

Oxidation of Thiolato Complexes of Ruthenium(III) by Peroxymonosulfate

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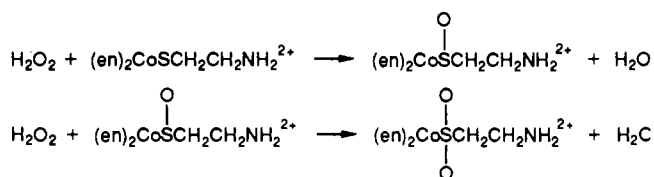
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The HSO_5^- oxidation of thiols coordinated to ruthenium(III) centers proceeds cleanly via two discrete steps to give the corresponding sulfenato and sulfinato complexes. First-order behavior was observed with respect to both complex ion and oxidant. The first oxidation step is sensitive to the nature of the sulfur substituent, and rates follow a Hammett correlation with $\rho = -0.66$. In contrast, the second reaction is relatively insensitive to the nature of the substituent. This paper describes the preparation of several (thiolato)ruthenium(III) complexes and their oxidation kinetics.

Introduction

Metal complexes possessing coordinated sulfur ligands are of interest in both inorganic and biochemical systems.¹ For example, redox proteins, such as the cytochromes and ferridoxins, have cysteine or methionine sulfurs coordinated to iron centers which allow for precise control of their redox reactivity.² In "simple" inorganic systems, the coordination of sulfur to a metal center, such as cobalt(III), allows for the unique and facile synthesis of sulfenato and sulfinato complexes using hydrogen peroxide as the oxidant.³ Deutsch et al. have studied the H_2O_2 redox kinetics of a variety of cobalt(III) and chromium(III) complexes as shown:⁴



From these studies two interesting observations emerge. First, the hydrogen peroxide oxidation of (thiolato)chromium(III) complexes, analogous to that of the cobalt(III) complexes shown, produces only aquachromium(III) as the final product. Presumably, a sulfenato intermediate is formed but is hydrolyzed rapidly to produce the observed product.^{3b} The difference in stability between these two metal centers has been ascribed to changes in the amount of sulfur to metal π bonding. Second, the nature of the thiol ligand coordinated (e.g. chelate ring size, steric requirements, or ancillary ligands) makes little if any difference in the rate of sulfur oxidation.⁵

In order to further the understanding of the differences in the stability and reactivity of coordinated thiolato, sulfenato, and sulfinato complexes, the oxidation of a series of (thiolato)ruthenium(III) complexes to sulfenato and sulfinato complexes has been examined. These complexes provide an interesting contrast to the aforementioned studies in that large differences in the oxidation rates of the coordinated sulfur are observed with varying R groups.

Experimental Section

Organic starting materials and solvents were of reagent grade and used without further purification (Aldrich). Pentaamminechlororuthenium(III) chloride was prepared according to literature methods from RuCl_3 (Strem).⁶

Stock solutions of trifluoromethanesulfonic acid and lithium hydroxide were prepared from anhydrous starting materials (Aldrich) and their concentrations determined by titration with standard NaOH or HCl (Acculute) solutions. Millipore water was used to make up all solutions.

Peroxymonosulfate stock solutions were prepared from Oxone (Aldrich) and standardized by iodometric titration. Although the titer of these solutions did not change upon standing for several days, fresh solutions were found to give the most reproducible results. This is presumably due to partial hydrolysis of peroxymonosulfate to sulfate and hydrogen peroxide. UV-visible spectra were obtained using a Cary 219 spectrophotometer and matched quartz cells. The rapid scanning spectrophotometer was a Harrick rapid scan monochromator interfaced with a Durrum DI10 stopped-flow instrument as designed by Dr. R. DeSa (OLIS). IR spectra were recorded with a Perkin-Elmer 1720X FT-IR instrument.

Elemental analyses were performed by Galbraith Laboratories.

