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Kinetics and Mechanism of Oxygen Atom Abstraction from Sulfenatocobalt(III) Complexes by Hydrated Methyldioxorhenium(V)

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Cationic sulfenatocobalt(III) complexes, with the remaining ligands amines, are deoxygenated upon reaction with hydrated methyldioxorhenium(V). The reactions of $(Am)_5Co-S(O)R^{2+}$ yield the thiolato complexes $(Am)_5Co-SR^{2+}$ and methyltrioxorhenium(VII), MTO. A kinetic study of these reactions was carried out, using the known reaction between MTO and hypophosphorous acid to prepare the Re(V) reagent in solution. The second-order rate constants between $(Am)_5Co-S(O)R^{2+}$ and $MeReO_2(aq)$, after correction for protonation, fall in the range 47−455 L mol^{-1} s^{-1} in aqueous solution at 25.0 °C and 1.0 M ionic strength. In the analysis of the pH effects, allowance was made for the formation of the protonated species $(Am)_5Co-S(OH)R^{3+}$ at high $[H_3O^+]$. The values of pK_a are in the range 0.49−0.96, as determined from fitting the rate−pH profiles.

Introduction

The rhenium(V) complex CH_3ReO_2, presumably the diaqua complex $CH_3ReO_2(OH_2)_2$ (aqua ligands hereinafter omitted), has been shown to abstract oxygen atoms from certain reagents, as in the reaction

$$XO + CH_3ReO_2 \rightarrow X + CH_3ReO_3 \qquad (1)$$

Examples of the XO reagents for this reaction include C_5H_5NO, R_2SO, Ar_3AsO, Ar_3SbO, etc.[1] The Re(V) reagent is so kinetically aggressive that even perchlorate ions react in a cascade of similar steps that eventually forms chloride ions:[2]

$$ClO_4^- \xrightarrow{CH_3ReO_2} ClO_3^- \xrightarrow{CH_3ReO_2} \rightarrow \rightarrow Cl^- \qquad (2)$$

The driving force for these reactions is the formation of a strong Re−O bond. The value of $\Delta G°$ for reaction 3 was

$$CH_3ReO_3(aq) \rightarrow CH_3ReO_2(aq) + O(g) \qquad (3)$$

established by kinetic methods to be 111 kcal mol^{-1}.[1] This value places a limit on the feasibility of substrates for reaction 2; phosphine oxides in place of perchlorate ions, for example, are unable to participate. On the other hand, the thermodynamic values tell only what is feasible. Dinitrogen monoxide, for example, does not react with CH_3ReO_2, despite the favorable value $\Delta G° = -30$ kcal mol^{-1}, which clearly shows the reaction is spontaneous.

Since oxygen atom transfers hold biological and industrial relevance,[3,4] and are of fundamental interest as well, it seemed useful to extend the essence of reaction 1 to a broader and potentially more demanding range of substrates. In this study we consider the reactions of certain sulfenato complexes that are the analogues of organic sulfoxides. Thiols (e.g., from cysteine) are oxidized in a protein environment.[5] It should be noted that considerable research on the oxidation of nickel and palladium sulfenates and sulfinates has been reported.[6] We have examined cobalt(III) complexes, $(Am)_5Co-S(O)_nR^{2+}$ (Am = amine, $n = 1, 2$).[5] The structural formulas of the sulfenato ($n = 1$) complexes are displayed in Chart 1 designated with the suffix **b**; the suffix **a** is used for thiolate ($n = 0$) and **c** for sulfinato ($n = 2$) complexes, whose structures are not explicitly shown.

Results and Discussion

The UV−vis spectral data of the thiolato- and sulfenatocobalt complexes are given in Table S-1 (Supporting Information). The thiolates have a characteristic LMCT band near 285 nm. The sulfenates have an intense peak near 365 nm. Certain special cases deserve mention. Complex **4** can exist as either of two isomers. The geometry for complex **4b** depicted in Chart 1 presents the structure determined from the ^{13}C NMR spectrum.[7] The trien complex **5a** was also made in the course of this study. It was fully characterized and analyzed. Since it was otherwise difficult to spectroscopically ascertain with certainty the geometry, its structure was determined by crystallography. [8] The trien ligand adopts the β mode of coordination in which three of the nitrogen atoms of the ligand are in the equatorial plane of the complex,[8] as displayed in Chart 1.

