.01	6.2	14
0.10[e]	0.89	2.12	6.99	10.9	12
0.10[e]	0.90	5.10	3.01	22.7	25
0.10[e]	0.97	2.32	6.62	11.0	11
0.10[f]	0.84	2.12	6.99	6.6	7.9
0.10[f]	1.43	1.57	6.99	8.6	6.0
0.10[f]	1.66	4.34	3.01	17.4	11
0.080	1.05	2.24	4.77	10.6	10
0.060	1.00	2.03	2.89	7.4	7.4
0.060	1.78	2.17	4.84	14.0	7.0
0.040	2.14	1.15	4.88	17.8	8.3
0.030[e]	1.99	1.01	3.01	9.3	4.7
0.030[e]	2.47	0.53	6.99	8.5	3.4
0.030	2.61	1.34	2.85	12.2	4.7
0.030[e]	3.97	2.03	3.01	35	8.8
0.020	2.25	0.77	1.89	7.2	3.2
0.020	4.79	1.13	2.79	21.1	4.4
0.010	1.42	0.079	2.84	1.25	0.88
0.010	2.84	0.16	2.84	3.3	1.2
0.010	5.67	0.32	2.84	5.15	0.91
0.010	5.76	0.24	3.81	7.1	1.2
0.0030	3.88	0.063	1.30	1.61	0.41
0.0030	5.91	0.094	0.90	3.3	0.56
0.0030	5.96	0.031	2.90	1.99	0.33
0.0030[e]	5.96	0.031	3.00	2.78	0.47
1.3×10^{-5}[g]	30.0	0.000 81	0.41	3.17	0.11
1.3×10^{-5}[g]	39.7	0.000 053	0.60	4.43	0.11
1.3×10^{-6}[h]	29.7	0.000 000 77	0.41	3.18	0.11
1.3×10^{-6}[h]	39.7	0.000 000 53	0.60	4.34	0.11

[a] Conditions: $[(\text{thiolato})\text{cobalt(III)}]_0 = (1.24\text{–}5.2) \times 10^{-5}$ M; $I = 0.10$ M, maintained by use of KNO_3 unless otherwise indicated. [b] Concentrations calculated by use of eqs 9 and 10; only traces of VO_2^+ are present. [c] Values obtained from slopes of plots of $-\ln(A_\infty - A)$ vs time, where k_{corr} = slope $- k_{H_2O_2}$. [d] Values calculated by use of the equation $k_{VO_5^-} = k_{corr}/[VO(O_2)_2^-]_0$. [e] Ionic strength maintained by use of $HClO_4$ and $LiClO_4$. [f] Ionic strength maintained at 1.0 M. The value of $K_2 = 1.3$ M was used in calculating the concentrations. [g] [acetate buffer] = 0.10 M. [h] [MES buffer] = 0.10 M.

Table V. Summary of Kinetic Results at 25 °C for the Oxidation of (Thiolato)cobalt(III) under Conditions Favoring $VO(O_2)^+$ Relative to $VO(O_2)_2^-$[a]

$[H^+]$, M	$10^3[VO(O_2)^+]_0$,[b] M	$10^7[VO(O_2)_2^-]_0$,[b] M	$10^4[H_2O_2]$,[b] M	$10^{-4}k_{VO_5^-}$,[c] M^{-1} s^{-1}
1.00	0.73–1.84	0.15–7.47	0.16–0.62	1.9 ± 0.2
0.50	0.93–1.81	1.12–23.5	0.23–2.51	1.4 ± 0.4
0.10	0.681	51.9	0.65	0.75 ± 0.04
0.10[d]	0.43–0.88	12.3–110	0.22–1.07	0.89 ± 0.23

[a] Conditions: $I = 1.0$ M, maintained by use of $LiClO_4$; $[H^+] = [HClO_4]$; $[V(V)]_{tot} = (1.00\text{–}2.00) \times 10^{-3}$ M; $[(\text{thiolato})\text{cobalt(III)}]_0 = (0.46\text{–}1.15) \times 10^{-4}$ M. Reactions were monitored at 323 nm unless otherwise indicated. [b] Values calculated by using $K_1 = 3.7 \times 10^4$ M^{-1} and $K_2 = 1.3$ M. [c] Individual values calculated by use of the equation $k_{VO_5^-} = (k_{obs} - k_{H_2O_2})/[VO(O_2)_2^-]_0$. Uncertainties are average deviations of 12, 14, 2, and 4 independent determinations of the entries in the order listed, respectively. [d] Reactions were monitored at 365 nm.

