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Kinetics and Mechanism of the Reaction of Hydrogen Peroxide with Thiolato Complexes of Cobalt(III) and Chromium(III). Comments on the Nucleophilicity of Coordinated Sulfur and the Stability of Coordinated Sulfenic Acids

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Kinetics of the reaction of H_2O_2 with the 11 thiolato complexes $[(H_2O)_5CrSCH_2CH_2NH_2]^{3+}$, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$, $[(H_2O)_4Cr(SCH_2COO)]^+$, $[(en)_2M(SCH_2CH_2NH_2)]^{2+}$, $[(en)_2M(SCH_2COO)]^+$, $[(en)_2M(SC(CH_3)_2COO)]^+$, $[(en)_2Cr(SCH_2CH_2COO)]^+$, and $[(en)_2Co(SCH(CH_3)COO)]^+$, where M = Co and Cr, have been investigated in aqueous media. All cobalt(III) complexes undergo 2-equiv oxidation to isolable S-bonded sulfenic acid complexes, while all chromium(III) complexes undergo Cr–S bond fission via a presumed unstable sulfenato–chromium(III) intermediate. The mechanism of these reactions is taken to be nucleophilic attack by coordinated sulfur on the O–O peroxide bond. With respect to this process, coordinated thiols are potent nucleophiles, about equivalent to thiosulfate. When bonded to cobalt(III), thiols are significantly better nucleophiles than when bonded to chromium(III), presumably due to greater π back-bonding in the cobalt system. The rate law takes the form rate = k_2[Nuc][H_2O_2], and typical rate and activation parameters are $k_2 = 1.13$ (2) $M^{-1} s^{-1}$, $\Delta H^* = 9.7$ (2) kcal/mol, and $\Delta S^* = -26$(1) eu (for $[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$, 25 °C, $\mu = [HClO_4]$ = 1.00 M). The reactivity patterns for H_2O_2 oxidation of analogous chromium and cobalt complexes are very similar but are different from the reactivity pattern exhibited for normal aquation of thiolato–chromium(III) complexes. All oxidation reactions show a slight acid dependence of the generalized form $k_2 = a + b[H^+]$, typical for oxidation by H_2O_2 and $H_3O_2^+$. The ratio b/a ranges from 1.5 to 3.0 M^{-1}, these small values being consistent with attack by cationic nucleophiles. The rate of H_2O_2 oxidation of a coordinated thiol is relatively insensitive to the nature of the thiolato complex (thiolato chelate ring size or steric requirements, ancillary ligands, etc.). However, the rate of H_2O_2 oxidation of a coordinated sulfur atom is very sensitive to the steric requirements of the sulfur atom, two-coordinate sulfur being oxidized more than 10^3 times faster than three-coordinate sulfur.

Introduction

In a previous paper[1] we have characterized stable, S-bonded, sulfenato–cobalt(III) complexes prepared by the H_2O_2 oxidation of chelated thiolato–cobalt(III) complexes (e.g., eq 1).

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + H_2O_2 \rightarrow$$
$$(en)_2Co(S(O)CH_2CH_2NH_2)^{2+} + H_2O \quad (1)$$

Since free sulfenic acids are very unstable molecules,[2,3] coordination to cobalt(III) induces a considerable stabilizing influence on the sulfenato moiety.[1,4–6] However, in earlier work[7] we had noted that the H_2O_2 oxidation of a monodentate thiolato–chromium(III) complex led to Cr–S bond fission with no indication of a sulfenato–chromium(III) intermediate (eq 2). This observation raises the possibility that chromium(III)

$$(H_2O)_5CrSC_6H_4NH_3^{3+} + H_2O_2 \rightarrow$$
$$(H_2O)_6Cr^{3+} + \text{organic products} \quad (2)$$
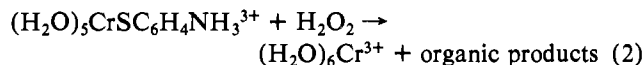
does not stabilize the sulfenato moiety to the same extent as does cobalt(III). As part of our continuing research into the chemistry of coordinated sulfenic acids, we decided to examine this possibility through investigation of the kinetics and mechanism of the H_2O_2 oxidation of analogous thiolato–cobalt(III) and thiolato–chromium(III) complexes (e.g., $[(en)_2M(SCH_2CH_2NH_2)]^{2+}$, where M = Co and Cr). This study was also designed to yield information on how various factors (central metal identity, nature of ancillary ligands, thiolato chelate ring size, steric strain, etc.) affect the nucleophilicity of the coordinated thiol. The nucleophilicity of coordinated sulfur seems to be very important in governing

the chemistry and reactivity of sulfur-containing complexes,[1,5,8–10] just as the nucleophilicity of noncoordinated sulfur molecules is crucial to the chemistry and reactivity of these species.[11,12] The results of these studies are described herein.

Experimental Section

Materials. All common laboratory chemicals were of reagent grade. Kinetic experiments employed triply distilled water[10] and doubly distilled perchloric acid (70–72%, G. F. Smith). Lithium perchlorate was prepared from Baker "Ultrex" lithium carbonate.[13] Dowex 50W-X2 (200–400 mesh) cation-exchange resin was cleaned as previously described.[14] Sephadex SP-C25 (sodium form) cation exchanger was prepared and stored as recommended by the manufacturer (Pharmacia). Perchlorate salts of (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)cobalt(III), (mercaptoacetato-*O,S*)bis(ethylenediamine)cobalt(III), (2-mercaptopropionato-*O,S*)bis(ethylenediamine)cobalt(III), (2-mercapto-2-methylpropionato-*O,-S*)bis(ethylenediamine)cobalt(III), (2-mercaptoethylamine-*N,S*)bis(ethylenediamine)chromium(III), and (mercaptoacetato-*O,S*)bis(ethylenediamine)chromium(III) were available from previous studies.[1,15,16] Solutions of pentaaquo(2-mercaptoethylammonium-*S*)chromium(III), pentaaquo(4-thioanilinium-*S*)chromium(III), and tetraaquo(mercaptoacetato-*O,S*)chromium(III) were prepared, and purified by ion-exchange chromatography, according to published procedures.[7,15,17] The disulfides 3,3'-dithiodipropionic acid and 2,2'-dimethyl-2,2'-dithiodipropionic acid were prepared by H_2O_2 oxidation of the corresponding thiols; thiopropionic acid was obtained from Aldrich, and thioisobutyric acid was kindly donated by H. J. Price of Eastman Kodak.

(3-Mercaptopropionato-*O,S*)bis(ethylenediamine)chromium(III) Perchlorate and (2-Methyl-2-mercaptopropionato-*O,S*)bis(ethylenediamine)chromium(III) Perchlorate, [(en)_2Cr(SCH_2CH_2COO)]ClO_4

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Table I. UV–Visible Spectrophotometric Parameters for Selected Chromium(III) and Cobalt(III) Complexes Containing O,S-Chelated Ligands

complex	λ_{max} $(\epsilon)^a$
Thiolato–Chromium(III) Complexes	
[(en)₂Cr(SCH₂COO)]⁺ ^{b}	500 (99), 385 (91), 310 (1000), 250 (7440)
[(en)₂Cr(SCH₂CH₂COO)]⁺	510 (88), 395 (65), 258 (6050)
[(en)₂Cr(SC(CH₃)₂COO)]⁺	495 (94), 385 (87), 310 (1100), 251 (7420)
Thiolato–Cobalt(III) Complexes^c	
[(en)₂Co(SCH₂COO)]⁺	518 (152) 282 (11 700)
[(en)₂Co(SC(CH₃)₂COO)]⁺	514 (153) 282 (10 900)
Sulfenato–Cobalt(III) Complexes^c	
[(en)₂Co(S(O)CH₂COO)]⁺	493 (350), 360 (6000), 285 (3100)
[(en)₂Co(S(O)C(CH₃)₂COO)]⁺	486 (440), 364 (4500), 289 (4700)