Efforts then were directed toward the sulfenato series. The conditions for preparing solutions of CH_3ReO_2 useful for kinetics are demanding. The acid concentration must be high; we chose 0.1−1.0 M H_3O^+ for the most part. Without that, the colorless solutions of CH_3ReO_2 turned a blue color that strongly

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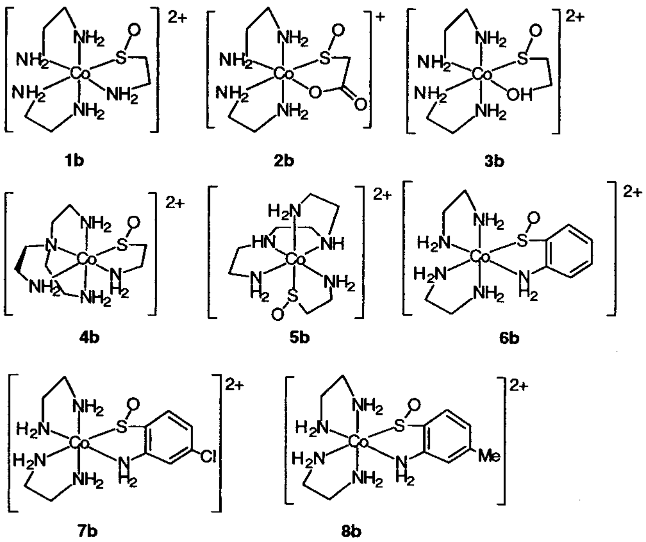
Chart 1



intensified with time, ultimately depositing a blue-black solid. This material contains an intact Re−CH_3 group, since its treatment with hydrogen peroxide generates the well-known peroxo complex $CH_3Re(O)(\eta^2\text{-}O_2)_2(OH_2)$.[1] Another requirement for the kinetic studies is that the total rhenium concentration be kept quite low (usually <0.25 mM) for the same reason. We presume the blue substance to be $[CH_3ReO]_2(\mu\text{-}O)_2$, by analogy to the derivative with Cp* in place of CH_3.[9] Solutions of CH_3ReO_2 were made by reducing CH_3ReO_3 with aqueous hypophosphorous acid:

$$CH_3ReO_3 + H_2P(O)OH \rightarrow CH_3ReO_2 + HP(O)(OH)_2 \qquad (4)$$

The reaction is not particularly rapid ($k_4 = 2.8 \times 10^{-2}$ L mol^{-1} s^{-1} at 298 K), but that causes no difficulty. Solutions of CH_3ReO_2 so prepared are stable for 1−3 h.

The general procedure for the kinetics studies was to generate CH_3ReO_2 first and then add the sulfenato complex. Its concentration could be set much smaller than that of CH_3ReO_2, given the strong absorption bands; thus, first-order kinetics were closely followed. The reactions occur as in

$$CH_3ReO_2 + (Am)_5Co-S(O)R^{2+} \rightarrow CH_3ReO_3 + (Am)_5Co-SR^{2+} \qquad (5)$$