Preparation of Complexes. Pentaammine(benzenethiolato)ruthenium(III) hexafluorophosphate, $[\text{Ru}(\text{NH}_3)_5\text{SC}_6\text{H}_5](\text{PF}_6)_2$, was prepared by the reaction of $[\text{Ru}(\text{NH}_3)_5\text{OH}_2](\text{PF}_6)_2$ with diphenyl disulfide in acetone as described by Taube et al.⁷ Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5\text{SC}_6\text{H}_5](\text{PF}_6)_2$: C, 12.3; H, 3.44; N, 11.9. Found: C, 12.8; H, 3.59; N, 11.0.

Pentaammine(thiosulfato)ruthenium(III) chloride, $[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$, was obtained by a variation of the method of Taube and Armor.^{7b} $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was dissolved in a minimum of water, and a 1.5-fold excess of sodium thiosulfate was added. The solution was allowed to sit for 30 min in the dark and then charged onto a SP-Sephadex column. The uncharged ruthenium(II) thiosulfate complex passed through the resin with water, and the orange ruthenium(III) complex formed a tight band at the top. Elution with 0.1 M HCl removed this complex from the resin, and rotoevaporation at 35 °C gave the thiosulfato complex. Anal. Calcd for $[\text{Ru}(\text{NH}_3)_5\text{S}_2\text{O}_3]\text{Cl}$: N, 20.9; H, 4.53%. Found: N, 20.5; H, 4.62.

trans-Aquatetraammine(thiolato)ruthenium(III) complexes were prepared as follows: A stoichiometric amount of ligand was added to 0.20 g of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ dissolved in 20 mL of water at 50 °C. The mixture was stirred on a hot plate for 15 min or until the solution turned a deep purple color. At this time, it was cooled and the excess ligand was removed. This crude mixture was diluted 10-fold and charged onto a SP Sephadex C-25 column (2 cm \times 5 cm). Elution with 0.15 M HCl separated a purple band followed by an orange species upon elution with stronger acid. The exact nature of this orange species is unknown but appears similar to that first reported by Taube et al.⁷ in the synthesis of (sulfido)ruthenium complexes.

The purple species is the desired product and may be isolated as a chloride salt by rotoevaporation of the eluant to dryness at 50 °C in

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Table I. UV-Vis Spectral Data for Complexes

thiol group	λ_{\max} (nm)	ϵ ($M^{-1} \text{ cm}^{-1}$)	ref
	[Ru(NH ₃) ₄ OH ₂ (SR)] ²⁺		
perfluorophenyl	474	1800	this work
	330	3800	
	230	22000	
	230	22000	
<i>p</i> -methylphenyl	493	710	this work
	329	2950	
	250	4580	
	240	2190	
phenyl	509	380	this work
	329	2300	
	240	2190	
	240	2190	
<i>p</i> -methoxyphenyl	496	150	this work
	327	880	
	266	1380	
	230 (sh)	1430	
<i>p</i> -nitrophenyl	489	708	this work
	325	3370	
	220 (sh)	2830	
	220 (sh)	2830	
	[Ru(NH ₃) ₅ SR] ²⁺		
ethyl	508	1900	8
thiosulfate	512	390	this work
	289	14100	
	509	8	
phenyl	509	8	8
	[Ru(NH ₃) ₄ OH ₂ (S(O) ₂ R)] ²⁺		
phenyl ^b	330	<i>a</i>	this work
	225	<i>a</i>	
phenyl ^c	410	<i>a</i>	this work
<i>p</i> -nitrophenyl	255	<i>a</i>	this work
<i>p</i> -chlorophenyl	228	<i>a</i>	this work

^a Prepared pure only in solution. ^b Pentammineruthenium(III) center. ^c Sulfenate ligand on a pentammineruthenium(III) center.

dimmed light. All complexes were photosensitive and were stored in the dark at 0 °C in a desiccator.

Kinetic Measurements. Kinetic measurements were made using a Durum Model D-110 stopped-flow spectrophotometer interfaced with a computerized data acquisition system. The observed rate constants were obtained from an exponential fit of the raw data utilizing a data processing routine developed by the OLIS Corp. In all cases, at least a 10-fold stoichiometric excess of oxidant over the ruthenium(III) complex was used to ensure pseudo-first-order conditions. Each rate constant is an average of three to five trials. Due to photodecomposition of the ruthenium complexes, solution preparation and kinetic measurements were performed in dimmed light. When possible, Raysorb glassware was used to prevent photodecomposition.