^{a} Wavelengths, λ, of maxima (max) are in nanometers. Molar extinction coefficients, ϵ, given in parentheses, are in M⁻¹ cm⁻¹. Spectra are recorded in dilute aqueous perchloric acid. ^{b} Data from ref 16. ^{c} Data from ref 1.

and [(en)₂Cr(SC(CH₃)₂COO)]ClO₄. These complexes were synthesized by reduction of the appropriate disulfide with ethylenediamine–chromium(II) mixtures according to a previously detailed procedure.[16] All manipulations were conducted under rigorously anaerobic conditions. In a typical preparation, 10 g of >5 N chromium metal (0.2 mol) was dissolved in 36.2 mL of 70% HClO₄ that had been diluted with water to a total volume of 300 mL. To this chromium(II) solution was added 0.4 mol of ethylenediamine as a 10% v/v aqueous solution. The resultant deep blue solution was oxidized with 0.1 mol of disulfide dissolved in methanol, and the reaction mixture was then vigorously stirred at room temperature for ca. 1 h. The purple mixture was filtered and the filtrate neutralized with HClO₄ before being reduced in volume to ca. 100 mL. Addition of an equal volume of saturated aqueous NaClO₄ solution to the concentrated filtrate, followed by cooling at ca. 4 °C overnight, yielded deep purple crystals. This product was recrystallized from aqueous NaClO₄ and then from water. Overall yield of the 3-mercaptopropionato product was usually less than 10%, while yield of the 2-methyl-2-mercaptopropionato product was usually in the range 20–40%. Anal. Calcd for [(en)₂Cr(SCH₂CH₂COO)]ClO₄: C, 22.37; H, 5.37; N, 14.91; S, 8.53; Cr, 13.84. Found: C, 22.22; H, 5.44; N, 14.82; S, 8.30; Cr, 14.04. Calcd for [(en)₂Cr(SC(CH₃)₂COO)]ClO₄: C, 23.56; H, 5.93; N, 13.74; S, 7.34; Cl, 8.69; Cr, 12.75. Found: C, 23.90; H, 6.04; N, 13.84; S, 7.69; Cl, 8.80; Cr, 12.71. UV–visible spectrophotometric parameters for these complexes are given in Table I.

Analyses. Elemental analyses of solid samples and analyses of aqueous solutions for total sulfur content were performed by Galbraith Laboratories, Inc. Total cobalt analyses were performed by a modified Kitson procedure[18] while total chromium was spectrophotometrically determined as chromate (ϵ_{373} 4815 M⁻¹ cm⁻¹) following alkaline H₂O₂ oxidation.[19] Stock solutions of H₂O₂ used in kinetic experiments were stored at ca. 4 °C in the dark and standardized every 2 weeks by spectrophotometric titration at 350 nm against standard Ce(IV) solutions. The reducing power of thiol solutions was determined by a modification of the method of Grassetti and Murray[20] in which 2-thiopyridone, produced by the thiol reduction of 2,2′-dithiodipyridine, is spectrophotometrically monitored.[21]

Equipment. UV–visible spectra were recorded on a Cary 14 spectrophotometer at room temperature. Kinetic data were obtained on a Cary 118B spectrophotometer equipped with a thermostated sample compartment that maintained the temperature to within ±0.1 °C, the temperature being known with an accuracy of ±0.3 °C. Computer calculations were performed on an IBM 370/168 or an AMDAHL 470/V6 located at the University of Cincinnati.

Kinetic Measurements and Calculations. All kinetic experiments were conducted in aqueous perchloric acid solutions maintained at a constant ionic strength of 1.00 ± 0.01 M with LiClO₄. Most experiments were conducted with μ = [HClO₄] = 1.00 ± 0.01 M. Reactions of cobalt(III) complexes were monitored at the 360-nm band characteristic of the S-bonded sulfenato product.[1] Reactions of chromium(III) complexes were monitored at the 250-nm ligand-to-metal charge-transfer (LTMCT) band characteristic of the thiolato starting material.[16] Reactions were conducted with pseudo-first-order concentration excesses of H₂O₂ and H⁺ maintained over the metal complex concentration (usualy present initially in the range (1–2) × 10⁻³ M) and were monitored for at least 4 half-lives. All reactions followed first-order kinetics; the two standard methods previously described[1] were used to calculate the pseudo-first-order rate constant, k^{obsd}, and its associated standard deviaton, σ_k, for a given kinetic experiment. Activation parameters were calculated within the Eyring formalism[22] by using a previously described nonlinear least-squares procedure.[23] In all calculations, individual values of k^{obsd} were weighted as $(1/\sigma_k)^2$. All reported errors are standard deviations.
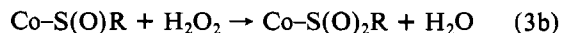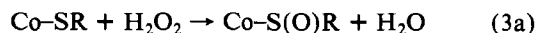
Procedures. Formal charges on complexes were inferred from the characteristics of their elution from Dowex 50W-X2 (200–400 mesh, H⁺ or Li⁺ form) ion-exchange columns which had been calibrated with ions of known formal charge.[10,17]

Results

Characterization. All of the thiolato–cobalt(III) complexes, all of the sulfenato–cobalt(III) complexes, and all but two of the thiolato–chromium(III) complexes used in thus study have been previously reported and characterized[1,7,15-17] (several by single-crystal X-ray structure analyses[1,24]). The two new additions [(en)₂Cr(SCH₂CH₂COO)]⁺ and [(en)₂Cr(SC-(CH₃)₂COO)]⁺ are characterized by (1) elemental analyses of isolated perchlorate salts which give empirical compositions in agreement with those predicted, (2) cation-exchange elution characteristics which are consistent with the assigned +1 formal charge, and (3) UV–visible spectrophotometric parameters (Table I) which are very similar to those observed[16] for the analogous complex [(en)₂Cr(SCH₂COO)]⁺, the formulation of which has been established by X-ray structure analysis.[24]

Table I lists spectrophotometric parameters for examples of the three types of complexes used in this study. Thiolato–chromium(III) complexes exhibit an intense LTMCT band at ca. 250 nm which is diagnostic for the presence of a Cr–S linkage.[16] Thiolato–cobalt(III) complexes exhibit an analogous band at ca. 280 nm,[8,25] the lower energy reflecting the greater oxidizing power of cobalt(III) relative to chromium(III). Sulfenato–cobalt(III) complexes exhibit a characteristic, intense band at ca. 360 nm,[1] although the origin of this band is not yet established, plus the LTMCT band at ca. 280 nm.[1]

