acid and thiocyanate are similar. Chloride dramatically increases the acceleration rate. It is possible that only in the chloride substitution reaction is the accelerating nature of the cis site showing up. The other bulky ions cannot get into the cis site as rapidly. This interpretation would be consistent with the I_a nature of the chromium(III) substitution reactions. The nitrate acceleration is uncertain due to scatter in the data.

Registry No. $Cr(OH_2)_6^{3+}$, 14873-01-9; $Cr(OH_2)_5(CH_3OH)^{3+}$, 29827-16-5; $Cr(OH_2)_5(NCS)^{2+}$, 22258-89-5; *trans*-$Cr(OH_2)_4(CH_3OH)(NCS)^{2+}$, 52003-12-0; *cis*-$Cr(OH_2)_4(CH_3OH)(NCS)^{2+}$, 52079-27-3; $Cr(OH_2)_3(CH_3OH)_2(NCS)^{2+}$, 52063-97-5; SCN^-, 302-04-5; F^-, 16984-48-8; CH_3OH, 67-56-1.

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Contribution from the Chemistry Division, Argonne National Laboratories, Argonne, Illinois 60439,
and from the Departments of Chemistry, University of Chicago, Chicago, Illinois 60637,
and University of Cincinnati, Cincinnati, Ohio 45221

Oxidation of Free and Coordinated Thiols by Neptunium(VI)[1a]

CHARLES J. WESCHLER,[1b,c] JAMES C. SULLIVAN,[1d] and EDWARD DEUTSCH*[1e]

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The Np(VI) oxidation of thioglycolic acid (tga) has been quantitatively investigated under conditions where the reaction involves a 1-equiv oxidation at sulfur. This reaction follows the rate law $-d(\ln [Np(VI)])/dt = (a + b/[H^+])[tga]$; at 25° and $\mu = 1.00\ F$ ($LiClO_4$), $a = 3.5 \pm 0.7\ F^{-1}\ sec^{-1}$, $b = 34.2 \pm 0.3\ sec^{-1}$, and the corresponding activation parameters are $\Delta H^*_a = 6 \pm 3$ and $\Delta H^*_b = 14.2 \pm 0.2$ kcal/mol and $\Delta S^*_a = -37 \pm 11$ and $\Delta S^*_b = -3.7 \pm 0.5$ eu. The Np(VI) oxidation of methyl thioglycolate follows a similar rate law with values of a and b at 25° and $\mu = 1.00\ F$ ($LiClO_4$) of $58 \pm 2\ F^{-1}\ sec^{-1}$ and $2.7 \pm 0.1\ sec^{-1}$, respectively. These results are interpreted as indicating that the net rate of oxidation of tga deprotonated at the carboxyl group (b^{COO}) is 12 times greater than the net rate of oxidation of tga deprotonated at the sulfhydryl group (b^S); however, the specific rate of oxidation of the latter form ($k_2^S = b^S/K^S$) is 10^3 times greater than that of the former ($k_2^{COO} = b^{COO}/K^{COO}$) since the acid dissociation constant of the carboxyl group (K^{COO}) is about 10^4 times greater than that of the sulfhydryl group (K^S). Qualitative observations have also been made on the Np(VI) oxidation of coordinated thiolato ligands in the complexes $[Cr(en)_2(SCH_2COO)]^+$, $[Co(en)_2(SCH_2COO)]^+$, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, $[Cr(en)_2(SCH_2CH_2COO)]^+$, $[Cr(en)_2(SC_6H_4COO)]^+$, and $[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$. The last two complexes consume roughly 1 equiv of Np(VI)/mol of complex and can be considered to undergo the same type of oxidation as free thiols. The other complexes undergo multiequivalent, multistep oxidations often involving oxidation of the thiol carbon backbone. Chromium(III)-thiolato complexes are oxidized much more rapidly than analogous cobalt(III) complexes and coordinated tga is oxidized much more rapidly than coordinated cysteamine or coordinated thiopropionic acid. Rationalizations to account for these observations are presented.

Introduction

Thiols contain the chemically most reactive functionality found in biological systems. A prominent feature of this reactivity is the ease of oxidation of thiols (RSH) to disulfides (RSSR), which in turn are resistant to further oxidation under mild conditions. The RSH-RSSR redox pair comprises an essential part of many electron-transport systems, the myriad biochemical roles of these systems having recently been reviewed.[2] Of particular interest to the inorganic chemist are the observations that in biological systems (1) transition metal complexes (*e.g.*, vitamin B_{12}[3]) are often associated with thiols and (2) the RSH-RSSR conversion is often mediated by metal-containing enzymes in relatively complicated reaction sequences (*e.g.*, phosphorylation of adenosine monophosphate can be coupled to the transfer of electrons from glutathione to cytochrome *c* in a reaction which requires oxidized glutathione as a catalyst[4]). In the hope of shedding some light on the chemistry of these complex natural processes, we have undertaken a detailed kinetic study of the relatively simple Np(VI) oxidation of free thioglycolic acid (tga) and its methyl ester in dilute aqueous solutions. Analogous studies with other metal ion oxidants have been reported,[5] but conclusions reached therein must be considered suspect in light of recent work showing that the stoichiometry of thiol oxidations is very sensitive to reaction conditions.[6] Indeed, the results reported in this study demonstrate that under properly controlled conditions the kinetics of metal ion oxidation of thiols are much simpler than previously appreciated.

Kinetic studies on the oxidation of free thiols also provide a standard to which the rates of oxidation of coordinated thiols may be compared. The oxidation of thiolato metal complexes is of considerable current interest in both biological and inorganic chemistry as evidenced by the following reports as to the possible courses such reactions may take: (a) autoxidation of $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$ leads to metal-sulfur bond fission and formation of the free disulfide;[7] (b) H_2O_2 oxidation of tris(cysteinato)cobaltate(III) proceeds by oxidation at the coordinated sulfur, with no cleavage of the metal-sulfur bond, to yield the S-bonded tris(cysteine)-sulfinato complex;[8] (c) oxidation of *O,S*-mercaptoacetatobis-

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[1] (a) A portion of this investigation was conducted under the auspices of the United States Atomic Energy Commission. (b) ANL-AUA-AEC Laboratory Graduate Participant, 1972-1973. (c) University of Chicago. (d) Argonne National Laboratory. (e) Presently located at University of Cincinnati.

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(ethylenediamine)chromium(III) by Np(VI) or Ce(IV) proceeds by oxidation at carbon and yields a monothiooxalato complex in which the sulfur has undergone no net oxidation and the metal-sulfur bond remains intact.[9] In an effort to elucidate the factors which determine which of these possible courses obtain in a particular system, we have also investigated the Np(VI) oxidation of several thiolato complexes of chromium(III) and cobalt(III).