Kinetic data were obtained by monitoring the loss of the sulfenato complex or occasionally the buildup of the thiolato product. In some instances, CH_3ReO_3, $H_2P(O)OH$, and $(Am)_5Co-S(O)R^{2+}$ were mixed concurrently. The two reaction stages, reaction 4 followed by 5, occurred in sequence. The rate of reaction 4 is much lower than that of reaction 5, and the rate of conversion of the sulfenate to the thiolate complex was governed by it. The rates from these experiments were proportional to each of the concentrations of $H_2P(O)OH$ and CH_3ReO_3, and gave rate constants in the range $k_4 = (2.4(1)-2.7(1)) \times 10^{-2}$ L mol^{-1} s^{-1} at 298 K. This agrees with the accepted value, $k_4 = 2.8(2) \times 10^{-2}$ L mol^{-1} s^{-1}.[1] The rate constant of reaction 4 was insensitive to the value of $[H^+]$ in the range 0.20−1.0 M. The rate constant of reaction 5 was also determined in aqueous acetonitrile (1:1): $k_4 = 3.7(3) \times 10^{-3}$ L mol^{-1} s^{-1} at 298 K, some 7 times lower than in aqueous solution. This is not simply the effect of a presumably innocent solvent change. It appears as if, to an appreciable but undetermined extent, that acetonitrile has replaced the solvating water molecules coordinated to the rhenium atom of CH_3ReO_2.

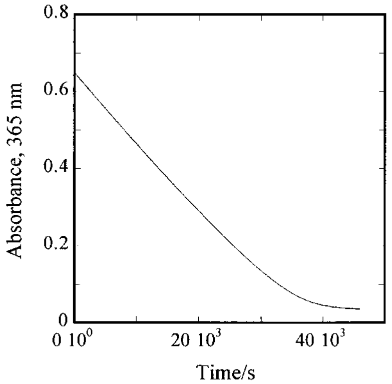


Figure 1. Absorbance−time recording of the reaction between $(\mathbf{1b})Cl_2$ (1.0 mM) and $H_2P(O)OH$ (50 mM) catalyzed by CH_3ReO_3 (84 μM). Conditions: 0.13 M HCl in 1:1 aqueous acetonitrile at 298 K.

It followed that a catalytic system could be constructed, featuring the repetitive cycling of the two rhenium species through reactions 4 and 5 in sequence, with the anticipated result

$$H_2P(O)OH + (Am)_5Co-S(O)R^{2+} \rightarrow HP(O)(OH)_2 + (Am)_5Co-SR^{2+} \qquad (6)$$

Figure 1 shows data for one such experiment for $(\mathbf{1b})Cl_2$. It was carried out with 84 μM MTO, 1.0 mM $(\mathbf{1b})Cl_2$, and 50 mM $H_2P(O)OH$. The absorbance of species **1b** fell to nearly zero, consistent with reaction 6 going to completion. During most of the course of the reaction, the data follow zero-order kinetics. This is consistent with reaction 4 being rate-controlling, since the concentration of $H_2P(O)OH$ remains effectively constant because it is present in large excess and because it is the catalyst and is continuously regenerated.

For the study of reaction 5, solutions of CH_3ReO_2 were prepared by the prior reaction of CH_3ReO_3 with excess $H_2P(O)OH$. After the necessary time had passed (5 half-lives for reaction 4), the sulfenatocobalt complex was then added. Its concentration was chosen to be $\leq 10[MeReO_2]_0$. The reaction was followed at one or more appropriate wavelengths. The data at each wavelength were fitted to pseudo-first-order kinetics. To do so, a nonlinear least-squares fit to the rate law in eq 7

$$Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\exp(-k_\psi t) \qquad (7)$$

was carried out. For each complex, the plot of k_ψ against the total rhenium concentration of the cobalt complex was linear. This treatment establishes that reaction 5 follows mixed second-order kinetics.

The sulfenatocobalt complexes are known to be weak Brønsted bases:

$$(Am)_5Co-S(OH)R^{3+} \rightleftarrows H^+ + (Am)_5Co-S(O)R^{2+} \qquad (K_a) \quad (8)$$

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(8) X-ray crystal data for $C_8H_{24}Cl_2CoN_5O_8S$: monoclinic, $P2_1/n$, a = 8.900(4) Å, b = 12.458(5) Å, c = 15.974(5) Å, b = 90.00(1), V = 1771.2(12) Å^3, Z = 4, T = 173(2) K, D_{calcd} = 1.801 g/cm^3, $R(F)$ = 14.78% [$I = 2\sigma(I)$]. Owing to the poor crystal quality only the atom connectivity was established with certainty. The software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