Product Analysis. As previously reported,[1] H₂O₂ oxidation of (thiolato)bis(ethylenediamine)cobalt(III) complexes leads to S-bonded sulfenato complexes which exhibit an intense absorption at ca. 360 nm (e.g., eq 1). Further oxidation converts the sulfenato complex to a sulfinato complex[26] with concomitant disappearance of the 360-nm band. Both the sulfenato and sulfinato complexes exhibit the characteristic LTMCT band at ca. 280 nm, indicating that the Co–S linkage remains intact during the thiolato → sulfenato → sulfinato conversions (eq 3a,b). This behavior was exhibited by all the

$$Co-SR + H_2O_2 \rightarrow Co-S(O)R + H_2O \quad (3a)$$

$$Co-S(O)R + H_2O_2 \rightarrow Co-S(O)_2R + H_2O \quad (3b)$$

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Table II. Rate Parameters Describing the Reaction of H_2O_2 with (Thiolato)chromium(III) Complexes[a]

rate = $(k_1 + k_2[H_2O_2])$[complex]

complex	t, °C	$10^4 k_1$, s^{-1}	k_2, M^{-1} s^{-1}
$[(en)_2Cr(SCH_2COO)]^+$	13.4	3.07 ± 0.09	0.58 ± 0.01
	25.0	11.1 ± 0.2	1.13 ± 0.02
	35.0	33.0 ± 1.5	2.14 ± 0.16
$[(en)_2Cr(SCH_2CH_2COO)]^+$	13.4	2.75 ± 0.04	0.60 ± 0.01
	25.0	10.4 ± 0.1	1.19 ± 0.01
	35.0	29.7 ± 2.4	2.03 ± 0.25
$[(en)_2Cr(SC(CH_3)_2COO)]^+$	25.0	7.94 ± 0.17	0.16 ± 0.01
	33.8	21.2 ± 0.2	0.26 ± 0.01
	41.0	49.6 ± 0.2	0.40 ± 0.02
$[(en)_2Cr(SCH_2CH_2NH_2)]^{2+}$	13.4	b	0.54 ± 0.01
	25.0	b	1.13 ± 0.02
	35.0	b	1.96 ± 0.06
$[(H_2O)_5Cr(SCH_2CH_2NH_3)]^{3+}$	15.5	0.650 ± 0.001	0.089 ± 0.002
	25.5	2.30 ± 0.21	0.176 ± 0.008
	35.5	5.41 ± 0.34	0.324 ± 0.020
$[(H_2O)_4Cr(SCH_2COO)]^+$	16.5	0.594 ± 0.047	0.222 ± 0.003
	26.6	2.10 ± 0.20	0.445 ± 0.006
	36.5	8.00 ± 0.34	0.745 ± 0.011
$[(H_2O)_5CrSC_6H_4NH_3]^{3+}$	15.5	b	0.0187 ± 0.0003
	26.0	b	0.0451 ± 0.0006
	35.7	b	0.0767 ± 0.0017

[a] $\mu = [HClO_4] = 1.00$ M. [b] k_1 is statistically insignificant.

cobalt(III) complexes investigated in this study, and thus the reported kinetic parameters describe the rate of reaction 3a.

Hydrogen peroxide oxidation of all the thiolato–chromium(III) complexes investigated leads to cleavage of the Cr–S bond, manifested by disappearance of the characteristic LTMCT band at ca. 250 nm and a plethora of reaction products. The kinetic parameters reported for these reactions therefore describe the rate of H_2O_2-induced Cr–S bond fission.

Several experiments were conducted in order to determine something of the nature and distribution of the reaction products resulting from oxidation of $[(en)_2Cr(SCH_2COO)]^+$. (1) Ion-exchange separation of the product mixture (Table A[27]) yields a collection of noncoordinated sulfur-containing fragments, which are eluted before the chromium-containing species, plus three chromium containing fractions of estimated formal charges +2, +3, and >+3. These fractions are hereafter designated as the wash and bands I, II, and III. (2) For three different reaction conditions, the results of analyses for total chromium content and net reducing ability of these four fractions are given in Table A.[27] In all cases the wash contains the greatest reducing ability and the least (<3%) amount of chromium; bands I–III all contain significant amounts (>10%) of chromium but relatively low reducing ability. It is important to note that both free thiols and $[(en)_2Cr(SCH_2COO)]^+$ react quantitatively with 2,2′-dithiodipyridine[20,21] to yield 2-thiopyridone; thus this analytical procedure monitors the sum of free and chromium-bound thiol. Dithiodiglycolic acid does not reduce 2,2′-dithiodipyridine, and under the specific conditions used in this analysis,[20,21] the cobalt(III) complex $[(en)_2Co(SCH_2COO)]^+$ generates less than 20% of the expected 2-thiopyridone. (3) The data of Table B[27] show that the reducing ability of bands I and II is much less than the total sulfur content of these bands, implying net oxidation of the thiolato moiety. (4) The UV–visible spectrophotometric parameters of bands I–III are given in Table C.[27] It should be noted that these bands may contain unseparated mixtures of product complexes, and therefore the given parameters may not describe pure chemical species. The visible spectra are generally similar to that of the starting material $[(en)_2Cr(SCH_2COO)]^+$ (Table I), but the UV spectra are significantly different. Band III has no LTMCT absorption, band II exhibits only a shoulder in the 250-nm region,

Table III. Rate Parameters Describing the Reaction of H_2O_2 with (Thiolato)cobalt(III) Complexes[a]

rate = $(k_1 + k_2[H_2O_2])$[complex]

complex	t, °C	$10^4 k_1$, s^{-1}	k_2, M^{-1} s^{-1}
$[Co(en)_2(SCH_2COO)]^+$	7.9	7.04 ± 0.13	1.11 ± 0.01
	16.5	9.28 ± 3.28	1.87 ± 0.03
	25.0	37.2 ± 0.9	2.54 ± 0.06
$[Co(en)_2(SCH(CH_3)COO)]^+$	16.5	b	1.20 ± 0.05
	25.0	b	2.20 ± 0.08
	37.3	b	4.03 ± 0.04
$[Co(en)_2(SC(CH_3)_2COO)]^+$	16.5	b	0.33 ± 0.01
	25.0	b	0.52 ± 0.01
	37.3	b	1.05 ± 0.05
$[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$	16.5	b	2.20 ± 0.02
	25.0	b	3.20 ± 0.03
	37.3	b	5.36 ± 0.06

[a] $\mu = [HClO_4] = 1.00$ M. [b] k_1 is statistically insignificant.

and band II exhibits a LTMCT band of decreased intensity. (5) Bands I and II lose the LTMCT intensity in acid solution (e.g., the 1.00 M $HClO_4$ medium in which the kinetics experiments were conducted) and rapidly regain it in neutral solution, reminiscent of the reversible thiolato chelate ring-opening and ring-closing reactions documented for $[(en)_2Cr(SCH_2COO)]^+$.[16]

Kinetics. Observed first-order rate parameters governing the reaction of H_2O_2 with seven thiolato–chromium(III) complexes as a function of $[H_2O_2]$ and temperature are given in Tables D–J.[27] In all cases k^{obsd} is linearly dependent on $[H_2O_2]$ as in eq 4 where the minor component represented by

$$k^{obsd} = k_1 + k_2[H_2O_2] \qquad (4)$$

the intercept term corresponds to normal aquation of the Cr–S bond.[7,15,17,25] Derived values of k_1 and k_2 for the thiolato–chromium(III) complexes are given in Table II.

Observed first-order rate parameters governing H_2O_2 oxidation of four thiolato–cobalt(III) complexes as a function of $[H_2O_2]$ and temperature are given in Tables K–N.[27] Again, k^{obsd} is linearly dependent on $[H_2O_2]$ as in eq 4, three out of the four k_1 values being statistically insignificant. Derived values of k_1 and k_2 for the thiolato–cobalt(III) complexes are given in Table III.

First-order rate parameters describing the acid dependence of the H_2O_2 oxidation of four thiolato–chromium(III) complexes and one thiolato–cobalt(III) complex are summarized in Table IV. In all cases k^{obsd} is linearly dependent on $[H^+]$

(27) Supplementary material. This includes all tables designated by alphabetic characters.