Experimental Section

Materials. Unless otherwise specified, all chemicals were of reagent grade. The preparation and standardization of perchloric acid, lithium perchlorate, neptunium(VI) perchlorate, and neptunium(V) perchlorate solutions have been previously described.[10] **Thioglycolic acid** was available from a previous study.[6] **Methyl thioglycolate**, obtained from Aldrich Chemical Co., was purified by vacuum distillation (41.1-41.7° (10.5 mm)). **Dithiodiglycolic acid**, from Aldrich, was purified by precipitating it from acetone solution with toluene and then crystallizing the precipitate two times from hot carbon tetrachloride: mp 102°. **2,2′-Dithiodipyridine**, from Aldrich, was used without purification; stock solutions of this reagent were freshly prepared each day. ***O,S*-Mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate, *N,S*-(2-mercaptoethylamine)bis(ethylenediamine)chromium(III) perchlorate**, and ***N,S*-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III) perchlorate** were available from previous studies.[11,12] ***O,S*-Mercaptoacetatobis(ethylenediamine)cobalt(III) perchlorate**[13] was converted to the chloride salt for a single crystal X-ray structure analysis which confirmed the composition of this complex.[14] *Anal.* Calcd for $[Co(en)_2(SCH_2COO)]Cl \cdot H_2O$: C, 22.33; H, 6.25; N, 17.36; Cl, 10.99; Co, 18.26; S, 9.94. Found: C, 22.19; H, 6.03; N, 17.30; Cl, 11.12; Co, 18.19; S, 8.84. ***O,S*-(2-Mercaptobenzoato)bis(ethylenediamine)chromium(III) perchlorate** and ***O,S*-(3-mercaptopropionato)bis(ethylenediamine)chromium(III) perchlorate**[15] were prepared by the general technique already outlined[11] except that dimethylformamide was used as solvent for the appropriate disulfides. *Anal.* Calcd for $[Cr(en)_2(SC_6H_4COO)]ClO_4$: C, 31.17; H, 4.76; N, 13.22; Cr, 12.27; S, 7.57. Found: C, 31.20; H, 4.79; N, 13.08; Cr, 12.38; S, 7.68. Calcd for $[Cr(en)_2(SCH_2CH_2COO)]ClO_4$: C, 22.37; H, 5.37; N, 14.91; Cr, 13.84; S, 8.53. Found: C, 22.22; H, 5.44; N, 14.82; Cr, 14.04; S, 8.30. **Tris(ethylenediamine)chromium(III) chloride**[16] was the only solid complex purified and used as a chloride salt; all other solid complexes were crystallized three times as their perchlorate salts before being used in oxidation studies. Solutions of the *cis*-$[Cr(en)_2(OH_2)(OOCCH_2SH)]^{2+}$ ion were prepared immediately prior to use by ion-exchange procedures already documented.[11]

Analyses. Nonmetal elemental analyses were performed by Galbraith Laboratories, Inc. The concentrations of neptunium(V) solutions were determined spectrophotometrically at 9805 Å (ϵ 403.1 M^{-1} cm^{-1});[10] neptunium(VI) solutions were standardized as neptunium(V) after reduction with excess sodium nitrite. The total chromium concentration of solutions was determined spectrophotometrically as chromate at 3730 Å (ϵ 4815 M^{-1} cm^{-1})[17] after oxidation with basic peroxide. The total cobalt concentration of solutions was determined using Kitson's spectrophotometric method[18] with a known cobalt(II) solution being carried through the analysis as an internal standard.[19] The concentration of free thiol in solution was spectrophotometrically determined by a modification of the method of Grassetti and Murray[20] as previously described.[6]

Equipment. Pmr spectra were recorded using a Varian A-60 at 37°. A Cary Model 14 recording spectrophotometer was used to determine molar extinction coefficients and reaction stoichiometries. Kinetic experiments were performed on a Model D-110 Durrum stopped-flow spectrophotometer equipped with a storage oscilloscope. The drive syringes and mixing chamber of this instrument were thermostated to ±0.1°. Standard nonlinear least-squares calculations were carried out on a Xerox Sigma 5 computer.

General Procedures. Unless otherwise indicated, all manipulations were performed under anaerobic conditions using solutions which had been deaerated with an argon stream. Stoichiometry experiments were usually carried out by rapidly injecting the oxidant solution into the vigrously stirred reductant solution; identical results were obtained by reversing the order of addition.

Kinetic Measurements. All kinetic experiments were performed in anaerobic aqueous solutions of $HClO_4$ that were maintained at constant ionic strength of 1.00 ± 0.01 *F* with $LiClO_4$. Concentration of free thiol was always at least 20 times the concentration of Np(VI), and the course of the reaction was monitored at a wavelength specific for Np(VI) (usually 340 nm). At least three independent oscilloscope traces were photographed for each individual kinetic experiment, and then 15-20 absorbance-time points were manually read from each photograph. The usual plots of log $(A_t - A_\infty)$ *vs.* time were linear for at least 95% of the reaction. Values reported in this paper for the observed first-order rate parameters, k, and their standard deviations, σ_k, were obtained from a nonlinear least-squares adjustment of the A_t–t data for each trace within the first-order rate expression

$$A_t = A_\infty + (A_0 - A_\infty)e^{-kt} \qquad (1)$$

where A_0, A_∞, and k are treated as adjustable parameters. For each trace, the values of A_t calculated from eq 1 and the optimized values of A_0, A_∞, and k always agreed with the observed values of A_t to a standard deviation of less than 1.0% full-scale deflection on the oscilloscope screen; on the average, agreement was 0.3% of full-scale deflection. Optimized values of A_0 and A_∞ always agreed with observed values to well within experimental error.

Results

Oxidation of Thioglycolic Acid (tga). In an earlier paper[6] it was shown that the Np(VI) oxidation of thiols proceeds with a reaction stoichiometry of 1.0 if a large excess of thiol is present and if the reaction mixture is free from oxygen; *e.g.*, for tga

$$2HOOCCH_2SH + 2NpO_2^{2+} \rightarrow 2NpO_2^{+} + (HOOCCH_2S\text{-})_2 + 2H^+$$

As noted in the Experimental Section, kinetic results reported in this paper were obtained under such conditions and under these conditions Np(VI) disappears in a first-order fashion. Table I summarizes values of the observed first-order rate parameters, k, as a function of initial tga concentration. It is seen that k increases linearly with $[\text{tga}]_0$ and the average value of the corresponding second-order rate constant, k', under the conditions of Table I is 36.8 ± 1.6 F^{-1} sec^{-1}. Addition of either of the reaction products Np(V) or dithiodiglycolic acid to the initial reactant solutions has no significant effect on the observed first-order rate parameter. Thus the empirical form of the rate law at constant hydrogen ion concentration is

$$-d[\text{Np(VI)}]/dt = k'[\text{Np(VI)}][\text{tga}] \qquad (2)$$

The variation of k' as a function of $[H^+]$ and temperature is summarized in Table II. At each temperature the data are adequately correlated by the relation

$$k' = a + b/[H^+] \qquad (3)$$

At 14.9, 24.9, and 34.9° respectively values computed for a (F^{-1} sec^{-1}) and b (sec^{-1}) are 2.3 ± 0.3 and 14.3 ± 0.1, 3.5 ± 0.7 and 34.2 ± 0.3, 3.3 ± 1.7 and 77.4 ± 0.8. The small positive values of a could reflect a rate term or they may result from changes in activity coefficients induced by substituting H^+ for Li^+ in the ionic medium.[21] Since there is no definitive method to distinguish directly between minor