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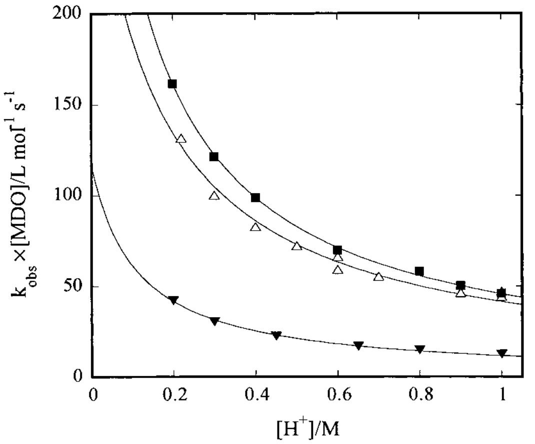

Figure 2. pH profiles for selected sulfenato complexes. The lines represent least-squares fitting to eq 9. Data are shown for complexes **1b** (open triangles), **4b** (filled triangles), and **6b** (squares).

Table 1. pK_a Values for Sulfenatocobalt(III) Complexes and Kinetic Data for Oxygen Atom Transfer Reactions from Sulfenatocobalt(III) and CH_3ReO_2 Complexes[a]

entry	k_5/(L mol^{-1} s^{-1})	pK_a (kinetics)	pK_a (equil)
1b	305(37)	0.74	~0.1
2b	355(24)	0.49	0.4−0.5
3b	220(46)	0.72	
4b	116(13)	0.96	
5b	47(2)	0.60	$0.1-0.1_3$
6b	430(20)	0.92	
7b	455(20)	0.92	0.05
8b	312(16)	0.72	
Me_2SO	15.2[b]	−1.5[c]	
PhS(O)Me	17[b]		
p-TolS(O)Me	21[b]		

[a] At 298 K and ionic strength 1.0 M. [b] Reference 1. [c] Reference 20.

Consequently, the reaction rates will likely show a pH effect, regardless of any involvement of H^+ (or lack thereof) in the mechanism, except in the case where the two cobalt species fortuitously have the same reactivity. The predominant species of the sulfenatocobalt reagents changes with the hydrogen ion concentration. Experiments were carried out in which [H^+] was varied in the range (usually) 0.10−1.00 M. In every case the apparent rate constant decreased with increasing [H^+], from which one infers that only $(Am)_5Co-S(O)R^{2+}$, and not its conjugate acid, reacts with CH_3ReO_2. This postulate seems quite reasonable because the proton of the conjugate acid would block the point of attack of the rhenium (or, would block the basic site that would reasonably be the atom that attacks the Lewis acid). To explore the validity of this postulate, the data at a given [H^+] were represented by an apparent second-order rate constant, k_{app}. Its value would vary with [H^+] according to

$$k_{app} = k_5/(1 + [H^+]/K_a) \tag{9}$$

where k_5 represents the actual second-order rate constant for the species $(Am)_5Co-S(O)R^{2+}$ reacting with CH_3ReO_2. The pH profiles for several sulfenato complexes are presented in Figure 2. The smooth curves through the points are the nonlinear least-squares fits to eq 9. The values of pK_a are given in Table 1.

This treatment allows a comparison between values of the kinetically determined parameter pK_a and those found by specific equilibrium determinations. One such value has been reported previously: pK_a = 0.15(3) for **1b**.[5a] Three other values of pK_a were determined directly during the course of these studies. The basis for these determinations is the significant change in the UV−vis spectrum that accompanies the shift in position of reaction 7. Figure S-3 shows a family of juxtaposed spectra of complex **1b** taken over the [H^+] range of interest.