Table IV. Rate Parameters Describing the Acid Dependence of the Reaction of H$_2$O$_2$ with (Thiolato)bis(ethylenediamine)chromium(III) and -cobalt(III) Complexes[a,b]

[H$^+$], M	$10^4 k^{obsd}$, s^{-1}				
	Cr(tga)	Cr(cys)	Cr(tpa)	Cr(tiba)	Co(cys)
0.2	9.59 ± 0.10	7.27 ± 0.02	11.76 ± 0.04	2.85 ± 0.03	21.00 ± 0.07
0.4	14.21 ± 0.10	9.83 ± 0.04	16.47 ± 0.03	4.63 ± 0.03	
0.6	18.30 ± 0.12	12.05 ± 0.05	20.66 ± 0.22	6.83 ± 0.04	31.01 ± 0.09
0.8	23.22 ± 0.08	14.64 ± 0.05	23.97 ± 0.22	8.60 ± 0.02	
1.0	26.42 ± 0.17	16.74 ± 0.06	27.19 ± 0.21	10.85 ± 0.04	40.90 ± 0.10

complex	$k^{obsd} = A + B[H^+]$		complex	$k^{obsd} = A + B[H^+]$	
	$10^3 B$, M^{-1} s^{-1}	$10^4 A$, s^{-1}		$10^3 B$, M^{-1} s^{-1}	$10^4 A$, s^{-1}
Cr(tga)	2.19 ± 0.06	5.47 ± 0.26	Cr(tiba)	0.98 ± 0.02	0.88 ± 0.02
Cr(cys)	1.23 ± 0.02	4.89 ± 0.09	Co(cys)	2.49 ± 0.01	16.03 ± 0.05
Cr(tpa)	2.13 ± 0.14	7.75 ± 0.50			

[a] Cr(tga) = [Cr(en)$_2$(SCH$_2$COO)]$^+$, Cr(tpa) = [Cr(en)$_2$(SCH$_2$CH$_2$COO)]$^+$, Cr(tiba) = [Cr(en)$_2$(SC(CH$_3$)$_2$COO)]$^+$, and M(cys) = [M(en)$_2$-(SCH$_2$CH$_2$NH$_2$)]$^{2+}$ (M = Co and Cr). Conditions: [complex]$_0$ = (1.0–1.5) × 10^{-4} M, [H$_2$O$_2$]$_0$ = 1.36 × 10^{-3} M, 25 °C, μ = 1.00 M (LiClO$_4$). [b] Cr(III) reactions were monitored at 255 nm and Co(III) reactions at 360 nm.

Table V. Selected Second-Order Rate Constants (at ~25 °C) and Activation Parameters Describing Reactions of H$_2$O$_2$ with Thiolato Complexes of Chromium(III) and Cobalt(III)

complex	rate = k_2[complex][H$_2$O$_2$][a]			
	t, °C	k_2, M^{-1} s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
(Thiolato)aquochromium(III) Complexes				
[(H$_2$O)$_5$CrSCH$_2$CH$_2$NH$_3$]$^{3+}$	25.5	0.176 ± 0.008	10.6 ± 0.9	−26.5 ± 2.9
[(H$_2$O)$_5$CrSC$_6$H$_5$NH$_3$]$^{3+}$	26.0	0.045 ± 0.001	10.8 ± 0.5	−28.5 ± 1.7
[(H$_2$O)$_4$Cr(SCH$_2$COO)]$^+$	26.6	0.445 ± 0.006	10.4 ± 0.3	−25.6 ± 0.9
(Thiolato)bis(ethylenediamine)chromium(III) Complexes				
[(en)$_2$Cr(SCH$_2$CH$_2$NH$_2$)]$^{2+}$	25.0	1.13 ± 0.02	9.71 ± 0.17	−25.8 ± 0.6
[(en)$_2$Cr(SCH$_2$COO)]$^+$	25.0	1.13 ± 0.02	9.30 ± 0.48	−27.0 ± 1.6
[(en)$_2$Cr(SCH$_2$CH$_2$COO)]$^+$	25.0	1.19 ± 0.01	9.99 ± 0.45	−24.7 ± 1.5
[(en)$_2$Cr(SC(CH$_3$)$_2$COO)]$^+$	25.0	0.16 ± 0.01	10.65 ± 0.55	−26.6 ± 1.8
(Thiolato)bis(ethylenediamine)cobalt(III) Complexes				
[(en)$_2$Co(SCH$_2$CH$_2$NH$_2$)]$^{2+}$	25.0	3.20 ± 0.03	7.28 ± 0.18	−31.8 ± 0.6
[(en)$_2$Co(SCH$_2$COO)]$^+$	25.0	2.54 ± 0.06	10.17 ± 0.90	−21.9 ± 3.1
[(en)$_2$Co(SCH(CH$_3$)COO)]$^+$	25.0	2.20 ± 0.08	9.68 ± 0.80	−24.6 ± 2.7
[(en)$_2$Co(SC(CH$_3$)$_2$COO)]$^+$	25.0	0.52 ± 0.01	9.25 ± 0.25	−28.7 ± 0.8

[a] μ = [HClO$_4$] = 1.00 M.

as in eq 5. Derived values of A and B for the five complexes investigated are also given in Table IV.
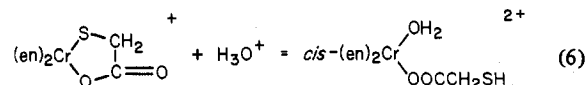
$$k^{obsd} = A + B[H^+] \qquad (5)$$

Derived activation parameters governing k_2 values for 11 thiolato complexes are summarized in Table V; these parameters correspond to [H$^+$] = 1.00 M. Derived activation parameters governing k_1 values for the thiolato–chromium(III) complexes were in good agreement with those previously determined[7,15,17,25] for normal aquation of the Cr–S bond.
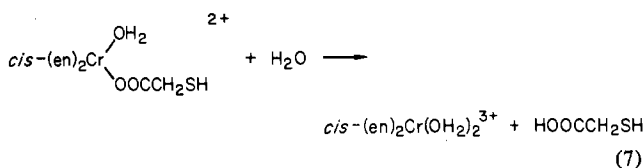
Discussion

Products of the H$_2$O$_2$ + [(en)$_2$Cr(SCH$_2$COO)]$^+$ Reaction. The salient net chemical change resulting from addition of H$_2$O$_2$ to thiolato–chromium(III) complexes is induced hydrolytic cleavage of the Cr–S bond. This cleavage leads to a plethora of reaction products; the identities and distribution of these products have not been fully defined. Experiments designed to elucidate at least the general nature of the product mixture resulting from H$_2$O$_2$ oxidation of [(en)$_2$Cr-(SCH$_2$COO)]$^+$ lead to the following conclusions. (1) The thiolato moiety does indeed suffer net oxidation, the reducing power of various product components being considerably less than the total sulfur content of these components (Table B[27]). We infer that sulfur has been oxidized from the −II state (RS$^-$, thiol) to at least the +II state (RSO$_2^-$, sulfinic acid) and possibly to the +IV state (RSO$_3^-$, sulfonic acid); the 0 oxidation state (RSO$^-$, sulfenic acid) may exist transiently, but noncoordinated sulfenic acids are notoriously unstable.[2,3] (2)

The distribution of chromium(III) products (Table A[27]) depends on reaction time, H$_2$O$_2$ concentration, and other less readily controlled parameters such as the length of time the product mixture spends on the ion-exchange column. Aside from the fact that the product mixture is complex, the only firm conclusion we can draw from these product distribution studies is that the reducing power of the product components decreases with increased exposure to H$_2$O$_2$. (3) The chromium(III)-containing products exhibit chemistry reminiscent of that observed[16,28] for [(en)$_2$Cr(SCH$_2$COO)]$^+$. First, they show increased Cr–S bond formation (enhanced intensity of the LTMCT band) in neutral solution and decreased Cr–S bond formation in acid solution; this is analogous to the acid-dependent chelate ring-opening–ring-closing equilibrium[16] (eq 6). Second, they readily lose sulfur-containing fragments

$$\text{(en)}_2\text{Cr} \begin{array}{c} S{-}CH_2 \\ | \\ O{-}C{=}O \end{array}^+ + H_3O^+ = \textit{cis-}\text{(en)}_2\text{Cr} \begin{array}{c} OH_2 \\ \\ OOCCH_2SH \end{array}^{2+} \qquad (6)$$

through presumed[28] hydrolysis of the C–O bond promoted by the anchimeric assistance provided by the neighboring sulfur group (eq 7). This type of reaction has been well documented[28] for a variety of bis(ethylenediamine)chromium(III) complexes containing O,S-chelated thioacids.

