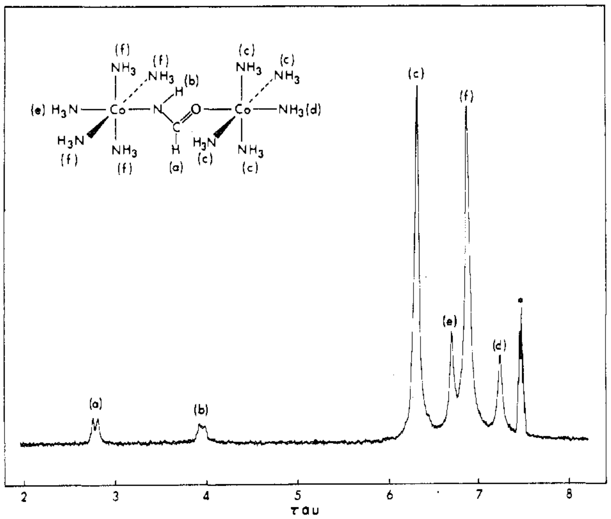

Figure 1. Pmr spectrum of μ-formamido-decaamminecobalt(III) perchlorate in dimethyl sulfoxide-d_6. The asterisk denotes the solvent peak.

It should be noted that this assignment of peak (e) requires a modification of our empirical rule[6] that the cis and trans NH_3 resonance should be separated by 0–0.6 τ unit for a nitrogen-coordinating ligand on $(NH_3)_5Co^{3+}$. The range must be extended now to cover from −0.2 to +0.6 τ unit.

Experimental Section

The preparation and characterization of *N,N*-dimethylformamidopentaamminecobalt(III) perchlorate has been described elsewhere.[3] The formatopentaamminecobalt(III) was prepared in the standard way[2] and purified by ion-exchange chromatography on Rexyn 102 (Fisher Scientific Co.) in the sodium ion form.

The μ-formamido-decaamminedicobalt(III) perchlorate was isolated as a pink crystalline by-product during the preparation of the nitrogen-bonded isomer of formamidopentaamminecobalt(III).[3] The same compound has also been prepared by heating 2.5 g of $(NH_3)_5CoOH_2(ClO_4)_3$ and 2.1 g of $(NH_3)_5CoNHCO(ClO_4)_2$ in 50 ml of trimethyl phosphate, over 5 g of Linde 3A molecular sieve, for 3 hr on a steam bath. The product was isolated by addition of *sec*-butyl alcohol as described previously.[3] The crude product may be purified by chromatography on the weak-acid cation-exchange resin Rexyn 102, in the sodium ion form. Elution was carried out with sodium acetate in increasing concentrations up to 2.0 *M*. This served to elute all impurities from the column and left the desired product, which is clearly highly charged since it cannot be eluted with a 2 *M* solution. The product was removed from the resin with dilute perchloric acid and was essentially quantitatively precipitated by adding concentrated perchloric acid to a final concentration of 1 *M*. *Anal.* Calcd for $(NH_3)_{10}Co_2NHCHO(ClO_4)_5$: C, 1.45; H, 3.86; N, 18.6. Found: C, 1.75; H, 3.86; N, 18.3.

The visible spectrum of the dimer in water shows maxima at 341 nm (ϵ 164 M^{-1} cm^{-1}) and 492 nm (ϵ 141 M^{-1} cm^{-1}). The infrared spectrum is complex but deuteration leaves a strong absorption at 1601 cm^{-1} (KBr disk) which may be assigned to the C=O stretching frequency. The pmr spectrum is shown in Figure 1 and discussed elsewhere in this paper.

The pmr samples for the NOE studies were all prepared by mixing about 0.1 g of the cobalt(III) complex, about 0.01 g of 2,4-dinitrobenzene (used as an integration standard),[7] 0.05 ml of TMS, and 1 ml of DMSO-d_6 over some molecular sieve in a tube with ground-glass joints suitable for attachment to a standard vacuum line. The sample was taken through three freeze–pump–thaw cycles and stored under vacuum for 3–4 hr for residual water to be removed by the molecular sieve. Then the solution was poured, while still under vacuum, through a glass wool plug into a standard nmr tube and sealed off.