Table 1 presents both sets of pK_a values. In some cases the agreement is excellent, in others only fair. Considering the extrapolations being made, the overall adherence to the proposed reaction scheme seems acceptable. Certainly there is no *simple* alternative that would suffice. In all cases pK_a(kinetic) < pK_a(equil). Equation 9 could be brought into agreement with the independent value of pK_a by having an added numerator term, as in

$$k_{app} = (k_5 + k_5'[H^+]^{-1})/(1 + [H^+]/K_a) \tag{10}$$

in which the term k_5' represents a *conjugate base* (CB) enhancement. This alternative is not without a certain appeal in the molecular mechanism, but no independent evidence for it could be obtained. Moreover, there is a case in which the two pK_a values agree well. There is no reason to admit the possibility of the CB interpretation in certain cases, only to disallow it in others. Furthermore, the k_5' value needed to accommodate the fits is unreasonably large. For these reasons we return to the simpler scheme.

The noteworthy features of the data are these: the sulfenato complexes transfer an oxygen atom to CH_3ReO_2 readily enough, whereas their O-protonated forms do not. The sulfinato complexes do not suffer oxygen loss upon treatment with CH_3ReO_2. That feature is not unique with these Co(III) complexes: sulfones themselves, R_2SO_2, do not transfer an oxygen atom to CH_3ReO_2, whereas sulfoxides do so readily. Clearly, coordination, ionic charge, etc. do not provide the difference. The failure of sulfones and sulfinatocobalt(III) complexes must also be examined in light of the comparative bond energies. It is well-known that sulfur−oxygen bond free energies of sulfones are greater than those of sulfoxides. This amounts to a difference of 25 kcal. For example, the family of reactions $R_2SO_n \rightarrow R_2SO_{n-1} + O(g)$ has the following values of bond dissociation energies (kcal mol^{-1}): 112 (R = Me) and 113 (R = Ph) for sulfones (n = 2), as compared to 86.6 (R = Me) and 89.3 (R = Ph) for sulfoxides (n = 1).[10]

We assert, however, that the higher value of the driving force is (a) thermodynamically insufficient to prevent the reaction of sulfones and sulfinates, given $\Delta G°$ = 111 kcal for reaction 3, (b) incidental, as bond enthalpy values, although providing a prerequisite for reaction, seem largely immaterial to the question of reactivity (it should be noted that even N_2O_{aq}, with $\Delta G°$ = 82 kcal, the weakest oxygen bond of all those considered, fails to react with CH_3ReO_2), and (c) not at all reflected in the rate constants for the transfer of an oxygen atom *to* a sulfur of an organic sulfide or sulfoxide,[11] as shown in

$$CH_3Re(O)_2(\eta^2\text{-}O_2) + R_2SO_{n-1} \rightarrow CH_3ReO_3 + R_2SO_n \tag{11}$$

for which $k(Ph_2S)^{11} = 1.2 \times 10^2$ L mol^{-1} s^{-1} and $k(Ph_2SO)$ = 0.91 L mol^{-1} s^{-1}. The analogous trend has been established for the sequence **1a** → **1b** → **1c**.[12] The analogous rate constants with these sulfur compounds are k(**1a**) = 4.3 × 10^3 L mol^{-1} s^{-1} and k(**1b**) = 3.05 × 10^2 L mol^{-1} s^{-1} at 298 K. With and without cobalt, the gross trend is much the same.

These values are instructive, illustrating that the stronger S−O bonds of the sulfones and sulfinatocobalt(III) complexes form more slowly. The rate constants are sufficiently similar that it

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seems as if ionic charge on the cobalt participant is nearly without effect, or at least not of a constant influence. What is important in determining the rates of the first step of reaction 11 relative to the second is, or appears to be, the existence or absence of an electronegative oxygen atom on the sulfur to which the oxygen is being transferred. These reactions, best regarded as the attack of a sulfur nucleophile on an oxygen of the η^2-peroxide group, are highly sensitive to the extra oxygen atom, the reactivity being reduced accordingly.