Thus, consideration of the simplest possible product distribution (three oxidation states of sulfur; monodentate, O,-

(28) Adzamli, I. K. M.S. Thesis, University of Cincinnati, 1975.

$$cis\text{-}(en)_2Cr\begin{array}{c} OH_2 \\ OOCCH_2SH \end{array}^{2+} + H_2O \longrightarrow$$

$$cis\text{-}(en)_2Cr(OH_2)_2{}^{3+} + HOOCCH_2SH$$

$$\text{(7)}$$

S-chelated, or O,O-chelated thioacid ligand derivative; loss of thioacid ligand derivative) leads to nine possible chromium-containing products and three types of noncoordinated sulfur-containing products. Accepting that the three bands isolated by ion-exchange separation of the product mixture (Tables A–C[27]) are themselves very likely to consist of mixtures of similar complexes containing sulfur in unknown oxidation states, we suggest the following possible compositions for bands I–III: band I, *cis*-[(en)$_2$Cr(OH$_2$)(OOCCH$_2$S-(O)$_n$H]$^{2+}$, with n = 0, 1, 2, and 3, in equilibrium with the chelated analogues; band II, isomeric mixture of [(en)Cr-(enH)(OH$_2$)$_2$(OOCCH$_2$S(O)$_n$H]$^{3+}$, with n = 0, 1, 2, and 3, in equilibrium with the chelated analogues; band III, *cis*-[(en)$_2$Cr(OH$_2$)$_2$]$^{3+}$ and isomers of [(en)Cr(enH)(OH$_2$)$_3$]$^{4+}$. It should be noted that in these types of complexes the Cr–N bond is susceptible to hydrolysis, and Cr–N bond fission occurs at roughly the same rate as Cr–S bond fission.[16,28,29]

Kinetics and Mechanism of H$_2$O$_2$ Oxidation. The mechanism of action of hydrogen peroxide as a 2-equiv oxidant has been extensively investigated and thoroughly reviewed, largely by Edwards and co-workers.[30-33] It is generally accepted that H$_2$O$_2$ oxidation of nucleophilic substrates occurs via nucleophilic attack of the substrate on the O–O bond of H$_2$O$_2$.[1,5,30-33] In view of the known nucleophilic character of coordinated sulfur,[1,8,9,34] in the following discussion we will assume that H$_2$O$_2$ oxidation of coordinated thiols proceeds by means of this general nucleophilic attack scheme.

A. Thiolato–Cobalt(III) Complexes. In three out of the four complexes examined, oxidation of the coordinated thiol to the coordinated sulfenic acid proceeds by the simple second-order rate law expected for the nucleophilic attack scheme (i.e., eq 8) at constant [H$^+$] (see Table III). However, the

$$\text{rate} = k_2[\text{complex}][H_2O_2] \tag{8}$$

[(en)$_2$Co(SCH$_2$COO)]$^+$ complex exhibits an "anomalous" peroxide-independent term, i.e., k_1 in eq 4. This minor term must be an artifact because no sulfenic acid is produced when peroxide is omitted from the reaction mixture. While this anomalous k_1 term may arise because the linear functional form used to describe the k^{obsd}–[H$_2$O$_2$] data is an oversimplification, we were unable to formulate a meaningful functional form which significantly improved the description. We suspect that this k_1 term arises because of the susceptibility to oxidation of the carbon adjacent to sulfur in [(en)$_2$Co-(SCH$_2$COO)]$^+$[35-37] (to yield [(en)$_2$Co(SC(O)COO)]$^+$), but the data are not sufficient to develop this hypothesis further.

There is remarkably little variation in k_2 for the four thiolato–cobalt(III) complexes studied (Table V), the observed range being only 0.52–3.2 M^{-1} s^{-1}; Herting et al.[5] determined k_2 for [(en)$_2$Co(SCH$_2$CH(COOH)NH$_2$)]$^{2+}$ to be 0.78 M^{-1} s^{-1} (20.3 °C, μ = 0.48 M, corrected to [H$^+$] = 1.00 M),
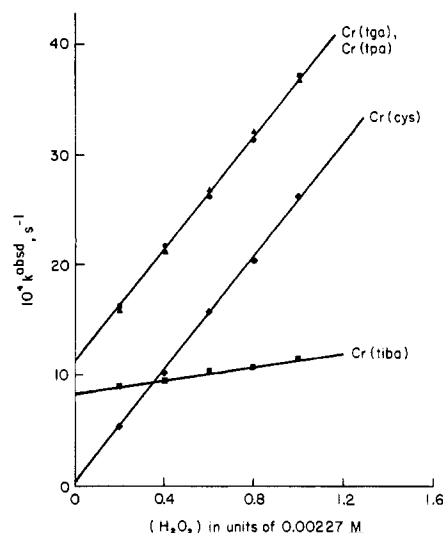
Figure 1. Plots of $10^4 k^{obsd}$ (in s^{-1}) vs. [H$_2$O$_2$] (in units of 0.002 27 M) for the complexes Cr(tga) ≡ [(en)$_2$Cr(SCH$_2$COO)]$^+$, Cr(tpa) ≡ [(en)$_2$Cr(SCH$_2$CH$_2$COO)]$^+$, Cr(tiba) ≡ [(en)$_2$Cr(SC(CH$_3$)$_2$COO)]$^+$, and Cr(cys) ≡ [(en)$_2$Cr(SCH$_2$CH$_2$NH$_2$)]$^{2+}$. Conditions: 25 °C, μ = [HClO$_4$] = 1.00 M. Data from Tables D–G.[27]

placing a fifth independent value within this narrow range. Thus the energetics of oxidation seem to be primarily determined by the cleavage of the peroxide O–O bond and only depend in a minor fashion on the nature of the coordinated thiol. Consistent with this view, the activation parameters observed for the four thiolato–cobalt(III) complexes (Table V) are all very similar, the small rate differences being reflected primarily in ΔH^*. The most significant variation in k_2 results from varying the steric requirements of the thiolato chelate backbone, the more sterically demanding thiol being less reactive. While this trend is in the direction expected on the basis of the nucleophilic attack scheme, the effect is rather small; [(en)$_2$Co(SCH$_2$COO)]$^+$ reacts only 4.9 times faster than [(en)$_2$Co(SC(CH$_3$)$_2$COO)]$^+$, consistent with the observation of Herting et al.[5] that [(en)$_2$Co(SCH$_2$CH(COOH)NH$_2$)]$^{2+}$ reacts only 2.6 times faster than [(en)$_2$Co(SC(CH$_3$)$_2$CH-(COOH)NH$_2$)]$^{2+}$. The small magnitude of this effect can be appreciated by considering that [(en)$_2$Co(SC(CH$_3$)$_2$COO)]$^+$ differs from [(en)$_2$CO(SCH$_2$COO)]$^+$ by approximately the same extent that neopentyl bromide differs from *n*-propyl bromide, and in organic nucleophilic reactions *n*-propyl bromide is ca. 10^4 times more reactive as a substrate than neopentyl bromide:[38,39]