The pmr spectra were recorded on a Varian HA 100 and all integrations were performed with the standard electronic integrator. Both the sample and internal integration reference (2,4-dinitrobenzene) peaks were integrated in each sweep through the spectrum. At least six integrations were performed at a particular irradiating power and the results averaged. A maximum deviation of about 3% was observed in the ratio of standard to sample integral under a given set of conditions.

Registry No. $(NH_3)_5CoOH_2(ClO_4)_3$, 13820-81-0; $(NH_3)_5CoNHCHO(ClO_4)_2$, 26729-10-2; $(NH_3)_5CoOCHN(Me)_2(ClO_4)_3$, 18897-02-4; $(NH_3)_5CoO_2CH(ClO_4)_2$, 28660-81-3; $(NH_3)_{10}Co_2NHCHO(ClO_4)_5$, 38894-74-5.

Acknowledgment. The authors wish to acknowledge the financial support for this research and fellowship support to R. J. B. from the National Research Council of Canada and to thank Mr. G. Bigam and Mr. D. Brisbane for running the pmr spectra.

---

(6) R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **9**, 1567 (1970).

(7) These quantities give about 0.2 *M* cobalt(III) and 0.06 *M* standard and make the single proton of the complex about equal in intensity to the four protons from the standard.

Contribution from the Department of Chemistry,
University of Chicago, Chicago, Illinois 60637, and the
Chemistry Division, Argonne National Laboratory,
Argonne, Illinois 60439

Reaction of Thiols with the One-Equivalent Oxidants Neptunium(VI) and Cerium(IV) in Aqueous Acidic Media[1]

D. K. Lavallee,[2] J. C. Sullivan,*[3] and E. Deutsch[2]

Received October 11, 1972

A determination of the stoichiometry of the reaction between a series of thiols and the 1-equiv oxidant Np(VI) was undertaken prior to dynamic studies on such systems. During the course of this study our attention was brought to the recent reports by Danehy and coworkers,[4] who investigated stoichiometries of thiol oxidations with the 2-equiv reagent iodine. These investigators demonstrated (a) that the excessive consumption of iodine (to yield products of higher oxidation states than disulfides) is dependent upon the concentration of thiol and (b) that thiols containing a free β-carboxylate group have the greatest tendency to be oxidized beyond the disulfide.

The data presented in this note demonstrate that the 1-equiv oxidants Np(VI) and Ce(IV) yield results that are similar to those obtained with iodine. The results obtained with Ce(IV) are in good agreement with thermometric titration data[5] but are not consistent with a previous report that the oxidation of mercaptocarboxylic acids by Ce(IV) stoichiometrically yields disulfides.[6] We have also demonstrated that both the stoichiometry and dynamics of oxidation of thiols by Np(VI) are markedly affected by the presence of molecular oxygen in the solutions.

Experimental Section

Materials. Unless otherwise specified, all chemicals are reagent

---

(1) A portion of this investigation was conducted under the auspices of the United States Atomic Energy Commission.

(2) University of Chicago.

(3) Argonne National Laboratory.

(4) (a) J. P. Danehy, *Int. J. Sulfur Chem. C*, 6, 159 (1971); (b) J. P. Danehy, B. T. Doherty, and C. P. Egan, *J. Org. Chem.*, 36, 2525 (1971); (c) J. P. Danehy, C. P. Egan, and J. Switalski, *ibid.*, 36, 2530; (d) J. P. Danehy and M. Y. Oester, *ibid.*, 32, 1491 (1967).

(5) W. A. Alexander, C. J. Mash, and A. McAuley, *Talanta*, 16, 535 (1969).