Results and Discussion

Characterization of Complexes. The pentaammineruthenium(III) complexes of thiosulfate, benzenethiol, and ethanethiol have previously been characterized by Taube and co-workers.⁷ The tetraammineaqua(thiolato)ruthenium(III) complexes were not amenable to elemental analysis due to decomposition wherein the thiol ligand was lost. UV-vis spectra of freshly prepared samples were recorded, and the results are summarized in Table I. The spectra are similar to those found in pentaammine(thiolato)ruthenium(III) complexes (visible peak at ~510 nm) but with an additional band present around 330 nm. The addition of dilute ammonia to an aqueous solution of this complex results in the gradual loss of the 330-nm band and generation of a spectrum identical to that of the pentaammine complex. From these observations and the tendency of sulfur to labilize ligands trans to itself, we formulate these complexes as *trans*-[Ru(NH₃)₄OH₂(SR)]²⁺.

Characterization of Reaction. The stoichiometry of the reaction was established by adding excess HSO₅⁻ to oxidize the ruthenium-bound thiol and determining the excess HSO₅⁻ by spectrophotometric titration using ferrocyanide. The stoichiometric ratio of HSO₅⁻ to Ru(III) complexes for the complexes studied was

Table II. Infrared Spectral Data for Sulfinato Complexes^a

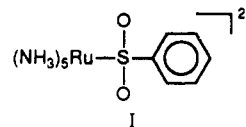
complex	S-O str freq (cm ⁻¹)	ref
[Co(NH ₃) ₅ SO ₂ Ph] ²⁺	1300, 1100	9
[Ru(NH ₃) ₅ SO ₂ Et] ²⁺	1365, 1075	this work
[Ru(NH ₃) ₅ SO ₂ Ph] ²⁺	1354, 1070	this work
[Ru(NH ₃) ₅ SO ₂ PhNO ₂] ²⁺	1355, 1065	this work

^a Obtained using KBr pellets.

found to be 2.1 ± 0.1 ; see supplementary material. From this information, the following general equation may be written:



Ion-exchange characteristics on SP-Sephadex resin indicate a 2+ charge for the ruthenium oxidation product. Isolation of a crude product as the chloride salt was possible for several thiol complexes, and the absorbances at 1100 and 1300 cm⁻¹ in the infrared are indicative of coordinated sulfones;⁹ see Table II. Since sodium benzenesulfinate is readily available and stable in aqueous media, the synthesis of the sulfinato complex was attempted by substitution onto pentaammineaquaruthenium(II) and subsequent oxidation to the +3 state using an equivalent amount of cerium(IV). Again, isolation of a pure solid product was unsuccessful, but the UV-vis characteristics of the complex produced in solution were the same as those obtained from the oxidation HSO₅⁻ process. From these observations and the propensity of HSO₅⁻ to react via oxygen transfer,^{10,11} the most probable formulation of the ruthenium(III) product is I.



Rapid-scanning spectroscopy indicates a two-step oxidation process for the benzenethiol complex; see supplementary material. The intermediate is assumed to be the sulfenate complex, and direct conversion of the thiolato to the sulfenate complex is indicated by the presence of an isosbestic point.

Kinetics of Oxidation Reaction. The kinetics of oxidation for the first step, monitored at the visible peak, were studied under pseudo-first-order conditions with the oxidant in excess. First-order traces were obtained for the disappearance of the visible peak, and monitoring at an appropriate wavelength (see supplementary material) gave the same rate constants for the appearance of the sulfenate intermediate. A plot of k_{obs} versus [HSO₅⁻] is linear with a zero y -intercept. The following rate law was obtained:

$$\text{rate} = k_{\text{obs}}[\text{Ru}]$$

Here $k_{\text{obs}} = k_1[\text{HSO}_5^-]$. No dependence on hydrogen ion was observed between 0.10 and 0.50 M (CF₃SO₃H). Table III lists values of k_1 for each of the complexes studied (observed rate constants in supplementary material).