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Table I. Rate Parameters Governing Oxidation of Thioglycolic Acid, tga, by Np(VI) as a Function of $[\text{tga}]_0$[a-c]

$[\text{tga}]_0, F$	k, sec^{-1}	k', F^{-1} sec^{-1}
0.0221	0.797 ± 0.006	36.1 ± 0.3
0.0221	0.807 ± 0.007	36.5 ± 0.3
0.0221	0.791 ± 0.005	35.8 ± 0.2
0.0223	0.870 ± 0.007	39.0 ± 0.3
0.0223	0.858 ± 0.007	38.5 ± 0.3
0.0223	0.861 ± 0.005	38.6 ± 0.2
0.0223	0.807 ± 0.006	36.2 ± 0.3
0.0223	0.853 ± 0.008	38.3 ± 0.4
0.0233	0.846 ± 0.007	36.3 ± 0.3
0.0233	0.840 ± 0.005	36.1 ± 0.2
0.0233	0.836 ± 0.008	35.9 ± 0.3
0.0233	0.844 ± 0.006	36.2 ± 0.3
0.0233	0.811 ± 0.008	34.8 ± 0.3
0.0621	2.36 ± 0.02	38.0 ± 0.3
0.0621	2.35 ± 0.02	37.8 ± 0.3
0.0621	2.38 ± 0.02	38.3 ± 0.3
0.326	12.6 ± 0.1	38.7 ± 0.3
0.326	12.3 ± 0.1	37.7 ± 0.3
0.326	11.8 ± 0.1	36.2 ± 0.3
1.227	42.5 ± 0.4	34.6 ± 0.3
1.227	40.6 ± 0.4	33.1 ± 0.3

[a] $[\text{tga}]_0$ ≡ initial concentration of thioglycolic acid; k ≡ observed first-order rate constant; $k' = k/[\text{tga}]_0$. [b] Conditions: 24.9°; $[\text{H}^+] = \mu = 1.00$ F; $[\text{Np(VI)}]_0 = (0.95\text{-}1.24) \times 10^{-3}$ F; λ 340 nm. [c] As described in text, multiple entries result from analysis of independent oscilloscope traces for a given set of reactant solutions.

Table II. Rate Parameters Governing Oxidation of Thioglycolic Acid by Np(VI) as a Function of Temperature and Acid Concentration[a,b]

14.9°		24.9°		34.9°	
$[\text{H}^+]$, F	k', F^{-1} sec^{-1}	$[\text{H}^+]$, F	k', F^{-1} sec^{-1}	$[\text{H}^+]$, F	k', F^{-1} sec^{-1}
0.056	249 ± 1	0.036	1036 ± 7	0.056	1480 ± 10
0.056	253 ± 1	0.036	1038 ± 7	0.056	1490 ± 10
0.056	254 ± 1	0.036	986 ± 8	0.056	1500 ± 10
0.100	144 ± 1	0.036	995 ± 6	0.056	1440 ± 10
0.100	148 ± 1	0.064	527 ± 4	0.100	754 ± 5
0.100	144 ± 1	0.064	530 ± 3	0.100	757 ± 6
0.150	98.2 ± 0.7	0.064	509 ± 3	0.150	507 ± 6
0.150	100.7 ± 0.7	0.064	517 ± 6	0.150	510 ± 3
0.150	98.2 ± 0.6	0.064	529 ± 5	0.150	525 ± 3
0.300	50.4 ± 0.4	0.064	517 ± 3	0.300	260 ± 1
0.300	51.4 ± 0.4	0.100	348 ± 3	0.300	260 ± 2
0.300	52.4 ± 0.3	0.100	366 ± 2	0.300	252 ± 2
0.500	31.5 ± 0.3	0.100	328 ± 3	0.500	156 ± 1
0.500	31.8 ± 0.2	0.144	235 ± 1	0.500	157 ± 1
0.500	31.8 ± 0.2	0.144	234 ± 1	0.500	157 ± 1
1.00	16.1 ± 0.1	0.144	234 ± 1	1.00	82.3 ± 0.5
1.00	16.1 ± 0.1	0.144	234 ± 1	1.00	83.6 ± 0.7
1.00	16.2 ± 0.1	0.304	114 ± 1	1.00	80.9 ± 0.4
		0.304	115 ± 1		
		0.304	114 ± 1		
		0.360	100 ± 1		
		0.360	98.2 ± 0.6		
		0.360	104 ± 1		
		0.544	68.3 ± 0.5		
		0.544	68.0 ± 0.4		
		0.544	69.8 ± 0.4		
		1.00	*c*		

[a] See footnotes *a* and *c* of Table I. [b] Conditions: $\mu = 1.00$ F; $[\text{Np(VI)}]_0 = (0.95\text{-}1.24) \times 10^{-3}$ F; $[\text{tga}]_0 = 0.022\text{-}1.23$ F; λ 340 nm. [c] Twenty-one data points from Table I fit here.

rate terms and activity effects, the data of Table II were successively treated within each hypothesis. First, all 74 rate constants at each $[\text{H}^+]$ and temperature were weighted as $1/\sigma_k^2$ and then fitted according to the expression

$$k' = [e^{[\text{H}^+](P_1+P_2\theta)}][kT/h][1/[\text{H}^+]]e^{-\Delta H^*{}_b/RT}e^{\Delta S^*{}_b/R} \quad (4)$$

where θ is the temperature in degrees centigrade, $(P_1 + P_2\theta)$ is the standard Harned factor β separated into temperature-independent and -dependent portions, and the subscript b refers to the slope of the k' *vs.* $1/[\text{H}^+]$ plot (eq 3). The values of the four parameters that best describe the data within eq 4 are $\Delta H^*{}_b = 14.3 \pm 0.2$ kcal/mol, $\Delta S^*{}_b = -3.6 \pm 0.5$ eu, $P_1 = 0.22 \pm 0.05$ F^{-1}, and $P_2 = -0.023 \pm 0.004$ F^{-1} deg^{-1}, the average deviation between calculated and observed rate constants being 2.9%. The value of β at 25° calculated from P_1 and P_2 is -0.35 F^{-1}, considerably outside the range 0-0.1 F^{-1} considered to be normal for $\text{H}^+\text{-Li}^+$ solutions.[21b] When the weighted rate data are fitted to the standard Eyring expression

$$k' = [kT/h]\{e^{-\Delta H^*{}_a/RT}e^{\Delta S^*{}_a/R} + [1/[\text{H}^+]e^{-\Delta H^*{}_b/RT}e^{\Delta S^*{}_b/R}\} \quad (5)$$

the values of the four parameters which best describe the data are $\Delta H^*{}_a = 6 \pm 3$ kcal/mol, $\Delta S^*{}_a = -37 \pm 11$ eu, $\Delta H^*{}_b = 14.2 \pm 0.2$ kcal/mol, and $\Delta S^*{}_b = -3.7 \pm 0.5$ eu with an average deviation between calculated and observed rate constants of 3.0%.