(6) J. Hill and A. McAuley, *J. Chem. Soc. A*, 156 (1968).

grade. Commercial **cysteine hydrochloride monohydrate** was crystallized three times from hot 20% HCl and then dried at 50° under vacuum (over P_2O_5) to yield the anhydrous compound[7] which was stored under vacuum (over P_2O_5). This product was used as a primary standard for the thiol analysis described below. Commercial **thiomalic acid**[8] was crystallized three times from water, then vacuum sublimed (125°, 0.1 mm),[9] and dried at 45° under vacuum (over P_2O_5). This material was used to estimate the accuracy of the thiol analysis (see below). Commercial **thioglycolic acid**[8] was dried *via* benzene azeotrope, then vacuum distilled (97°, 8 mm), and stored under argon in sealed ampoules. **Cysteamine hydrochloride** was obtained from BDH and used without further purification. 2,2'-Dithiodipyridine was obtained from Aldrich Chemical Co. and was used without further purification.

Stock solutions of this reagent (44 mg diluted to 10.0 ml with absolute ethanol) were freshly prepared each day. **Citrate buffer** was prepared by neutralizing a 0.2 *F* solution of citric acid with 50% NaOH until pH 5.0. Solutions of Np(VI) in 0.01 *F* $HClO_4$ were freshly prepared and standardized each day by previously described procedures.[10] Solutions of Ce(IV) in 1 *F* H_2SO_4 were prepared and standardized by the usual techniques. Solutions of thiols were prepared in deaerated 0.01 *F* $HClO_4$ (or 1 *F* H_2SO_4 for Ce(IV) experiments) and then were standardized *vs.* cysteine hydrochloride by the following procedure.

Thiol Analysis. The concentration of free thiol (RSH) in solution was quantitatively determined using a modification of the method of Grassetti and Murray[11] in which 2-thiopyridone, produced by the reduction of 2,2'-dithiodipyridine with RSH, was spectrophotometrically monitored. A thiol solution of unknown concentration was quantitatively diluted with deaerated water until it was *ca.* 10^{-3} *F* in RSH (also preferably no more than 1.0 *F* in H^+); 1.00 ml of this solution and 0.1 ml of stock 2,2'-dithiodipyridine solution were combined and diluted to 10.0 ml with deaerated citrate buffer (citrate was employed in order to sequester metal ions which otherwise might have precipitated or catalyzed the autoxidation of 2-thiopyridone).

The optical density of this solution, *vs.* a water blank, was determined (in triplicate) in a 1.00-cm cell at 3430 Å using a Cary 14MR spectrophotometer. Known solutions of primary standard cysteine hydrochloride, prepared by weight, were used to establish that Beer's law is followed over the [RSH] range (0.1359–1.027) × 10^{-4} *F*, the resultant straight line being described by the equation OD = (0.024 ± 0.003) + (7906 ± 31)[RSH] (there were ten independent OD–[RSH] determinations, error limits are standard deviations, standard deviation in OD is 0.0035 unit). Appropriate blanks showed that the absorbance due to Np and Ce species under the conditions of the analysis was negligible. Stock solutions of all thiols (except the primary standard cysteine hydrochloride) were analyzed by this procedure. The purified sample of thiomalic acid assayed as 99.6% pure, relative to cysteine hydrochloride.

Techniques. Unless otherwise indicated, all manipulations were performed under an inert atmosphere (argon or carbon dioxide) using solutions which had been deaerated with an argon stream. Stoichiometry experiments were usually carried out by rapidly injecting 2 ml of oxidant solution into an equal volume of vigorously stirred thiol solution. Identical results were obtained when the thiol was injected into the oxidant solution and when the two solutions were mixed using a Durrum Model D-110 stopped-flow spectrophotometric apparatus (mixing time *ca.* 2 msec). The error limits for each stoichiometry determination were calculated from the standard deviations of the Beer's law parameters (see above), an estimated maximum uncertainty of 1% in the individual optical density observations, and the usual relationship governing error propagation. Since the determination of stoichiometry is based upon analysis of excess thiol present after reaction, the uncertainty of the calculated stoichiometry increases as the initial ratio of thiol to oxidant, ([thiol]/[oxidant])$_0$, increases. For this reason, no experiments with ([thiol]/[oxidant])$_0$ > 6.2 were undertaken.