The nature of the sulfur substituent dramatically influences the rate of this reaction for the series of substituted phenyl complexes. The reaction rate decreases in the presence of electron-withdrawing substituents. Correlation of the rate of this reaction with the degree of electron withdrawal via a Hammett plot is shown in Figure 1. The Hammett plot has a negative slope ($\rho = -0.66$) indicating that withdrawal of electron density at the coordinated sulfur greatly reduces its ability to attack the peroxy oxygen on peroxymonosulfate. This behavior is in contrast to that observed by Deutsch et al. for the hydrogen peroxide oxidation

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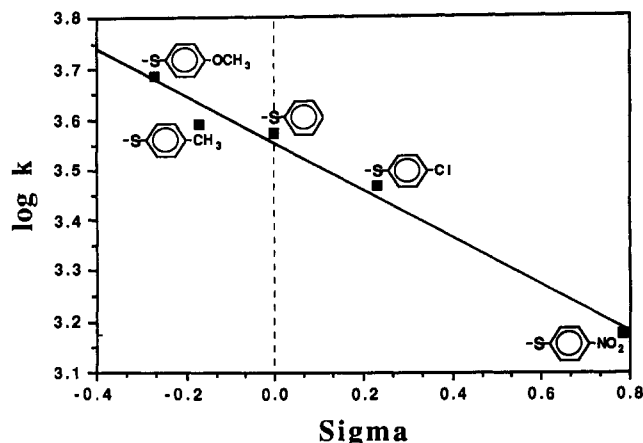
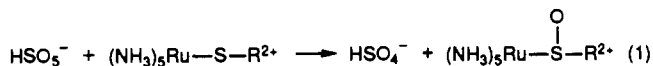


Figure 1. Hammett correlation plot for the HSO_5^- oxidation of a series of substituted benzenethiols coordinated to $[\text{Ru}^{\text{III}}(\text{NH}_3)_4(\text{OH}_2)]$. Conditions: $T = 25.0^\circ\text{C}$, $I = 1.00\text{ M}$ (lithium triflate), and $[\text{H}^+] = 0.10\text{ M}$ (triflic acid).

of cobalt(III) and chromium(III) complexes.⁴ In these investigations, little change in the reaction rates were observed. This may be due to only small changes in the electron-withdrawing/electron-donating character of the ligands chosen or to effects of first row versus second row transition metal centers. For ruthenium(III), the potential for better π -overlap between the sulfur d-orbitals and the metal d-orbitals may be expected with ruthenium compared to the first row metals. Studies with other metal thiolato complexes are currently in progress to investigate the role of the metal.

A mechanism may be written for this step involving nucleophilic attack of the coordinated sulfur on the peroxy oxygen of HSO_5^- to generate a coordinated sulfenato (eq 1). Although



attempts to isolate this complex proved unsuccessful, for the benzenethiol complex, rapid-scanning UV-vis spectrophotometry did allow for a crude spectral characterization (Table I). Due to the instability of the complexes, no oxygen tracer studies were feasible. It is assumed therefore that the sulfenato oxygen arises from the peroxide oxygen of the HSO_5^- moiety.¹¹

The second oxidation process was also examined under pseudo-first-order conditions. Plots of k_{obs} versus $[\text{HSO}_5^-]$ were linear with a positive y -intercept (observed rate constants in supplementary material). No hydrogen ion dependence was observed between 0.10 and 0.50 M acid. The following rate law may be written:

$$\text{rate} = k_{\text{obs}}[\text{Ru}]$$

Here $k_{\text{obs}} = k_2[\text{HSO}_5^-] + k_3$. Values of k_2 and k_3 are listed in Table III. In this step, k_2 is the oxidation rate and k_3 is the hydrolysis rate of the sulfenato intermediate. Evidence for the hydrolysis pathway, k_3 , comes from ion-exchange experiments. Reaction mixtures of the benzenethiolato complex were ion exchanged over Sephadex-CM-C25 resin in the sodium ion form. The eluate showed a UV spectrum which corresponded to that of free benzenesulfinate or benzenesulfonate if excess oxidant was present. Similar hydrolyses have been observed for chromium(III)-sulfinato complexes.^{3b}