The nature of the S−O bond in sulfoxides has been debated.[13] The issue centers on whether a true (full) double bond exists. In view of the large dipole moments of dialkyl- and diarylsulfoxides, little π-bonding may exist.[13] Consequently these bonds are weaker than in, for example, phosphine and arsine oxides. Moreover, the typical bond strength of a sulfoxide is ca. 25 kcal mol^{-1} weaker than that of a sulfone. An exception arises when an electronegative atom or group is placed on the sulfur, which strengthens the S−O bond; for example, F_2SO and $(MeO)_2SO$ have bond strengths of ca. 118 kcal, compared to 87 kcal for M.[14]

The stability of the sulfenatocobalt(III) complexes has been attributed, at least in part, to π back-bonding of the $(t_{2g})^6$ configuration into a vacant π orbital on sulfur,[5b] in competition with the O → S π bonding. This competition for vacant orbitals on sulfur makes it seem reasonable that the sulfenatocobalt complexes are more reactive than organic sulfoxides. This effect manifests itself elsewhere. Sulfenatochromium(III) complexes, not stabilized in this fashion, are not formed upon oxidation of the thiolato complexes.[5b] In addition, this orbital picture explains the basicity of the oxygen atom of the sulfenato complexes, reaction 8, despite the overall 2+ ionic charge.

With that in mind, we return to the principal subject. Oxygen transfer from the SO/SO_2 group, attached to cobalt(III) or not, can also be depicted as a nucleophilic reaction in which the oxygen attacks the d^2 rhenium(V) center. The rhenium(V) center is surely electropositive; oxygen attack on it will be more favored for the sulfenate (lacking a second electronegative oxygen atom) over the sulfinate.

Experimental Section

Materials. High-purity water was obtained by passing laboratory-distilled water through a Millipore-Q water purification system. Many substances were obtained from commercial sources, although certain disulfides, 2-amino-4-chlorophenyl disulfide and 2-amino-4-methylphenyl disulfide, were prepared from a literature procedure in which dinitrotrisulfides were first obtained from 4-chloro-3-nitrotoluene or 2,5-dichloronitrobenzene.[15] The substituted dinitrodisulfides bis(2-amino-4-methylphenyl) trisulfide and bis(2-amino-4-chlorophenyl) trisulfide were reduced with $LiAlH_4$.[16] The reaction in ether was quenched with a minimum amount of water and then filtered. The substituted disulfides were recovered once the ether was removed, and the thiol was oxidized by air. No IR bands were observed in the S−H region, 2550−2600 cm^{-1}, indicating complete oxidation.

Thiolates and sulfenates were prepared according to literature procedures or slight modifications thereof. *Caution; some of the compounds were isolated as perchlorate salts; although no problems were encountered, the possibility of explosion hazard should be noted.* Chart 1 shows the sulfenate series; an analogous series of thiolates (**a**) and sulfinates (**c**) can be considered. The following compounds were synthesized by literature methods[5,17] and isolated: (**1a**)Cl$_2$,[5,17] (**1b**)Cl$_2$,[5,17] (**2a**)(ClO$_4$)$_2$,[17] (**3a**)ClO$_4$,[18] (**4a**)(ClO$_4$)$_2$,[7] and (**5a**)(ClO$_4$)$_2$.[18] Compound (**6a**)(ClO$_4$)$_2$ was prepared by a variant of the literature method,[19] in which 6 M HOTf (CF_3SO_3H) was added instead of concentrated $HClO_4$ and cobalt triflate used in place of the perchlorate. Argon was passed through to evaporate the remaining THF, giving a precipitate that was taken up in the minimum amount of water. Cooling gave a tarry residue, which was again dissolved in the minimum amount of water and filtered. Excess sodium perchlorate was then added; crystals formed on allowing this preparation to stand overnight at 10 °C. The following compounds were prepared analogously: (**7a**)(ClO$_4$)$_2$, (**8a**)(ClO$_4$)$_2$. The following analyses were carried out:

	found (calcd)		
compound	C	H	N
(**5a**)(ClO$_4$)$_2$ ($C_8H_{24}N_5SCoCl_2O_8$)	19.75 (20.02)	4.83 (5.04)	14.22 (14.59)
(**6a**)(ClO$_4$)$_2$ ($C_{10}H_{22}N_5SCoCl_2O_8$)	24.34 (23.92)	4.23 (4.42)	13.69 (13.95)
(**7a**)(ClO$_4$)$_2$ ($C_{10}H_{21}N_5SCoCl_3O_8$)	22.17 (22.38)	3.54 (3.94)	12.74 (13.05)
(**8a**)(ClO$_4$)$_2$ ($C_{11}H_{24}N_4SCoCl_2O_8$)	25.70 (25.59)	4.46 (4.65)	12.87 (13.56)