Table VI. Summary of Rate Constants at 25 °C for the Oxidation of (Thiolato)cobalt(III) by Oxo Peroxo Complexes of d^0 Transition-Metal Ions[a]

peroxo species	rate const, M^{-1} s^{-1}	ref
$VO(O_2)(O_2H)(pic)^-$	87	this work
$VO(O_2)_2(pic)^{2-}$	13	this work
$VO(O_2)_2(ox)^{3-}$	12[b]	this work
$VO(O_2)_2(H_2O)_2^-$	11	this work
$MoO(O_2)_2(H_2O)_2$	1.9×10^4	1
$MoO(OH)(O_2)_2(H_2O)^-$	2.4×10^3	1
$MoO(O_2)_2(ox)^{2-}$	3.9×10^4	4
$WO(O_2)_2(H_2O)_2$	3.7×10^5	1
$WO(OH)(O_2)_2(H_2O)^-$	3.7×10^4	1
$VO(O_2)(dipic)(H_2O)^-$	$\leq(1\text{–}3) \times 10^{-3}$	this work
H_2O_2	$1.2 + 1.8[H^+]$	16–18

[a] Rate constants are for the rate law = k[(thiolato)cobalt(III)][peroxo species]. [b] Value determined at pH 5.1 and 20.6 °C.

termined are at least approximately correct, we cannot satisfactorily explain the pH dependence.

Vanadium(V) peroxo complexes in the absence of stabilizing heteroligands are formed in acidic solution, as shown in eqs 9 and 10. Under most conditions $VO(O_2)^+$, $VO(O_2)_2^-$, and H_2O_2 are present in appreciable amounts that depend sensitively on reactant concentrations and pH. However, under the experimental conditions for the last four entries in Table IV, the only peroxo complex of significance is $VO(O_2)_2^-$ and the limiting value of $k_{VO_5^-}$, 11 M^{-1} s^{-1}, is very likely the rate constant for this complex. The pH dependence of the remaining data in Table IV can be correlated by eq 15, which implies parallel paths for the reaction of

$$k_{VO_5^-} = 11\ M^{-1}\ s^{-1} + \{(1.5 \pm 0.1) \times 10^4\ M^{-2}\ s^{-1}\}[H^+] \qquad (15)$$

oxodiperoxovanadium(V) with the thiolato complex. The rate expression for the reaction of $VO(O_2)_2^-$ with I^- has the same functional form, and a mechanistic discussion of possible origins of the hydrogen ion dependent term has been presented by Secco.[21] We reject a scheme similar to that proposed for $VO(O_2)_2(pic)^{2-}$, since no evidence for protonation $VO(O_2)_2^-$ was obtained in careful spectral and equilibrium studies.[19-21] However, it is surprising to us that the aquo complex would be at least 4 orders of magnitude less basic than the picolinato species.

In spite of the substantial data presented in Tables IV and V, we are unable to assign even an upper limit for the reaction of $VO(O_2)^+$ with the (thiolato)cobalt(III) complex. This peroxo complex is so unreactive, apparently, that even the inevitable traces of the oxodiperoxo species can compete favorably. The $VO(O_2)(dipic)^-$ system, although not without its own complications, was more successful in that diperoxo impurities can be eliminated or at least severely curtailed.

We have assembled in Table VI are available rate constants for the oxidation of (thiolato)cobalt(III) by pentagonal-bipyramidal, oxo peroxo complexes of d^0 transition-metal ions. The oxodiperoxovanadium(V) complexes are approximately 10^4 times more reactive than the monoperoxo species $VO(O_2)(dipic)(H_2O)^-$, and the results for $VO(O_2)(H_2O)_4^+$ also suggest a very low rate. Clearly, the oxodiperoxo configuration confers a special reactivity

Table VII. Summary of Peroxo and Metal–Peroxo Bond Distances in Crystal Structures of Pentagonal-Bipyramidal V(V), Mo(VI), and W(VI) Oxo Peroxo and Oxo Diperoxo Complexes