R = H, CH$_3$
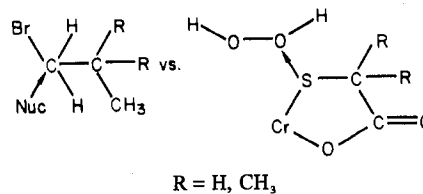
The different sensitivities of the two systems to steric requirements can be understood on the basis that sulfur is larger, but yet has a smaller coordination number, than carbon. Thus sulfur encounters much less of an energy barrier in going from two- to three-coordinate (in order to achieve the redox transition state) than carbon does in going from four- to five-coordinate (in order to achieve the substitution transition state). However, when sulfur is three-coordinate in the ground state,

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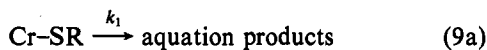
Table VI. Summary of Available Kinetic Data Describing the Acid Dependence of the H$_2$O$_2$ Oxidation of Sulfur-Containing Nucleophiles

$$\text{rate} = (a + b[\text{H}^+])[\text{Nuc}][\text{H}_2\text{O}_2]^a$$

nucleophile	a, M^{-1} s^{-1}	b, M^{-2} s^{-1}	b/a, M^{-1}	ref
Anionic				
S$_2$O$_3{}^{2-}$	0.025	1.7	68	12
SCN$^-$	5.2 × 10^{-4}	0.025	48	12
Neutral				
(HOCH$_2$CH$_2$)$_2$S	2.2 × 10^{-3}	0.023	10	12
O(CH$_2$CH$_2$)$_2$S	2.6 × 10^{-3}	0.035	14	12
(NH$_2$)$_2$C=S	0.07	1.42	20	12
(NHCH$_3$)$_2$C=S	0.094	0.60	6	12
(NHCH$_2$CH$_3$)$_2$C=S	0.086	0.53	6	12
Cationic				
[(en)$_2$Co(NO$_2$)(NCS)]$^+$	4.6 × 10^{-5}	1.3 × 10^{-3}	28	12
[(NH$_3$)$_5$CoNCS]$^{2+}$	5.3 × 10^{-5}	9.8 × 10^{-4}	19	12
[(en)$_2$Co(S(O)CH$_2$CH$_2$NH$_2$)]$^{2+}$	3.4 × 10^{-4}	5.1 × 10^{-4}	1.6	1
[(en)$_2$Co(SCH$_2$CH$_2$NH$_2$)]$^{2+}$	1.18	1.8	1.5	b
	0.94	≈1.2	≈1.3	5
[(en)$_2$Co(SCH$_2$CH(COOH)NH$_2$)]$^{2+}$	0.24	0.54	2.2	5
[(en)$_2$Cr(SCH$_2$CH$_2$NH$_2$)]$^{2+}$	0.36	0.90	2.5	b
[(en)$_2$Cr(SCH$_2$COO)]$^+$	0.38^c	0.80^c	2.1	b
[(en)$_2$Cr(SCH$_2$CH$_2$COO)]$^+$	0.50^c	1.00^c	2.0	b
[(en)$_2$Cr(SC(CH$_3$)$_2$COO)]$^+$	0.036^c	0.11^c	3.0	b

^{a} Conditions: 25 °C, H$_2$O solvent, variable ionic strength. ^{b} This work. ^{c} Calculated as described in the text by using data from ref 16 and 28 and from Table IV.

and, therefore, must become four-coordinate in the redox transition state, the rate of the reaction is dramatically reduced. Thus, k_2 for H$_2$O$_2$ oxidation of [(en)$_2$Co(S(O)CH$_2$CH$_2$NH$_2$)]$^{2+}$ to [(en)$_2$Co(S(O)$_2$CH$_2$CH$_2$NH$_2$)]$^{2+}$ is only[1] 8.6 × 10^{-4} M^{-1} s^{-1} (conditions as in Table V), compared to k_2 = 3.2 M^{-1} s^{-1} for H$_2$O$_2$ oxidation of [(en)$_2$Co(SCH$_2$CH$_2$NH$_2$)]$^{2+}$ to [(en)$_2$Co(S(O)CH$_2$CH$_2$NH$_2$)]$^{2+}$ (Table V). Consistent with the nucleophilic attack scheme, this large rate difference resides in the ΔH^* term (15 vs. 7 kcal/mol), the entropies of activation being about the same (−26 vs. −32 eu). The rate of H$_2$O$_2$ oxidation of coordinated sulfur is therefore much more sensitive to the steric requirements of the sulfur atom being oxidized than to the steric requirements of the chelate backbone.

B. Thiolato–Chromium(III) Complexes. The rates and mechanism of acid-catalyzed aquation of the Cr–S bond in thiolato–chromium(III) complexes have been extensively studied.[7,15–17,28] This process occurs in parallel with the H$_2$O$_2$-induced Cr–S bond cleavage (eq 9a–c), Figure 1 illustrates the relationships between k_1 and k_2 values for four (thiolato)bis(ethylenediamine)chromium(III) complexes (see also Table II). The three complexes [(en)$_2$Cr(SCH$_2$COO)]$^+$, [(en)$_2$Cr(SCH$_2$CH$_2$COO)]$^+$, and [(en)$_2$Cr(SCH$_2$CH$_2$NH$_2$)]$^{2+}$ all have the same k_2 value (slope); however, [(en)$_2$Cr(SCH$_2$CH$_2$NH$_2$)]$^{2+}$ has a markedly smaller k_1 value (intercept) than the other two. Since the k_1 values govern normal aquation of the Cr–S bond, this different distribution of k_1 and k_2 values shows that the energetics of Cr–S bond fission are *not* important in achieving the redox transition state, even though Cr–S fission results from the redox process. Supportive of this conclusion is the observation that the pattern of k_2 values for the (thiolato)bis(ethylenediamine)chromium(III) complexes mimics the pattern exhibited for the analogous cobalt(III) complexes which do not suffer Co–S bond fission during the oxidation process. This pattern can be summarized as follows: three different thiolato–chromium(III) complexes have essentially the same k_2 value, indicating that the ener-

getics of O–O bond fission dominate the oxidation process; increasing the steric requirements of the thiolato chelate backbone only moderately decreases k_2, the ratio of k_2 values for [(en)$_2$M(SC(CH$_3$)$_2$COO)]$^+$ and [(en)$_2$M(SCH$_2$COO)]$^+$ being 4.9 when M = Co and 7.1 when M = Cr.

Variation of the ancillary ligands in thiolato–chromium(III) complexes from en to H$_2$O decreases the rate of H$_2$O$_2$ oxidation (Table V), although the effect is not large (for [L$_4$Cr(SCH$_2$COO)]$^+$, $k_{2,\text{en}}/k_{2,\text{H}_2\text{O}}$ = 2.5). This is consistent with the nucleophilic attack scheme since en is a better electron donor than H$_2$O, making the coordinated sulfur in the en complex a better nucleophile. It is interesting to note that if rearrangement of the chromium(III) coordination sphere contributed significantly to the energetics of the oxidation process, the en complexes would be expected to react more slowly. Since the en complexes in fact react more rapidly, such rearrangement does not markedly affect the activation energy; this is consistent with the above conclusion that it is the energetics of O–O bond fission that dominate the oxidation process.

The fact that [(H$_2$O)$_5$CrSCH$_2$CH$_2$NH$_3$]$^{3+}$ reacts with H$_2$O$_2$ more rapidly than does [(H$_2$O)$_5$CrSC$_6$H$_4$NH$_3$]$^{3+}$ (ratio of k_2 values = 3.9; Table V) is attributed to the greater steric requirements of the aromatic anilinium group relative to the aliphatic 2-ethylammonium group.