Oxidation of Methyl Thioglycolate (Me(tga)). Prior to investigating the oxidation of Me(tga) by Np(VI) it was confirmed that the rate of ester hydrolysis is not competitive with the oxidation process. Using pmr techniques, the half-lives for ester hydrolysis in 0.4 and 1.0 F HClO_4 (37°, $[\text{Me(tga)}]_0 \simeq 1$ F) were found to be 211 and 52.5 min, respectively. Appropriate care was exercised in the preparation and handling of Me(tga) solutions to minimize ester hydrolysis during oxidation studies.

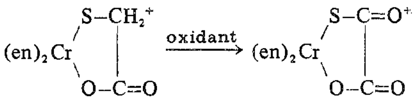
At constant $[\text{H}^+]$ oxidation of Me(tga) by Np(VI) is presumed to follow the rate law

$$-\text{d}[\text{Np(VI)}]/\text{d}t = k'[\text{Np(VI)}][\text{Me(tga)}] \quad (2\text{a})$$

by analogy to the tga system (eq 2). Table III summarizes the dependence of k' on $[\text{H}^+]$; correlating this data within eq 3 results in $a = 58 \pm 2$ F^{-1} sec^{-1} and $b = 2.7 \pm 0.1$ sec^{-1}.

Oxidation of Dithiodiglycolic Acid (dtdga). When Np(VI) is added to dtdga in 1.0 F HClO_4 at 25°, Np(V) is produced with a half-life of 6.5 hr ($[\text{Np(VI)}]_0 = 6.3 \times 10^{-3}$ F, $[\text{dtdga}]_0 = 19.1 \times 10^{-3}$ F). This corresponds to a first-order rate parameter of *ca.* 3×10^{-5} sec^{-1}.

Oxidation of $[\text{Cr(en)}_2(\text{SCH}_2\text{COO})]\text{ClO}_4$ (Cr(tga)). We recently reported on the chemistry of the oxidation of Cr(tga) by Np(VI) or Ce(IV).[9] These reactions yield the monothiooxalato complex A



Cr(tga) A

4 equiv of Np(VI) being consumed per mole of Cr(tga) when Np(VI) is used as oxidant.[9] Our attempts to characterize the dynamics of the Np(VI) oxidation showed that this reaction is too complicated to be readily amenable to detailed kinetic analysis. Table IV summarizes some qualitative observations on this system when stoichiometric amounts of reagents are employed. The reaction consists of one or more fast steps

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[21] (a) For a general discussion of this phenomenon see H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1959, Chapter 14. (b) For previously observed effects of this phenomenon see T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965); D. L. Toppen and R. G. Linck, *ibid.*, 10, 2636 (1971); C. Lavallee and T. W. Newton, *ibid.*, 11, 2616 (1972); C. Lavallee and E. Deutsch, *ibid.*, 11, 3133 (1972).

Table III. Rate Parameters Governing Oxidation of Methyl Thioglycolate by Np(VI) as a Function of Acid Concentration[a]

$[H^+]$, F	k', F^{-1} sec^{-1}	$[H^+]$, F	k', F^{-1} sec^{-1}
0.050	110 ± 1	0.500	62.1 ± 0.4
0.050	117 ± 1	0.500	64.6 ± 0.5
0.050	110 ± 1	0.500	63.8 ± 0.4

[a] Conditions: 25.0°; $\mu = 1.00\ F$; $[\mathrm{Me(tga)}]_0 = 4.04 \times 10^{-3}\ F$; $[\mathrm{Np(VI)}]_0 = 0.514 \times 10^{-3}\ F$; λ 300 nm.

Table IV. Observations on the Rate of Np(VI) Oxidation of Cr(tga)[a,b]

10^3[Np(VI)]$_0$, F	10^3[Cr(tga)]$_0$, F	$[H^+]$, F	Observations
19.6	4.93	0.01	Initial fast portion followed by slower portion; total reaction over within 10 sec[c]
2.07	0.480	0.01	Initial fast portion followed by slower portion; total reaction over within 100 sec[c]
0.894	0.227	0.01	Three equivalents of Np(V) produced within first 5 sec; fourth equivalent produced within 200 sec[d]
0.894	0.227	0.11	Three equivalents of Np(V) produced with first 5 sec; gradual further growth of Np(V), but fourth equivalent not produced with 2400 sec[d]
0.894	0.227	0.56	Three equivalents of Np(V) produced within first 5 sec; no significant amount of Np(V) produced within next 300 sec[d]

[a] Cr(tga) ≡ $[\mathrm{Cr(en)_2(SCH_2COO)}]\mathrm{ClO_4}$. [b] Conditions: 25°; no $\mathrm{LiClO_4}$ added; $[\mathrm{Np(VI)}]_0 = 4[\mathrm{Cr(tga)}]_0$. [c] Reaction monitored at 590 nm on a Durrum stopped-flow spectrophotometer. [d] Reaction monitored at 980.5 nm on a Cary 14 spectrophotometer.

Table V. Absorption Spectra (320–700 nm) of Selected Cobalt(III) Complexes[a]

Complex	$\lambda_{\max}$ (ϵ)
Acid	
P_2[b]	500 (133), 350 (157)
$[\mathrm{Co(en)_2(OOCCOO)}]^+$[c]	499 (112), 356 (145)
cis-$[\mathrm{Co(en)_2(OH_2)_2}]^{3+}$[d]	495 (71), 355 (66)
cis-$[\mathrm{Co(en)_2(OH_2)(OOCCH_2OH)}]^{2+}$[e]	498 (100), 360 (80)
cis-$[\mathrm{Co(en)_2(OH_2)(OOCCH_3)}]^{2+}$[f]	498 (100), 360 (78)
Base	
P_2[b]	513 (150), 355 (234)
cis-$[\mathrm{Co(en)_2(OH)_2}]^+$[d]	520 (95), 370 (110)
cis-$[\mathrm{Co(en)_2(OH)(OOCCH_3)}]^+$[f]	512 (102), 365 (85)

[a] Wavelength in nm; value inside parentheses is molar extinction coefficient in F^{-1} cm^{-1}. [b] This work. Pink reaction product of Np(VI) + $[\mathrm{Co(en)_2(SCH_2COO)}]^+$ of 2+ formal charge. [c] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jap.*, 28, 572 (1955). [d] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, 6, 1265 (1952). [e] R. H. Lane, Ph.D. Dissertation, University of Florida, 1971. [f] V. Carunchio, G. Illuminati, and G. Ortaggi, *Inorg. Chem.*, 6, 2168 (1967).

in which 3 mol of Np(V) is produced per mole of Cr(tga) initially present, followed by a much slower step which produces the last mole of Np(V). If the initial concentration of Cr(tga) is represented as X, then that of Np(VI) is $4X$, and the data in Table IV show that the rate of the slow step is proportional to X and *not* to X^2; the rate of the slow step is also decreased by increasing acid concentration.