	V(V)[b]			Mo(VI)[b]		
bond[a]	dist, Å	no.	ref	dist, Å	no.	ref
$(O–O)_{peroxo}$, $MO(O_2)$	1.432 (5)	6	27–32	1.431 (17)	8	9, 33
$(O–O)_{peroxo}$, $MO(O_2)_2$	1.465 (4)	8	22, 34–40	1.471 (11)	18	9, 41
$M–O_{peroxo}$, $MO(O_2)$	1.876 (7)	6	27–32	1.918 (5)	8	9, 33
$M–O_{peroxo}$, $MO(O_2)_2$	1.879 (6), 1.914 (14)	8	22, 34–40	1.924 (12), 1.961 (13)	18	9, 41

crystal	O–O dist,[c] Å	M–O dist,[d] Å	ref
$K_3[VO(O_2)_2(ox)]\cdot H_2O$	1.451 (6), 1.460 (6)	1.861 (5), 1.923 (12)	34
$K_2[MoO(O_2)_2(ox)]$	1.466 (2), 1.480 (2)	1.940 (2), 1.959 (2)	42
$K_2[WO(O_2)_2(ox)]$	1.496 (10), 1.510 (10)	1.934 (7), 1.966 (2)	43
$(NH_4)_3F[MoF_4O(O_2)]$	1.434 (8)	1.903 (5), 1.917 (5)	44
$(NH_4)_3F[WF_4O(O_2)]$	1.435 (20)	1.905 (12), 1.937 (12)	44

[a] The peroxo ligands in the oxodiperoxometalates are asymmetrically bonded to the metal. [b] Average values of the bond distances are listed; the number of structures considered is listed under number. Numbers in parentheses are average deviations of the mean values for the individual structures. [c] Estimated standard deviations are shown in parentheses. [d] Mean values with deviations from the mean shown in parentheses are listed for the oxo diperoxo complexes.

to the d^0 complex. We have previously obtained results[4] that indicate a much lower reactivity of an intermediate formulated as $MoO_2(O_2)(ox)(H_2O)^{2-}$ compared to the more stable diperoxo form $MoO(O_2)_2(ox)^{2-}$. The aquated monoperoxo species $Ti(O_2)^{2+}$ is much less reactive than even H_2O_2 toward a variety of oxidizable substrates.[5,6] While we have examined the reactions of the vanadium peroxo complexes only with (thiolato)cobalt(III), our previous studies indicate that the $k_{peroxo}:k_{H_2O_2}$ *ratio* is approximately independent of the substrate provided an inner-sphere pathway is available.

While the oxodiperoxovanadium(V) complexes are much more reactive than the monoperoxo forms, their rate constants are only marginally larger than those determined for hydrogen peroxide. Protonation, presumably at a peroxo ligand, enhances the reactivity but only by a relatively small amount. Little difference is seen if heteroligands rather than coordinated water molecules are present. What is of paramount importance in determining the activation of coordinated peroxide is the identity of the metal center in the oxo diperoxo complexes. The rate constants for H_2O_2 and the oxo diperoxo V(V), Mo(VI), and W(VI) species stand in the approximate order $1:10:10^4:10^5$. The more extensive studies with Mo(VI) and W(VI) indicate that the order applies for both oxygen atom transfer and inner-sphere, one-electron oxidations and that direct attack by the substrate at the peroxo ligand predominates. The relative acidities of the $MO(O_2)_2(H_2O)_2$ complexes are V(V) < Cr(VI) < Mo(VI) < W(VI), an ordering that parallels their reactivities (although data for Cr(VI) are very scarce).[23-26]

In spite of the abundance of kinetic, equilibrium, and structural data for the peroxo complexes, it is difficult to rationalize the enormous range of reactivities. Since breaking of the peroxo bond occurs in the rate-determining step of the reactions we have considered, one approach is to consider the $(O–O)_{peroxo}$ and $M–O_{peroxo}$ bond distances in available crystal structures. We have summarized these distances for structures determined with diffractometer data and with estimated standard deviations ≤0.010 Å in Table VII. We note that, for a given metal center (top half of Table VII), there is a significant increase in the O–O bond distance in the oxo diperoxo complexes relative to the oxo peroxo forms. In addition, while one $M–O_{peroxo}$ distance for each peroxo ligand in oxodiperoxometalates is comparable to those in the oxo peroxo species, there is a significant lengthening of the other bond.[45] Both of these features are consistent with a greater reactivity of the oxo diperoxo species. However, it is not clear that the structural data allow a convincing rationale as to why the oxo diperoxo complexes of Mo(VI) and especially W(VI) are so much more reactive than those of V(V). It may be that theoretical computations can provide valuable insights; a few calculations with the more symmetrical tetraperoxo complexes have been reported, but activation of the peroxo ligands in these species is not known.[46,47]

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