C. Acid Dependence. Oxidations of nucleophilic substrates by H$_2$O$_2$ are, without known exception,[1,30–33] acid catalyzed according to the general relationship of eq 10. For the two

$$\text{rate} = (a + b[\text{H}^+])[\text{Nuc}][\text{H}_2\text{O}_2] \qquad (10)$$

substrates [(en)$_2$M(SCH$_2$CH$_2$NH$_2$)]$^{2+}$ (M = Co and Cr), normal aquation of the metal–sulfur bond does not compete with H$_2$O$_2$ oxidation, and thus the observed rate law governing oxidation (eq 5) corresponds directly to eq 10 with $a = A/[\text{H}_2\text{O}_2]$ and $b = B/[\text{H}_2\text{O}_2]$. The two sets of a and b values resulting from the appropriate A and B values of Table IV are listed in Table VI. However, for the three complexes [(en)$_2$Cr(SCH$_2$COO)]$^+$, [(en)$_2$Cr(SCH$_2$CH$_2$COO)]$^+$ and [(en)$_2$Cr(SC(CH$_3$)$_2$COO)]$^+$, normal acid-catalyzed aquation of the Cr–S bond does compete with H$_2$O$_2$ oxidation, and thus the observed rate parameters A and B reflect the acid dependencies of both processes (eq 9a and 9b). For these three complexes eq 11a–c can be written. With the values of $k_{\text{aq,0}}$

Cr–SR $\xrightarrow{k_1}$ aquation products (9a)

H$_2$O$_2$ + Cr–SR $\xrightarrow{k_2}$ oxidation products (9b)

$k^{\text{obsd}} = k_1 + k_2[\text{H}_2\text{O}_2]$ (at constant [H$^+$]) (9c)

$$k^{obsd} = k_{aq,0} + k_{aq,H}[H^+] + (a + b[H^+])[H_2O_2] \quad (11a)$$

$$a = (A - k_{aq,0})/[H_2O_2] \quad (11b)$$

$$b = (B - k_{aq,H})/[H_2O_2] \quad (11c)$$

and $k_{aq,H}$ established in previous studies[16,28] and the values of A and B from Table IV, eq 11b and 11c yield the values of a and b listed in Table VI. (For the complex $[(en)_2Cr(SCH_2CH_2COO)]^+$ this procedure involves an approximation[28] which does not affect the calculation of a and can introduce a maximum error of only 10% in the calculation of b.)

Table VI collects all the data known to us that is relevant to the acid dependence of H_2O_2 oxidation of sulfur-containing nucleophiles. The approximate data of Herting et al.[5] for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ are in good agreement with our determination for this complex, and their data for $[(en)_2Co(SCH_2CH(COOH)NH_2)]^{2+}$ fall nicely within the pattern of our results for thiolato complexes.

Within the nucleophilic attack scheme for H_2O_2 oxidations, it is generally accepted that the rate law expressed by eq 10 results from protonation of H_2O_2.[1,30–33] Water is a better leaving group than OH^-, and, therefore, protonation of H_2O_2 promotes nucleophilic cleavage of the O–O bond. In this view, b is the composite rate parameter governing attack on $H_3O_2^+$ while a is the rate parameter governing attack on H_2O_2. On the basis of simple electrostatics, Hoffmann and Edwards[30] have argued that the ratio b/a should be largest for anionic nucleophiles, intermediate for neutral nucleophiles, and smallest for cationic nucleophiles. The data of Table VI show that this generalization holds if the two complexes with coordinated isothiocyanate are discounted. The isothiocyanato complexes become concordant if one accepts the view that they fall more naturally into the classification of neutral nucleophiles since in these complexes the remote sulfur atom carries a formal charge of zero.

The data of Table VI also show that the b/a ratio for the sulfenic acid complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ is essentially the same as that for the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. Therefore, the previously hypothesized[1] deactivating interaction between $H_3O_2^+$ and the sulfenyl oxygen atom, based on limited data which indicated an unusually low b/a ratio for oxidation of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, may be discounted.

Hoffmann and Edwards[30] have also noted that for a restricted set of nucleophiles a plot of log b vs. log a is roughly linear with a slope of ca. 1.0; the nucleophiles chloride and bromide were not used in this plot, and they do not fall on the indicated line. Clearly, for a log b vs. log a plot to be linear with unit slope, the ratio b/a must be approximately constant for all members of the data set. From the data in Table VI, this condition is met for the thiolato and sulfenato complexes over more than a three orders of magnitude variation in a; for these seven complexes a plot of log b vs. log a has a slope of 1.02 ± 0.04 with a correlation coefficient of 0.995 (unit weighting of log b values). When all 16 nucleophiles are considered, there is indeed a trend of increasing log a with increasing log b, but it would be overly optimistic to describe this trend as a linear relationship; for the 16 nucleophiles of Table VI, a plot of log b vs. log a has a slope of 0.79 ± 0.08 with a correlation coefficient of 0.928 (unit weighting of log b values). Considering the variation of b/a with the formal charge of the nucleophile, a linear relationship between log b and log a is expected only when nucleophiles of the same charge type are considered.

Nucleophilicity of Coordinated Sulfur. Comparison of the a terms given in Table VI and in the compilation of Hoffmann and Edwards[30] shows that, with respect to attack on H_2O_2, coordinated thiols are the most potent nucleophiles that have yet been investigated in detail. While the b terms for coor-

dinated thiols suffer somewhat from the positive formal charge on the complex, these terms are at least as large as those observed for thiosulfate and thiourea. It is expected that noncoordinated thiols would be better nucleophiles than coordinated thiols, but data on the aqueous H_2O_2 oxidation of free thiols are scarce. One brief study on cysteine and cysteamine[40] reports that the second-order rate parameter governing H_2O_2 oxidation of the zwitterion $[^+H_3NCH_2CH_2S^-]$ is 10 M^{-1} s^{-1} (aqueous solution, room temperature, undefined ionic strength, varying pH). While this parameter is indeed larger than the a values observed for oxidation of coordinated cysteamine (Table VI), the effect is less than one order of magnitude and is therefore suspiciously small. The effect will be even smaller if one accepts the contention[40] that oxidation of the cysteamine zwitterion is promoted by internal hydrogen bonding to H_2O_2, and oxidation of the anion $[H_2NCH_2CH_2S]^-$ is considerably slower. It should be noted that NCS^- also suffers only one order of magnitude decrease in nucleophilicity upon coordination to cobalt(III) (see Table VI), but in the isothiocyanato complexes the sulfur atom is two atoms removed from the cobalt center. Since the thiolato sulfur atom is directly coordinated to the cobalt center, coordination should deactivate the thiolato sulfur atom much more than the NCS^- sulfur atom. Clearly, more definitive data on the H_2O_2 oxidation of noncoordinated thiols are needed.

Taking the reported[40] rate for H_2O_2 oxidation of cysteamine as the best estimate available, the relative nucleophilicities toward peroxide oxygen of the three-coordinate sulfur atom in the sulfenato complex $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$, the two-coordinate sulfur atom in the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$, and the one-coordinate sulfur atom in the zwitterion $[^+H_3NCH_2CH_2S^-]$ are 1/3500/30000. As expected, nucleophilicity decreases with increasiang coordination number and concomitant steric requirements of the sulfur atom.

Chromium(III) vs. Cobalt(III). The data of Table V show that the nucleophilicity of thiolato sulfur coordinated to cobalt(III) is greater than the nucleophilicity of thiolato sulfur coordinated to chromium(III). For the three thiolato complexes $[(en)_2M(SCH_2CH_2NH_2)]^{2+}$, $[(en)_2M(SCH_2COO)]^+$, and $[(en)_2M(SC(CH_3)_2COO)]^+$, the ratios $k_{2,Co}/k_{2,Cr}$ are 2.83 ± 0.06, 2.25 ± 0.06, and 3.2 ± 0.2, respectively. This small but real effect can be understood if it is assumed that there is at least some π back-bonding character in the M–S bond. Since cobalt(III) has six t_{2g} electrons and chromium(III) has only three, metal to sulfur π bonding places more electron density on the sulfur atom coordinated to cobalt(III) and consequently causes this species to be the more effective nucleophile.[42] π bonding from cobalt(III) to sulfur in thiolato and thioether complexes has previously been invoked[9] to account for some of the spectral properties of these complexes.