In contrast to the first reaction, the second reaction is relatively insensitive of the nature of the coordinating thiol. This is thought to be due to the strong electron-withdrawing nature of the sulfenato oxygen overshadowing the effects of the phenyl group substituents. The two complexes with the greatest amount of withdrawing character from the phenyl ring, however, perfluorobenzenethiol and *p*-nitrobenzenethiol, do show a significant rate

Table III. Rate Constants for the Peroxymonosulfate/Ruthenium Thiol Oxidation Reactions

ligand substituent	$[\text{H}^+]$ (M)	$10^{-3}k_1^a$	$10^{-1}k_2^a$	$10^2k_3^b$
[Ru(NH ₃) ₄ (OH ₂)(SR)] ²⁺ (R = Substituted Thiophenol)				
perfluoro	0.5	0.050 ± 0.002		
	0.1	0.054 ± 0.002		
<i>p</i> -chloro	0.5	2.6 ± 0.2	4.3 ± 0.4	3.1 ± 0.3
	0.1	2.9 ± 0.3	4.5 ± 0.4	2.4 ± 0.2
<i>p</i> -methoxy	0.1	4.4 ± 0.4	5.8 ± 0.6	2.1 ± 0.2
	0.5	4.1 ± 0.40	2.8 ± 0.3	8.1 ± 0.7
<i>p</i> -methyl	0.1	3.8 ± 0.3	3.0 ± 0.3	1.0 ± 0.1
	0.5	1.50 ± 0.1	0.29 ± 0.02	4.0 ± 0.4
<i>p</i> -nitro	0.1	3.0 ± 0.3	2.4 ± 0.2	2.6 ± 0.3
	0.5	3.3 ± 0.3	2.7 ± 0.2	2.8 ± 0.2
SO ₃	0.1	[Ru(NH ₃) ₅ SR] ²⁺		
	0.5	0.35 ± 0.02	4.5 ± 0.4	1.8 ± 0.2
ethyl	0.1	38 ± 3	4.6 ± 0.4	1.3 ± 0.1
	0.5	31 ± 3	5.7 ± 0.5	<i>c</i>
phenyl	0.1	4.0 ± 0.4	4.9 ± 0.4	<i>c</i>
	0.5	4.0 ± 0.4	3.3 ± 0.3	2.7 ± 0.2

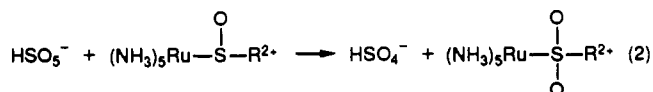
^a Units of $\text{M}^{-1}\text{s}^{-1}$, at 25.0°C , $I = 1.00\text{ M}$ (lithium triflate), $[\text{H}^+]$ adjusted using triflic acid. k_1 and k_2 are for the two oxidation reactions. ^b Units of s^{-1} and 25.0°C , $I = 1.00$ (lithium triflate), $[\text{H}^+]$ adjusted using triflic acid. k_3 is the aquation reaction of the sulfenato complex. ^c Unable to observe second reaction, possibly due to hydrolysis of the sulfenato complex.^{3b}

Table IV. Rate Constants for Oxidations of Thiolato Complexes^a

complex	oxidant	k_1 ($\text{M}^{-1}\text{s}^{-1}$)	k_2 ($\text{M}^{-1}\text{s}^{-1}$)	ref
[Co(en) ₂ cys] ²⁺	H ₂ O ₂	0.50		4
[Co(en) ₂ cys] ²⁺	HSO ₅ ⁻	40 ± 2		<i>b</i>
[Co(NH ₃) ₅ S ₂ O ₃] ⁺	HSO ₅ ⁻	700	40	11
[Ru(NH ₃) ₅ S ₂ O ₃] ⁺	HSO ₅ ⁻	350 ± 20	45 ± 4	this work
[Ru(NH ₃) ₅ (thiophenol)] ²⁺	H ₂ O ₂	50 ± 5		<i>b</i>
[Ru(NH ₃) ₅ (thiophenol)] ²⁺	HSO ₅ ⁻	4000 ± 400	33	this work

^a Ionic strength = 1.0 M (LiCF₃SO₃), $[\text{H}^+] = 0.10\text{ M}$ HCF₃SO₃, $T = 25.0^\circ\text{C}$. ^b Johnson, M. D.; Nickerson, D. Unpublished data.

decrease compared to the other complexes studied. In fact, for the perfluoro complex, no second step was observed at all. Apparently, too much electron density has been withdrawn by the fluoro groups for the sulfur to be an effective nucleophile toward the peroxy oxygen on HSO_5^- . A mechanism may be written for this second step (eq 2).