Table I. Stoichiometry of the Reaction of Thiols with 1-equiv Oxidants

Index	10^3 [thiol]$_0$	10^3 [oxidant]$_0$	$\left(\frac{[\text{Thiol}]}{[\text{oxidant}]}\right)_0$	$\left(\frac{[\text{Oxidant}]}{[\text{thiol}]}\right)_{\text{consumed}}$ [a]
Np(VI) + Thiomalic Acid[b]				
1	17.16	9.65	1.78	1.137 ± 0.014
2	17.10	9.86	1.73	1.113 ± 0.016
3	1.716	0.965	1.78	1.32 ± 0.02
4	1.710	0.986	1.73	1.33 ± 0.02
5	0.349	0.202	1.73	2.14 ± 0.07
6	0.171	0.0986	1.73	2.37 ± 0.09
7	1.073	1.010	1.06	1.654 ± 0.015
8	2.684	1.010	2.66	1.43 ± 0.05
9	5.27	1.023	5.15	1.63 ± 0.14[c]
10	5.27	0.986	5.34	1.45 ± 0.12
11	5.34	0.986	5.42	1.59 ± 0.14
12	7.36	1.188	6.19	1.21 ± 0.09
13	7.36	1.188	6.19	0.93 ± 0.05[d]
Ce(IV) + Thiomalic Acid[e]				
14	1.788	1.048	1.71	1.37 ± 0.02
15	17.88	10.48	1.71	1.134 ± 0.013
Np(VI) + Thioglycolic Acid[b]				
16	2.06	1.010	2.04	1.24 ± 0.02
17	5.15	1.010	5.10	1.22 ± 0.08
18	17.26	9.90	1.74	1.065 ± 0.011
19	27.62	4.50	6.14	1.00 ± 0.06
Ce(IV) + Thioglycolic Acid[e]				
20	1.726	1.048	1.65	1.199 ± 0.014
21	17.26	10.48	1.65	1.044 ± 0.009
Np(VI) + Cysteine Hydrochloride[b]				
22	18.99	11.19	1.70	1.089 ± 0.011
23	9.50	5.60	1.70	1.093 ± 0.011
24	1.899	1.119	1.70	1.099 ± 0.011
25	3.80	1.119	3.40	1.09 ± 0.03
Np(VI) + Cysteamine Hydrochloride[b]				
26	17.50	10.17	1.72	1.023 ± 0.009
27	17.50	10.17	1.72	1.019 ± 0.009
28	18.38	9.92	1.85	1.033 ± 0.011
29	1.750	1.017	1.72	1.066 ± 0.011
30	18.38	3.968	4.63	1.01 ± 0.04
Ce(IV) + Cysteamine Hydrochloride[e]				
31	18.38	10.48	1.75	1.089 ± 0.012
32	1.838	1.048	1.75	1.209 ± 0.016

[a] Errors are based on an assumed 1% uncertainty in observed optical density reading. [b] Conditions: [$HClO_4$] = 0.01 *F*; *T* = 25°; under argon atmosphere unless otherwise specified. [c] Solutions mixed using the Durrum stopped-flow apparatus. [d] Using air-saturated solutions. [e] Conditions: [H_2SO_4] = 0.50 *F*; *T* = 25°; under argon atmosphere.