Oxidation of $[\mathrm{Co(en)_2(SCH_2COO)}]\mathrm{ClO_4}$ (Co(tga)). When excess Np(VI) is added to Co(tga) in 0.010 F $\mathrm{HClO_4}$ at 25°, Np(V) is produced at a much slower rate than in the corresponding Cr(tga) reaction. After 4–8 min (depending on the initial concentration of Np(VI); $[\mathrm{Co(tga)}]_0$ = *ca.* $2.5 \times 10^{-4}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Co(tga)}]_0$ = 7.7–30.8) the yield of Np(V) levels at about 4 mol of Np(V)/mol of Co(tga) initially present (*i.e.*, $[\mathrm{Np(V)}]/[\mathrm{Co(tga)}]_0 = 4$). When this reaction is carried out at a higher acid concentration (0.60 F $\mathrm{HClO_4}$, other conditions similar), it takes 100 min for $[\mathrm{Np(V)}]/[\mathrm{Co(tga)}]_0$ to reach 2.3–2.7.

Ion-exchange analysis of the 0.010 F $\mathrm{HClO_4}$-Co(tga) product mixture shows the presence of two major cobalt-containing products, P_1 and P_2. P_1 is brown and has elution characteristics consistent with a 1+ formal charge. This product could not be completely separated from Np(V) and Np(VI) (1+ and 2+ formal charges, respectively) and therefore its ultraviolet spectrum and the extinction coefficient of its peak at 505 nm could not be determined. P_2 is pink, has elution characteristics consistent with a 2+ formal charge, and gives a negative test for cobalt(II). The visible spectrum of this product in 0.10 F $\mathrm{HClO_4}$ differs markedly from its spectrum in base (see Table V), suggesting the presence of coordinated water; the ultraviolet spectrum in acidic medium exhibits just one band ($\lambda_{\max}$ 225 nm; ϵ 18,000 F^{-1} cm^{-1}) indicating the absence of coordinated sulfur.[11] When the oxidation of Co(tga) is carried out under more vigorous conditions (oxidant = Ce(IV), $[\mathrm{Co(tga)}]_0 = 0.010\ F$, 1.0 F $\mathrm{H_2SO_4}$), P_2 is the only cobalt-containing product observed and the odor of $\mathrm{H_2S}$ is easily detected over the reaction solution.

By increasing the initial concentrations of Np(VI) and Co(tga) about 100-fold ($[\mathrm{Co(tga)}]_0 = 0.057\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Co(tga)}]_0 = 4.2$) it is possible to detect and isolate a minor reaction product P_3 which is not observed at the lower concentrations used above. P_3 is purple and is slowly eluted from Dowex 50-X2 with 6.0 F HCl indicating a formal charge of 3+ or greater. On the basis of three independently collected samples, P_3 is identified as a $\mathrm{Np^V}$–$\mathrm{Co^{III}}$ complex with Co:Np ratio of 1.07 ± 0.09. The spectrum of this product ($\lambda_{\max}$ 451, 575, 620, 1000, and 1020 nm; ϵ 53, 61, 47, 208, and 34 F^{-1} cm^{-1}, respectively) is consistent with its formulation as a binuclear complex. Especially indicative in this context is the shift of the characteristic 980.5-nm band of free $\mathrm{NpO_2^+}$ to a longer wavelength (1000 nm); similar shifts are observed for this band in other Np(V) binuclear complexes.[22] Over a period of 1 week in 6.0 F HCl at 25°, P_3 slowly dissociates yielding free Np(V).

Oxidation of $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}](\mathrm{ClO_4})_2$ (Cr(cys)). When excess Np(VI) is added to Cr(cys) in 0.010 F $\mathrm{HClO_4}$ at 25°, a two-stage reaction is again observed. The faster portion is complete within 1 min; the amount of Np(V) produced in this stage varies from 2.9 to 3.7 equiv/mol of Cr(cys) initially present, increasing as does the initial concentration of Np(VI) ($[\mathrm{Cr(cys)}]_0$ = *ca.* $2 \times 10^{-4}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(cys)}]_0$ = 5.2–15.4). The slower portion continuously yields Np(V), $[\mathrm{Np(V)}]/[\mathrm{Cr(cys)}]_0$ attaining an overall value of 4.5 within 1 hr of mixing.

Oxidation of $[\mathrm{Co(en)_2(SCH_2CH_2NH_2)}](\mathrm{ClO_4})_2$ (Co(cys)). When excess Np(VI) is added to Co(cys) in 0.010 F $\mathrm{HClO_4}$ at 25° ($[\mathrm{Co(cys)}]_0 = 2.18 \times 10^{-4}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Co(cys)}]_0$ = 16.1), no Np(V) can be detected even after several hours.

Oxidation of $[\mathrm{Cr(en)_2(SCH_2CH_2COO)}]\mathrm{ClO_4}$ (Cr(tpa)). The reaction of excess Np(VI) with Cr(tpa) in 0.010 F $\mathrm{HClO_4}$

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[22] (a) J. C. Sullivan, *J. Amer. Chem. Soc.*, 84, 4256 (1962); (b) J. C. Sullivan, *Inorg. Chem.*, 3, 315 (1964); (c) R. K. Murmann and J. C. Sullivan, *ibid.*, 6, 892 (1967).

at 25° again proceeds in two stages. The initial portion is complete within 4 min after mixing and yields 3.05 ± 0.05 mol of Np(V)/mol of Cr(tpa) initially present (average of four independent determinations, $[\mathrm{Cr(tpa)}]_0 = ca.\ 2.6 \times 10^{-4}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tpa)}]_0 = 5.7\text{-}10.9$). The subsequent slow stage produces Np(V) well past $[\mathrm{Np(V)}]/[\mathrm{Cr(tpa)}]_0 = 4$. When the acid concentration is lowered to *ca.* $10^{-5}\ F$, other conditions similar, the rate of the slow portion is considerably increased (the fast stage still proceeds with 3:1 stoichiometry). No spectral evidence for a binuclear $\mathrm{Np^{V}\text{-}Cr^{III}}$ product could be obtained at either of the acidities investigated.

Oxidation of $[\mathrm{Cr(en)_2(SC_6H_4COO)}]\mathrm{ClO_4}$ (Cr(tba)). The reaction of excess Np(VI) with Cr(tba) in 0.010 *F* $\mathrm{HClO_4}$ at 25° once again proceeds in two distinct stages. The first stage takes place on the stopped-flow time scale and produces 1.5 mol of Np(V)/mol of Cr(tba) initially present. The following observations are pertinent to this portion of the reaction. (1) At 580, 530, and 420 nm, the absorbance of the reactant solution initially increases before decaying to the expected final value. This observation is taken to imply the existence of a transient reaction intermediate with extinction coefficients at the above wavelengths that are greater than those of Cr(tba). (2) If $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0 = 1.5$ (*i.e.*, stoichiometric concentrations for this portion of the reaction), then plots of $1/(A_t - A_\infty)$ *vs.* time are linear for the decay of the intermediate and the slopes of these plots are not affected by changing the concentrations of the reactants. (3) If $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0$ is greater than 8.0, then plots of $\log (A_t - A_\infty)$ *vs.* time are linear for the decay of the intermediate. In the range $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0 = 1.5\text{-}8.0$, composite rate plots are observed. (4) Addition of Np(V) to the reactants decreases the rate of intermediate formation, the rate of intermediate decay, and the maximum observed absorbance, A_{max}. The rate of intermediate decay is inversely proportional to the concentration of Np(V) added. (5) Varying $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0$ from 1.0 to 8.0 has no effect on the observed value of A_{max}; decreasing this ratio to 0.5 decreases A_{max}. (6) Varying $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0$ from 1.5 to 8.0 has no effect on the observed value of A_∞; decreasing this ratio to 1.0 or 0.5 increases A_∞.