Conclusions

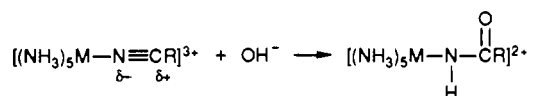
Oxidations of coordinated sulfur using peroxymonosulfate proceed at a greater rate than analogous hydrogen peroxide reactions. For [Co(en)₂cysN₃S]²⁺ a rate enhancement of 10² is observed for HSO_5^- over H₂O₂; see Table IV. This trend is consistent for other hydrogen peroxide/monoperoxosulfate couples.¹² Such differences may be understood by comparison of the leaving groups for the two processes. For H₂O₂ oxidations, the leaving group is OH⁻ whereas for HSO_5^- oxidations, the leaving group is HSO_4^- . In view of the superior ability of HSO_4^- to act as a leaving group compared to hydroxide ion, these monoperoxosulfate oxidations would be expected to proceed more rapidly. Similar conclusions have been made for the higher oxidation rates of H₃O₂⁺ compared to H₂O₂.⁵

Changing the nature of the ancillary sulfur ligand has a dramatic effect on the oxidation rates of ruthenium(III) thiolato complexes. For aromatic thiols, electron-withdrawing substituents lower the electron density at the sulfur site and decrease

(12) Johnson, M. D.; Nickerson, D. Unpublished results.

the ability of the sulfur to act as a nucleophile. Electron-donating substituents increase the electron density at the sulfur site and increase the sulfur's nucleophilicity. The oxygen in sulfenato complexes withdraws electron density from the sulfur and decreases the nucleophilicity of the sulfur.

The effect of varying the metal center between first- and second-row metals may be seen by comparing two metal complexes where the sulfur-containing ligand remains the same, e.g., $[(\text{NH}_3)_5\text{-RuSSO}_3]^+$ and $[(\text{NH}_3)_5\text{CoSSO}_3]^+$. As shown in Table IV, the oxidation rate constant for the ruthenium(III) complex is half that found for the cobalt(III) complex. This rate decrease must reflect differences in the amount of electron-withdrawing character of the two metals. Similar behavior is found in the hydration of nitrile ligands to form coordinated carboxamides via nucleophilic attack by a hydroxide ion.¹³



The greater amount of polarization experienced by the nitriles on ruthenium(III) causes significantly more *rapid* hydration compared to cobalt(III) nitriles due to less electron density residing on the ruthenium nitrile carbon. The same effect would *decrease*

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the reaction rate in the sulfur oxidations since the sulfur undergoes nucleophilic attack on the peroxy oxygen. Withdrawal of electron density at the sulfur results in a poorer nucleophile thereby decreasing the reaction rate. A comparison of the nucleophilicity of coordinated sulfur ligands was reported by Root and Deutsch for the methylation of coordinated thiols. In their study, the reactivity of a ruthenium(II) thiolate complex and cobalt(III), chromium(III), and nickel(II) thiolate complexes were compared. Enhanced nucleophilicity for the Ru(II) complex was observed and attributed to the π back-bonding tendency of the Ru(II) center.¹⁴ Unfortunately, the specific role of the metal center is somewhat clouded because the reactions compared were carried out in a wide range of solvents, both aliphatic and aromatic thiolates were methylated, and the secondary ligands on the metal center were varied dramatically. In our study, the only parameter varied was the metal center.

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Supplementary Material Available: Tables of stoichiometric and kinetic data and a figure showing rapid-scan spectra (5 pages). Ordering information is given on any current masthead page.

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