Results and Discussion

The data which are summarized in Table I support the following observations on the stoichiometry of the reaction of thiols with Np(VI) and Ce(IV). (1) There is generally more than 1 mol of oxidant consumed per mole of thiol oxidized. (2) The extent of overoxidation is reproducible. See for example experiments 1 and 2 or 3 and 4; the second experiment of each pair was performed on a different day from the first, with independently prepared solutions. (3) For all thiols, except cysteine hydrochloride, as ([thiol]/[oxidant])$_0$ is held constant (*i.e.*, at the same point in a hypothetical titration), the reaction stoichiometry approaches 1.0 as the initial concentration of thiol, [thiol]$_0$, increases. This is in qualitative agreement with Danehy's observations on iodine oxidations. We have no ready explanation for the apparent insensitivity of cysteine hydrochloride overoxidation to ([thiol]/[oxidant])$_0$. (4) In the narrow range that it was possible to cover, there does not seem to be a significant effect of varying ([thiol]/[oxidant])$_0$

---

(7) (a) I. M. Kolthoff and W. Stricks, *J. Amer. Chem. Soc.*, **72**, 1952 (1950); (b) M. X. Sullivan, W. C. Hess, and H. W. Howard, *J. Biol. Chem.*, 145, 621 (1942); (c) K. Shinohara, *ibid.*, 112, 671 (1935–1936).

(8) Samples kindly donated by Evans Chemetics, Inc.

(9) F. B. Martinez and M. del C. M. Mourino, *Inform. Quim. Anal.*, 16, 61 (1962).

(10) J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *J. Amer. Chem. Soc.*, 82, 5288 (1960).

(11) D. R. Grassetti and J. F. Murray, Jr., *Arch. Biochem. Biophys.*, 119, 41 (1967).

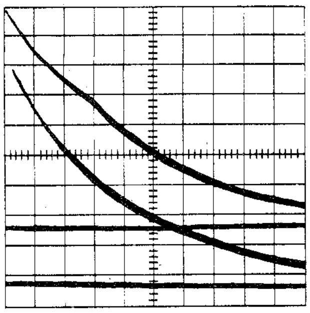

Figure 1. Reaction between Np(VI) and thiomalic acid, followed on a Durrum Model D-110 stopped-flow spectrophotometer. The upper trace was obtained using air-saturated solutions; the lower trace was obtained under anaerobic conditions. Conditions: 25°, λ 3400 Å, I = [HClO$_4$] = 2.00 F, [Np(VI)]$_0$ = 1.065 × 10^{-3} F, [thiomalic acid]$_0$ = 7.20 × 10^{-2} F, vertical scale = 0.02 optical density unit/division, and horizontal scale = 0.50 sec/division.

at constant initial concentration of oxidant, [oxidant]$_0$. (5) The extent of overoxidation is a function of the nature of the thiol. For the thiols studied, the susceptibility to overoxidation increases in the order cysteamine < cysteine < thioglycolic acid < thiomalic acid for Np(VI) as the oxidant and cysteamine $\simeq$ thioglycolic acid < thiomalic acid for Ce(IV) as oxidant. Again, these results are in general agreement with Danehy's observation that thiols containing a β-carboxylate function are most susceptible to overoxidation.[4] (6) For thioglycolic acid and thiomalic acid, there does not seem to be much difference in the extent of overoxidation caused by Np(VI) or Ce(IV). However, cysteamine hydrochloride is more susceptible to overoxidation by Ce(IV) than by Np(VI). (7) When Np(VI) oxidizes thiomalic acid in the presence of molecular oxygen, the reaction stoichiometry drops to less than 1 mol of oxidant consumed for every mole of thiol oxidized (compare experiments 12 and 13). This implies that molecular oxygen is effecting net oxidation of thiol during the reaction (note that, under the conditions of these reactions, molecular oxygen normally does not oxidize thiols at an appreciable rate).

Further evidence that molecular oxygen severely interferes with the normal course of thiol oxidation by 1-equiv oxidants is provided by Figure 1 wherein two stopped-flow traces of the reaction between Np(VI) and thiomalic acid are reproduced. The conditions under which these traces were obtained are exactly identical (see caption: at this wavelength the trace is monitoring the concentration of Np(VI)) except that the lower trace was obtained under anaerobic conditions. It is easily seen that the presence of molecular oxygen inhibits the rate of disappearance of Np(VI) in the early part of the reaction, an effect which could readily be mistaken for the formation of a neptunium–thiol intermediate.