Attempts to identify the chromium-containing product, or products, of the oxidation of Cr(tba) with 1.5 equiv of Np(VI) have led to the following observations. (1) The product(s) has (have) an absorption maximum at 525 nm with an effective extinction coefficient less than that of Cr(tba) at its absorption maximum of 490 nm. (2) The product(s) cannot be eluted from Dowex 50W-X2 ion-exchange resin with 6.8 *F* $\mathrm{NaClO_4}$, indicating a formal charge of 3+ or greater. (3) Addition of sodium tetraphenylborate to the product mixture separates the chromium-containing product(s) from neptunium species, but the resulting precipitate is insoluble in water. Elemental analysis of this solid gives a Cr:S:N ratio of 1:1:4, the same as in Cr(tba); comparative infrared spectra indicate that this solid is not the tetraphenylborate salt of Cr(tba).

The slow stage of the Np(VI) oxidation of Cr(tba) continuously produces Np(V). For $[\mathrm{Cr(tba)}]_0 = 1.30 \times 10^{-3}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(tba)}]_0 = 8.63$, and $[\mathrm{H^+}] = 0.010\ F$, the ratio of Np(V) produced to Cr(tba) initially present is 1.8 within seconds of mixing, 2.0 about 10 min after mixing, 2.2 after 20 min, 2.4 after 40 min, 2.6 after 60 min, and in excess of 4.0 within 4 hr of mixing. Increasing the acidity increases the rate of the slow stage and accentuates the leveling of $[\mathrm{Np(V)}]/[\mathrm{Cr(tba)}]_0$ at 3.0; at $[\mathrm{H^+}] = 3.45\ F$, other conditions similar, $[\mathrm{Np(V)}]/[\mathrm{Cr(tba)}]_0 = 2.5$ within 1 min of mixing, 2.87 after 3 min, 2.95 after 5 min, and 3.01 after 8 min. No spectral evidence for a binuclear $\mathrm{Np^{V}\text{-}Cr^{III}}$ product could be obtained at either of the acidities investigated.

Oxidation of $[\mathrm{Cr(en)_2(OH_2)(OOCCH_2SH)}](\mathrm{ClO_4})_2$ (Cr(OH₂)(tga)). As in the oxidation of Cr(tba), addition of excess Np(VI) to $\mathrm{Cr(OH_2)(tga)}$ in 0.010 *F* $\mathrm{HClO_4}$ at 25° results in an initial rapid yield of 1.5 equiv of Np(V) per mole of $\mathrm{Cr(OH_2)(tga)}$ initially present. This is then followed by a much slower Np(V) production; for $[\mathrm{Cr(OH_2)(tga)}]_0 = 1.94 \times 10^{-4}\ F$ and $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(OH_2)(tga)}]_0 = 5.26$, the ratio $[\mathrm{Np(V)}]/[\mathrm{Cr(OH_2)(tga)}]_0$ is 1.53 within 1 min of mixing, 1.58 after 12 min, and 1.66 after 45 min. This rate of Np(V) production is not affected by increasing acid concentration to 0.80 *F* but is decreased by decreasing $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(OH_2)(tga)}]_0$ to 2.63 (with $[\mathrm{Cr(OH_2)(tga)}]_0 = 3.88 \times 10^{-4}\ F$); under these conditions $[\mathrm{Np(V)}]/[\mathrm{Cr(OH_2)(tga)}]_0$ is 1.34 after 2 min and 1.45 after 40 min.

Oxidation of $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$ (Cr(en)). When excess Np(VI) is added to Cr(en) in 0.010 *F* $\mathrm{HClO_4}$ at 25°, no detectable Np(V) is produced over a period of 1 hr ($[\mathrm{Cr(en)}]_0 = 1.37 \times 10^{-3}\ F$, $[\mathrm{Np(VI)}]_0/[\mathrm{Cr(en)}]_0 = 7.4$).

Discussion

Oxidation of Free Thiols. Under the reaction conditions outlined earlier (large excess of thiol, complete exclusion of oxygen) the Np(VI) oxidation of thioglycolic acid (tga) proceeds according to the relatively simple rate law

$$-\mathrm{d}(\ln\ [\mathrm{Np(VI)}])/\mathrm{d}t = (a + b/[\mathrm{H^+}])[\mathrm{tga}] \qquad (6)$$

Considering the relative acidities of Np(VI) and tga, the $b/[\mathrm{H^+}]$ rate term plausibly reflects an activated complex wherein a proton has been lost from tga. Since there are two possible sites of deprotonation in tga, the following steps must be considered

$$\mathrm{HOOCCH_2SH} \overset{K^{\mathrm{COO}}}{=} [\mathrm{OOCCH_2SH}]^- + \mathrm{H^+}$$

$$\mathrm{HOOCCH_2SH} \overset{K^{\mathrm{S}}}{=} [\mathrm{HOOCCH_2S}]^- + \mathrm{H^+}$$

$$\mathrm{Np(VI)} + \mathrm{HOOCCH_2SH} \xrightarrow{k_1} \mathrm{Np(V)} + {}^1/_2(\mathrm{HOOCCH_2S}\text{-})_2 + \mathrm{H^+}$$

$$\mathrm{Np(VI)} + [\mathrm{OOCCH_2SH}]^- \xrightarrow{k_2^{\mathrm{COO}}} \mathrm{Np(V)} + {}^1/_2(\mathrm{HOOCCH_2S}\text{-})_2$$

$$\mathrm{Np(VI)} + [\mathrm{HOOCCH_2S}]^- \xrightarrow{k_2^{\mathrm{S}}} \mathrm{Np(V)} + {}^1/_2(\mathrm{HOOCCH_2S}\text{-})_2$$

This mechanism leads to the rate expression

$$-\mathrm{d}(\ln\ [\mathrm{Np(VI)}])/\mathrm{d}t = \left[\frac{k_1 + k_2^{\mathrm{COO}}K^{\mathrm{COO}}/[\mathrm{H^+}] + k_2^{\mathrm{S}}K^{\mathrm{S}}/[\mathrm{H^+}]}{1 + K^{\mathrm{S}}/[\mathrm{H^+}] + K^{\mathrm{COO}}/[\mathrm{H^+}]}\right][\mathrm{tga}] \qquad (7)$$

where [tga] represents the total concentration of thioglycolic acid in all its forms. K^{COO} is known to be about $2.1 \times 10^{-4}\ F$ (K_1 of tga at 25°)[23] and K^{S} may be estimated to be about $10^{-8}\ F$ (the acid dissociation constant of methyl thioglycolate is $1.2 \times 10^{-8}\ F$ at 25°).[23] Thus both K^{S} and K^{COO} are much smaller than $[\mathrm{H^+}]$ for all hydrogen ion concentrations considered in this study and eq 7 reduces to the form of eq 6 with $a = k_1$ and $b = k_2^{\mathrm{S}}K^{\mathrm{S}} + k_2^{\mathrm{COO}}K^{\mathrm{COO}}$. It is convenient to define $b^{\mathrm{S}} = k_2^{\mathrm{S}}K^{\mathrm{S}}$ and $b^{\mathrm{COO}} = k_2^{\mathrm{COO}}K^{\mathrm{COO}}$ and therefore b for tga is $b^{\mathrm{S}} + b^{\mathrm{COO}}$ (see Table VI).