Perchlorate complexes are convenient for isolation, but are entirely unsuited for these studies because reaction 2 occurs readily. The thiolato complexes were stirred with Dowex 1-X8 anion-exchange resin in the chloride ion form for at least 10 min. Sulfenato complexes are so soluble that, except for (**1b**)Cl$_2$, crystallizing them from solution is difficult. They were formed in solution by oxidation with hydrogen peroxide[5] once the resin had been removed by filtration. In the case of solution complexes **2b**, **3b**, **4b**, and **5b**, the ca. 2 mM solution was treated with hydrogen peroxide; it was added in 80% of the requisite quantity to avoid overoxidation. Complexes **6b**, **7b**, and **8b** were converted at the ca. 10 mM level to the sulfenato complex in solution, which was diluted to 2 mM and converted to the chloride form by the ion-exchange procedure described previously.

Kinetic Studies. Rate constants were determined spectrophotometrically at 25.0 ± 0.1 °C. In all the kinetics experiments in aqueous solution the ionic strength was adjusted to 1.00 M with HCl and LiCl. Stock solutions of MTO in 1.00 M HCl were prepared daily and used within 24 h. The MTO concentration was checked by its UV spectrum: $\lambda_{max} = 239$ and 270 nm ($\epsilon = 1900$ and 1300 L mol^{-1} cm^{-1}, respectively). The UV−vis spectra of the thiolato and sulfenato complexes are given in Table S-1.

Control experiments were performed to show that there is no uncatalyzed reaction between the sulfenato complexes and hypophosphorous acid. In a few reactions, the sulfenatocobalt(III) complex was used in excess. In such cases either MTO or $H_2P(O)OH$ was added last, and the disappearance of the cobalt complex monitored at 360 nm, where it has an intense absorption band (Table S-1). More commonly, the solution of CH_3ReO_2 was prepared first, monitoring the solution at 290 nm, and waiting about 4 half-times for reaction 4. The sulfenate complex was then added, and the kinetics monitored at $\lambda_{max} = 360{-}372$ nm. Concentrations used were 50 mM $H_2P(O)OH$, 0.22 mM total rhenium, and 0.010−0.015 mM cobalt. In a few experiments buildup of the thiolate complex was monitored at 282 nm.

Data were analyzed according to first-order kinetics, eq 7. In the case of **3b** the initial rate method was used. The absorbance values were converted to concentrations, and the values fit to a ninth-order polynomial, which gives the initial rate v_i. The initial rate was obtained by dividing v_i by $[\mathbf{3b}]_0$. The v_i of a polynomial function of 4−9 terms proved largely immaterial, although the scatter of the initial rates so calculated was ca. 8−10%.

Spectrophotometric Titrations. The UV−vis spectra of selected sulfenatocobalt complexes were recorded at different H_3O^+ concentrations in the range 0.1−1.0 M, with the ionic strength adjusted to 1.00 M. The data, mostly in the region 360−367 nm, were fit to an equation that describes the equilibrium in reaction 8 in terms of the acid concentration, the total cobalt concentration, and the molar absorptivities

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of acid and base forms. Least-squares fitting gave the value of the acid ionization constant K_a.

$$\frac{\text{Abs}}{l[\text{Co}]_T} = \frac{\epsilon_B K_a + \epsilon_A[\text{H}^+]}{K_a + [\text{H}^+]} \tag{12}$$

In one case the sulfenato was titrated with small aliquots of sodium hydroxide. The same data analysis applies.

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Supporting Information Available: Table giving UV−vis spectral data for thiolato- and sulfenatocobalt(III) compounds, figure showing juxtaposed UV−vis spectra for **1b**, and plots of kinetic data to illustrate agreement with selected mathematical forms and to evaluate numerical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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