The results reported in this work may be qualitatively explained by a mechanism analogous to that proposed by Danehy.[4] Within the systems we have considered, this scheme postulates a sequence of 1-equiv oxidation reactions to generate first a free radical RS· and then a reactive intermediate sulfenium ion, RS$^+$. Competing reactions of RS$^+$ with RSH and H$_2$O and the reaction of RS· with oxygen allow a facile rationalization of our observations. In the case of thiomalic acid, the reaction of RS$^+$ with water may be assisted by the presence of the β-carboxylate function.[4]

To summarize, in the reactions of the 1-equiv oxidants Np(VI) and Ce(IV) with thiols, the stoichiometry depends upon the initial concentration of thiol and the presence of β-carboxylate functions in the thiol. The presence of molecular oxygen in the solutions has an effect on both the dynamic and thermodynamic aspects of these reactions. These observations should be taken into consideration in any further work in this field.

Registry No. Neptunium, 7439-99-8; cerium, 7440-45-1; thiomalic acid, 70-49-5; thioglycolic acid, 68-11-1; cysteine, 4371-52-2; cysteamine, 60-23-1; oxygen, 7782-44-7.

Acknowledgment. E. D. gratefully acknowledges financial support from ARPA and from a DuPont Young Faculty Grant.

Contribution from the Chemistry Department,
Edinburgh University, Edinburgh, Scotland

Dissociation and Ionization of Difluorocyanophosphine

P. W. Harland, D. W. H. Rankin, and J. C. J. Thynne*[1]

Received October 13, 1972

Although the chemistry of the fluorophosphines has received much attention recently,[2] there has been only a limited study[3] of the results of electron impact on these molecules and in particular no studies of negative ion formation. We have accordingly measured positive–and negative–ion formation by difluorocyanophosphine.

Experimental Section

The experiments were performed using a Bendix time-of-flight mass spectrometer, Model 3015. The technique employed has been described previously.[4-6]

Difluorocyanophosphine was prepared by passing gaseous difluorobromophosphine over solid silver cyanide at 300°K, the product being condensed at 177°K. After vacuum distillation several times the product showed no traces of impurity when analyzed by infrared spectrometry.

Results and Discussion

(1) Positive Ion Formation. The principal ions observed in the positive ion mass spectrum of PF$_2$CN are PF$_2$CN$^+$ (22), PFCN$^+$ (9.1), PF$_2$$^+$ (100), PF$^+$ (9.2), and CN$^+$ (3.3); their relative intensities at 70 eV are shown in parentheses.

In Table I are shown the measured appearance potential data for these ions.

(i) PF$_2$$^+$. This ion is presumably formed by reaction 1

$$\mathrm{PF_2CN + e \rightarrow PF_2^+ + CN + 2e} \qquad (1)$$

at the energy shown in Table I. No value has been reported for the ionization potential of PF$_2$. A reasonably reliable value may be estimated as follows *via* a value of 15.4 ± 0.2 eV which we have measured in this laboratory for A(PF$_2$$^+$) from phosphorus trifluoride: the energy of decomposition of gaseous PF$_3$, PF$_3$(g) → P(g) + 3F(g), may be calculated to

---

[1] To whom correspondence should be addressed at the Department of Trade and Industry, Shell Mex House, Strand, London W.C.2, England.

[2] J. F. Dixon, *Advan. Inorg. Chem. Radiochem.*, 13, 364 (1970).

[3] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 88, 3729 (1966).

[4] K. A. G. MacNeil and J. C. J. Thynne, *Int. J. Mass Spectrom. Ion Phys.*, 3, 35 (1969).

[5] K. A. G. MacNeil and J. C. J. Thynne, *J. Phys. Chem.*, 75, 2584 (1971).

[6] P. W. Harland and J. C. J. Thynne, *J. Phys. Chem.*, 75, 3517 (1971).