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(23) H. A. Sober, Ed., "Handbook of Biochemistry," 2nd ed, The Chemical Rubber Co., Cleveland, Ohio, 1970, p J-223.

Table VI. Summary of Rate Parameters for the Np(VI) Oxidation of Thiols[a, b]

Parameter	Me(tga)	tga
a, F^{-1} sec^{-1}	58 ± 2[c]	3.5 ± 0.7[c]
b, sec^{-1}	2.7 ± 0.1[c]	34.2 ± 0.3[c]
b^{S}, sec^{-1}	2.7 ± 0.1[c]	2.7[d]
K^{S}, F	1.2×10^{-8} [e]	1.2×10^{-8} [d]
$k_2{}^{\mathrm{S}}$, F^{-1} sec^{-1}	2×10^{8} [f]	2×10^{8} [f]
b^{COO}, sec^{-1}		$34.2 - 2.7 = 31.5$[f]
K^{COO}, F		2.1×10^{-4} [e]
$k_2{}^{\mathrm{COO}}$, F^{-1} sec^{-1}		1.5×10^{5} [f]

[a] Me(tga) ≡ methyl thioglycolate; tga ≡ thioglycolic acid. [b] Conditions: 25°, $\mu = 1.00$ *F*. [c] Measured parameter. [d] Parameter assumed equal to corresponding Me(tga) parameter. [e] Value of parameter taken from ref 23. [f] Calculated parameter.

In order to gain some information as to the relative importance of the two possible inverse hydrogen ion paths (oxidation of tga deprotonated at sulfur *vs.* oxidation of tga deprotonated at the carboxyl group), we briefly investigated the acid dependence of the Np(VI) oxidation of methyl thioglycolate (Me(tga)) in which there is no ambiguity as to the site of deprotonation. Under similar conditions this reaction also proceeds by a rate law of the form of eq 6, but the observed value of b is considerably smaller than that seen in the tga case (b(Me(tga)) = 2.7 ± 0.1 sec^{-1} *vs.* b(tga) = 34.2 ± 0.3 sec^{-1}). Since the b term for Me(tga) must result from deprotonation of the sulfhydryl group, as a first approximation we can take this value to equal b^{S} for tga oxidation. Thus oxidation of deprotonated tga occurs along parallel paths with the net rate of oxidation of tga deprotonated at the carboxyl group (b^{COO}) being *ca.* 12 times greater than the net rate of oxidation of tga deprotonated at the sulfhydryl group (b^{S}). From this first approximation it can be calculated that the specific rate for Np(VI) oxidation of $[\mathrm{HSCH_2COO}]^-$ ($k_2{}^{\mathrm{COO}}$) is *ca.* 1.5×10^5 F^{-1} sec^{-1}; by making the additional approximation that K^{S} for tga is about equal to the acid dissociation constant of Me(tga), it can also be calculated that the specific rate for Np(VI) oxidation of $[\mathrm{SCH_2COOH}]^-$ or $[\mathrm{SCH_2COOCH_3}]^-$ ($k_2{}^{\mathrm{S}}$) is *ca.* 2×10^8 F^{-1} sec^{-1} approaching the diffusion-controlled limit. Therefore the observed smaller net rate of oxidation of $[\mathrm{SCH_2COOH}]^-$ relative to $[\mathrm{HSCH_2COO}]^-$ is due to the acid dissociation constant of the sulfhydryl group being sufficiently smaller than that of the carboxyl group so that the very fast rate of oxidation of $[\mathrm{SCH_2COOH}]^-$ is overridden (see Table VI).

It is of interest to note that the a term (which for the above mechanism is just k_1, the specific rate of oxidation of the protonated form) is much larger for Me(tga) than for tga (58 ± 2 *vs.* 3.5 ± 0.7 F^{-1} sec^{-1}; it should be reemphasized that this latter value may reflect a medium effect and therefore may not be a true rate parameter). This qualitative difference may at least partially be understood in terms of the greater electron-donating strength of $-\mathrm{COOCH_3}$ relative to $-\mathrm{COOH}$ decreasing the barrier to oxidation at sulfur. This inductive effect will be mitigated for the b^{S} term, which is the product of a specific rate ($k_2{}^{\mathrm{S}}$) and an equilibrium constant (K^{S}), since increased electron density on sulfur will increase $k_2{}^{\mathrm{S}}$ while decreasing K^{S}. Therefore the assumption introduced above that b^{S} for Me(tga) equals b^{S} for tga is not unreasonable.

Oxidation of Coordinated Thiols. The qualitative observations made in this work on the oxidation of coordinated thiols do not allow specific mechanistic conclusions to be drawn. However, on the basis of reaction stoichiometry, the complexes investigated can be separated into three classes: class I, consuming *ca.* 4 equiv of Np(VI): Cr(tga) ≡ $[\mathrm{Cr(en)_2(SCH_2COO)}]^+$, Co(tga) ≡ $[\mathrm{Co(en)_2(SCH_2COO)}]^+$, Cr(cys) ≡ $[\mathrm{Cr(en)_2(SCH_2CH_2NH_2)}]^{2+}$, Cr(tpa) ≡ $[\mathrm{Cr(en)_2(SCH_2CH_2COO)}]^+$; class II, consuming significantly less than 4 equiv of Np(VI): Cr(tba) ≡ $[\mathrm{Cr(en)_2(SC_6H_4COO)}]^+$, Cr(OH$_2$)(tga) ≡ $[\mathrm{Cr(en)_2(OH_2)(OOCCH_2SH)}]^{2+}$; class III, not oxidized by Np(VI): Co(cys) ≡ $[\mathrm{Co(en)_2(SCH_2CH_2NH_2)}]^{2+}$, Cr(en) ≡ $[\mathrm{Cr(en)_3}]^{3+}$. Only for Cr(tga) has the product of Np(VI) oxidation been unambiguously determined; this product has been established to be the *S,O*-monothiooxalato complex $[\mathrm{(en)_2Cr(SOCCOO)}]^+$, A, which may undergo acid hydrolysis to yield $\mathrm{H_2S}$.[9] The slower oxidation of the analogous Co(tga) leads to a more complex product mixture, but the basic chemistry of the two reactions seems to be the same. Both complexes consume 4 equiv of Np(VI). On the basis of elution characteristics and uv-visible spectra, the brown oxidation product of Co(tga), $\mathrm{P_1}$, can reasonably be identified as the *S,O*-monothiooxalato complex analogous to A, $[\mathrm{(en)_2Co(SOCCOO)}]^+$, and the pink product, $\mathrm{P_2}$, can reasonably be identified as $[\mathrm{(en)_2Co(OH_2)(OOCCOOH)}]^{2+}$, the acid aquation product of $\mathrm{P_1}$ (Table V lists the spectra of complexes structurally related to $\mathrm{P_2}$). In addition, when vigorous reaction conditions are employed (Ce(IV) in 1 *F* $\mathrm{H_2SO_4}$), only $\mathrm{P_2}$ and $\mathrm{H_2S}$ are detected; this is consistent with $\mathrm{P_1}$ giving rise to $\mathrm{P_2}$ and $\mathrm{H_2S}$ *via* acid hydrolysis.