Chromium(III) complexes are well-known to be more susceptible to substitution reactions than analogous cobalt(III) complexes,[29,41] and this generalization has been shown to be true for comparable thiolato complexes.[12] The greater lability of Cr–S bonds relative to Co–S bonds may be at least partially ascribed to the greater potential for π bonding in the cobalt(III) system which increases the bond order of the cobalt–sulfur linkage. It therefore seems reasonable to ascribe the instability of sulfenato–chromium(III) complexes to the inherent instability of the Cr–S bond. In this view, H_2O_2 oxidation of a coordinated thiol to a coordinated sulfenic acid is rate determining—if the central metal is cobalt(III), the

(40) Barton, J. P.; Packer, J. E.; Sims, R. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1547.

(41) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; pp 145 ff, 169.

(42) A reviewer has noted that greater sulfur-to-metal π bonding for Cr(III) relative to Co(III) would lead to the same effect.

sulfenato product is stable enough to be observed and isolated;[1] but if the central metal is chromium(III), Cr–S bond fission occurs too rapidly for the sulfenato intermediate to be detected. This scenario is consistent with the previously described reactivity patterns for aquation and oxidation of thiolato–chromium(III) complexes (illustrated in Figure 1) which preclude significant Cr–S bond fission in the redox transition state.

Summary

The major conclusions and hypotheses presented in the previous sections can be summarized as follows. Coordinated thiols react with H_2O_2 via nucleophilic scission of the O–O bond to yield coordinated sulfenic acids. When coordinated to cobalt(III), the S-bonded sulfenato moiety is moderately stable, and the sulfenato–cobalt(III) product can be detected and isolated.[1] When coordinated to chromium(III), the inherent instability of the Cr–S bond causes the S-bonded sulfenato moiety to be unstable, and the presumed sulfenato–chromium(III) intermediate is not observed. Coordinated thiols are very good nucleophiles, reacting with H_2O_2 at about the same rate as $S_2O_3^{2-}$. Thiols coordinated to cobalt(III) are slightly better nucleophiles than thiols coordinated to chromium(III), presumably because π back-bonding from the t_{2g}^6 cobalt(III) center puts more electron density on the coordinated sulfur atom.[42] The rate of H_2O_2 oxidation of a coordinated thiol is relatively insensitive to the nature of the thiolato complex (thiolato chelate ring size, steric requirements of the thiol backbone, ancillary ligands, etc.). However, the rate of H_2O_2 oxidation of a coordinated sulfur atom is very sensitive to the steric requirements of the sulfur atom, the two-coordinate sulfur of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ being oxidized more than three orders of magnitude faster than the three-coordinate sulfur of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

Registry No. $[(en)_2Cr(SCH_2CH_2COO)]ClO_4$, 51911-43-4; $[(en)_2Cr(SC(CH_3)_2COO)]ClO_4$, 60195-76-8; Cr(tpa), 51911-42-3; Cr(tiba), 60195-75-7; Co(tga), 42901-31-5; Co(tiba), 68645-86-3; Cr(tga), 41654-60-8; Cr(cys), 48131-66-4; $[(H_2O)_5Cr(SCH_2CH_2NH_3)]^{3+}$, 59033-97-5; $[(H_2O)_4Cr(SCH_2COO)]^+$, 32696-60-9; $[(H_2O)_5Cr(SC_6H_4NH_3)]^{3+}$, 38833-30-6; $[Co(en)_2(SCH(CH_3)COO)]^+$, 60828-74-2; Co(cys), 42901-32-6; H_2O_2, 7722-84-1.

Supplementary Material Available: Table A, analysis of products resulting from H_2O_2 oxidation of $[Cr(en)_2(SCH_2COO)]^+$; Table B, analysis of products from oxidation of $[Cr(en)_2(SCH_2COO)]^+$; Table C, spectra of products from H_2O_2 oxidation of $[Cr(en)_2(SCH_2COO)]^+$. First-order rate parameters for the reaction of H_2O_2 with: Table D, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$; Table E, $[Cr(en)_2(SCH_2COO)]^+$; Table F, $[Cr(en)_2(SCH_2CH_2COO)]^+$; Table G, $[Cr(en)_2(SC(CH_3)_2COO)]^+$. First-order rate parameters for the H_2O_2-catalyzed aquation of: Table H, $[(H_2O)_4Cr(SCH_2COO)]^+$; Table I, $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$; Table J, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$. First-order rate parameters for the oxidation of: Table K, $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$; Table L, $[Co(en)_2(SCH_2COO)]^+$; Table M, $[Co(en)_2(SCH(CH_3)COO)]^+$; Table N, $[Co(en)_2(SC(CH_3)_2COO)]^+$ (14 pages). Ordering information is given on any current masthead page.

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Oxidation, Reduction, and Copper–Carbon Bond Formation in the Reactions of Copper(II) Tetraglycine with Pulse Radiolytically Generated Free Radicals

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The reactions of copper(II) tetraglycine ($Cu^{II}G_4$) with a variety of aliphatic free radicals and with $\cdot Br_2^-$ and $\cdot OH$ have been investigated by the pulse radiolytic technique. Three types of reaction are observed: (i) oxidation of $Cu^{II}G_4$ to $Cu^{III}G_4$ by $\cdot Br_2^-$ and $\cdot OH$; (ii) rapid reduction to copper(I) by $\cdot CH_2OH$, $\cdot CO_2^-$, and $(CH_3)_2\dot COH$; (iii) formation of unstable copper(III)–carbon-bonded intermediates with lifetimes from several milliseconds to several seconds with $\cdot CH_2C(CH_3)_2OH$, $\cdot CH_2CO_2^-$, and $\cdot CH_2C(OH)CH_3$ radicals. Rate constants are reported for formation and decomposition of all intermediates, and the relative instability of neutral $Cu^{III}(H_{-2}G_4)$ compared to $Cu^{III}(H_{-3}G_4)^-$ is confirmed by direct observation.

Introduction

Formation of Cu^{III}–C-bonded intermediates has been suggested as part of a general mechanism for Cu^{II} oxidation of aliphatic free radicals which are not strong reducing agents,[2] and, indeed, such an intermediate has been reported in the reaction of $Cu^{II}(aq)$ with $\cdot CH_2CO_2^-$ radicals.[3]

In a recent pulse radiolytic study,[4] it was shown that $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CO_2^-$ free radicals react with

$Cu^{II}G_3$ (G_3 = triglycine peptide) via $Cu^{II}G_3 + \cdot R \rightarrow Cu^{III}G_3$–$R \rightarrow Cu^{I}G_3$ + products. At physiological pH, the unstable intermediates containing the $Cu^{III}G_3$–C bond have lifetimes of about 1 s. As this reaction sequence might be of general importance, indicating that "oxidizing" aliphatic free radicals might be scavenged by copper–protein complexes in biological systems, we decided to extend this study to the reactions of free radicals with $Cu^{II}G_4$. (The symbol G_4 is used here as a general term for tetraglycine; $H_{-2}G_4^{3-}$ and $H_{-3}G_4^{4-}$ are molecules with deprotonation at two and three peptide nitrogens, respectively, as well as at the carboxyl group.) It was suspected that, as $Cu^{III}G_4$ is more stable than $Cu^{III}G_3$,[5,6] the $Cu^{III}G_4$–R

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