A comparison of the results obtained with reactions of class I and class III leads to three generalizations. First, the reactions which involve consumption of *ca.* 4 equiv of Np(VI) proceed *via* intermediates, which in some instances can be formulated as neptunium-metal binuclear complexes.[22] Second, complexes with coordinated thioglycolic acid (tga) are more rapidly oxidized than the analogous complexes with coordinated cysteamine (cys) or thiopropionic acid (tpa). This may arise from the facts that in the tga five-membered chelate ring oxidation of the ring carbon is sterically favored by formation of a planar intermediate and that only in the tga complex is there possibility of resonance stabilization of reaction intermediates and/or transition states involving the carbon bound to sulfur. Third, the rate of oxidation of chromium(III)-thiolato complexes is greater than that of the analogous cobalt(III) complexes; this comparative kinetic behavior may be rationalized as a reflection of the significantly shorter cobalt-ligand bond lengths[14] and is also consistent with the correlation noted by Parshall that ligands coordinated to paramagnetic metal centers are more susceptible to 1-equiv reactions than when coordinated to diamagnetic centers.[24]

The consumption of *ca.* 1 mol of Np(VI)/mol of class II compound is postulated to produce the appropriate disulfide. Additional consumption of Np(VI) with Cr(OH$_2$)(tga) is considered to be due to the usual overoxidation of thiols at low thiol:oxidant ratios[6] and to the presence of some Cr(tga) (reaction stoichiometry 4.0[9]) which naturally grows into solutions of Cr(OH$_2$)(tga) *via* closure of the thioglycolate ring.[11] Thus when the sulfur of tga is not coordinated to a metal center, the methylene group exhibits no special susceptibility to oxidation and oxidation of sulfur occurs in the usual fashion. Cr(tba) falls within class II presumably because

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(24) We are indebted to Dr. G. W. Parshall of Du Pont's Central Research Department for making this correlation known to us and suggesting its applicability to this system.

of oxidant-catalyzed Cr–S bond fission similar to that reported for another aryl-thiolato complex $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$.[12] This reaction consumes 1 equiv of Np(VI)/mol of Cr(tba) to produce a disulfide which is hypothesized to be the spectrophotometrically detected reaction intermediate. The observed reaction stoichiometry of 1.5 can be rationalized by a scheme in which one aromatic ring of the disulfide is further oxidized *via* a coupling reaction. All observations on the Np(VI) oxidation of Cr(tba) may be understood by considering these two successive reactions as well as slower further oxidation of the aromatic rings.

Summary

Under properly controlled conditions the Np(VI) oxidation of free thiols occurs by 1-equiv oxidation at sulfur to yield disulfides. Deprotonation of the sulfhydryl group strongly promotes this oxidation, presumably by favoring formation of a neptunium(VI)-sulfur bond; in thioglycolic acid deprotonation of the carboxyl group is also effective. Equivalent chemistry is observed for the complex $Cr(OH_2)$-(tga) which has a free sulfhydryl group and for Cr(tba) which behaves as though it has a free thiol group because of oxidant-catalyzed Cr–S bond fission.

In complexes containing chelated alkyl thiols, Np(VI) oxidation proceeds by a multiequivalent process often involving oxidation of the thiol carbon backbone. Ancillary ethylenediamine ligands are not oxidized by Np(VI). Chromium(III)-thiolato complexes are oxidized much more rapidly than analogous cobalt(III) complexes and coordinated tga is oxidized more rapidly than coordinated cys or tpa. Thus, of the alkyl-thiolato complexes investigated, Cr(tga) is oxidized the most rapidly and gives the simplest product mixture, while Co(cys) does not react at all with Np(VI). Further studies are planned to elucidate the factors responsible for these effects.

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Registry No. tga, 68-11-1; Np, 7439-99-8; Me(tga), 2365-48-2; dtdga, 505-73-7; Cr(tga), 41212-24-2; Co(tga), 51911-41-2; Cr-(cys), 41777-30-4; Co(cys), 40330-50-5; Cr(tpa), 51911-43-4; Cr-(tba), 51922-74-8; $Cr(OH_2)$(tga), 51922-34-0; Cr(en), 14023-00-8.

Contribution from the Los Alamos Scientific Laboratory,
University of California, Los Alamos, New Mexico 87544

Gas-Phase Composition and Structure of Metal Oxide Tetrafluorides[1]

ROBERT T. PAINE* and ROBIN S. McDOWELL

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The composition of the gaseous equilibrium vapors over the solids $MoOF_4$, WOF_4, and $ReOF_4$ have been studied by mass spectrometry. In each case the principal component is the respective monomeric species; $MoOF_4$ and WOF_4 vapors contain in addition a few per cent of oligomers. The infrared spectra of the vapors at room temperature have been recorded in the region 2000–400 cm^{-1} using a 10-m multipass cell. All three molecules have similar monomer spectra with one M=O stretch, ν_1, near 1050 cm^{-1} and two M–F stretches, ν_2 and ν_7, near 700 cm^{-1}. Analysis of the spectra strongly supports a C_{4v} molecular symmetry.

Introduction

The molecular stereochemistry of transition metal fluoride and oxide fluoride compounds is diverse and of considerable interest due to the expected structural differences among the solid, liquid, and gaseous states. In addition, several of these molecules have potential for stereochemically nonrigid structures or Jahn–Teller distortions. Vibrational spectroscopy should be a sensitive probe for these stereochemical deviations.

The structural systematics in metal oxide tetrafluorides are of special interest. Currently only seven have been reported to exist: MOF_4, M = Cr,[2] Mo,[3] W,[3] Tc,[3] Re,[3,4] Ru,[3] and Os.[5] Each compound is a crystalline solid at room temperature and only $CrOF_4$ has a vapor pressure greater than 0.5 Torr at 23°. At least three different solid-state structure types have been discovered and all contain oligomeric units. The $CrOF_4$,[2] $MoOF_4$,[6,7] $TcOF_4$,[7] and $ReOF_4$[7,8] structures (monoclinic cell, VF_5 type) consist of octahedra of light atoms joined in endless chains by cis-bridging fluorine atoms. A metastable structure based on a trimeric unit containing bridging fluorine atoms also has been reported for $ReOF_4$[9] and $TcOF_4$.[10] The WOF_4[11,12] structure (monoclinic cell, NbF_5 type) consists of light-atom octahedra linked into a tetrameric array by cis-bridging fluorine atoms. The solid-state molecular structures of $OsOF_4$ (orthorhombic cell[5]) and $RuOF_4$ have not yet been determined.

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