Despite the interesting biological distributions of I and III,[5] the second-order dependence of the formation reaction of $[Tc]_m$ and the k_f value of 0.015 $M^{-1}\ s^{-1}$ results in half-lives on the order of days at the submicromolar concentrations required for the synthesis of radioimaging agents in nuclear medicine, which precludes their use for this purpose. Finally, the relatively small values of K_{eq} means that these complexes can dissociate back to monomeric (probably Tc^V) species in an oxidizing environment of low technetium concentration, which may have affected their uptake by mammalian tissues.

Isomerization. The decompositon in DCB observed when sufficient picoline was not present, which was partially reversible on the addition of picoline, suggests that picoline is a good leaving group in the μ-oxo molecules, as it is in *trans*-$[O_2(pic)_4Tc^V]^+$.[3] This is confirmed by the substitution of picoline onto the dissymmetric lutidine complex to form I. Conversely, the failure of even high concentrations of chloride to have any effect on the decompostion of III in dichlorobenzene suggests that it is not an initial leaving group in the isomerization reaction. At higher temperatures, decomposition of III was evident even in the presence of high concentrations of picoline, suggesting that transformation of the species lacking one or more picoline ligands can proceed more rapidly than replacement by solvent picoline under sufficiently energetic conditions. Lack of chloride also allows for decomposition in picoline solution, suggesting that this can also serve as a reasonable leaving group.

The kinetic and equilibrium parameters are remarkably similar in either DCP or picoline, indicating a similar mechanism in both solvents. A truly dissociative mechanism involving picoline loss as the rate-limiting step would exhibit a rate law inverse in picoline concentration, while an associative mechanism dependent on picoline attack would yield a rate law first-order in picoline. The small difference in rates, when the isomerization reaction was run in 0.1–1.1 M picoline in dichlorobenzene or even in neat picoline, shows that the isomerization not only is independent of picoline in this concentration range but is also fairly independent of the solvent. It appears that excess picoline is necessary to maintain the dinuclear complexes by inhibiting their decay to species lacking this ligand; however, when it is ligated, it still serves as a good leaving group on chloride attack. Assuming that chloride addition is rate-limiting, a reasonable mechanism for the isomerization reaction is given by Scheme III.

Scheme III

$$Cl^- + III \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cl(pic)_3ClTcOTcCl_4(pic)]^- + pic$$

$$[Cl(pic)_3ClTcOTcCl_4(pic)]^- + pic \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cl(pic)_4ClTcOTcCl_4(pic)]^-$$

$$[Cl(pic)_4ClTcOTcCl_4(pic)]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I + Cl^-$$

The relatively high ΔH^* and positive ΔS^* suggest that bond breaking plays some role in the rate-limiting step, and the similar activation parameters for the isomerization and decomposition reactions imply that loss of the pyridine ligand is involved. Owing to the strong electronic interaction between the two metal atoms, charge can be passed from one technetium center to the other via the metal–μ-oxo π-bonds. Consequently, addition of a chloride to one Tc may labilize bonds on the second. It is even possible that a picoline transfers from one side of the molecule to the other in concert with chloride dissociation. The reverse reaction, which has a smaller ΔH^* (94.3 kJ/mol in DCB and 105 kJ/mol in picoline) and a negative ΔS^* (–76.4 J/(mol K) in DCB and –59 J/(mol K) in picoline), may be somewhat more associative in its rate-limiting step. Assuming the first and last steps to be rate limiting in the forward and reverse directions, respectively, the net rate law and equilibrium constant for the reaction become

$$\frac{d[I]}{dt} = (k_f[III] - k_r[I])[Cl^-] \qquad K_{iso} = \frac{k_f}{k_r}$$

where $k_f = k_1k_3/(k_3 + k_{-1})$ and $k_r = k_{-3}k_3/(k_3 + k_{-1})$, which is consistent with the empirical rate law.

This mechanism, the decomposition through pyridine loss, and the substitution of one pyridine ligand for another suggest that the pyridine and chloride ligands can be sequentially replaced by other molecules, so that other heterocyclic ligands such as imidazole or purines may be incorporated into the μ-oxo complexes.

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Supplementary Material Available: Derivations of rate equations and tables giving data for all graphs in this paper (8 pages). Ordering information is given on any current masthead page.

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Kinetic Study of the Oxygen-Transfer Reactions from the Oxo Diperoxo Complexes of Molybdenum(VI) and Tungsten(VI) to (Thiolato)- and (Sulfenato)cobalt(III) Complexes

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The (thiolato)cobalt(III) complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ is oxidized first to $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$ and then much more slowly to $(en)_2Co(S\{O\}_2CH_2CH_2NH_2)^{2+}$ by the oxo diperoxo complexes of Mo(VI) and W(VI). Nearly quantitative oxygen atom transfer from peroxide to the coordinated sulfur acceptor accompanies these reactions. The reactions are strictly catalytic with respect to the d^0 metal ions, provided sufficient hydrogen peroxide is present to maintain them as oxo diperoxo complexes. The activation of the coordinated peroxo group is impressive; the relative reactivities for each substrate stand in the order $WO(O_2)_2 > WO(OH)(O_2)_2^- > MoO(O_2)_2 > MoO(OH)(O_2)_2^- \gg H_2O_2$. Second-order rate constants and, with the exception of those for $WO(O_2)_2$, activation parameters for all these reactions were determined. The data are insufficient to distinguish whether nucleophilic attack by coordinated sulfur occurs directly at the peroxo ligand or after prior coordination at Mo(VI) or W(VI).

Introduction

The early transition elements in their highest oxidation states rapidly combine with hydrogen peroxide to form peroxo complexes with large formation constants.[1,2] The reactivities of these peroxo complexes toward a variety of reducing agents have been examined, both in organic solvents and in aqueous solution.[2-7] In many

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(1) Connor, J. A.; Ebsworth, E. A. V. *Adv. Inorg. Chem. Radiochem.* **1964**, *6*, 279.

(2) Mimoun, H. In *The Chemistry of Peroxides*; Patai, S., Ed.; Interscience: New York, 1983; pp 463–482.

(3) Sheldon, R. A.; Kochi, J. K. In *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; pp 48–97.

(4) Secco, F. *Inorg. Chem.* **1980**, *19*, 2722.

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cases impressive activation of the η^2-bound peroxo group relative to hydrogen peroxide is observed. Oxygen atom transfer from peroxide to the substrate has been demonstrated or assumed for many of the systems examined. The formulations of the peroxo complexes in solution are reasonably well established and vary depending on the d^0 metal ion, the concentration of excess hydrogen peroxide present, and the pH (especially in aqueous solution). The reactivities of the various peroxo complexes toward a common substrate can be enormously variable. In our opinion the reasons for this variation are poorly understood. The intimate mechanisms of the reactions have not been established in most cases, although coordination of the substrate at the metal center followed by oxygen atom transfer from the neighboring peroxo ligand is often proposed, especially in poorly coordinating solvents.[9] However, direct attack by the substrate at the peroxo ligand has also been invoked.[10-12] It is not clear to us why, in either case, an η^2-bound peroxo group would be so impressively activated in many cases relative to hydrogen peroxide.

We have undertaken a systematic study of the redox reactions of several of these peroxo complexes with common substrates in aqueous solution.[6,7,13-16] The resulting reactivity of the peroxo complex is then referenced to the corresponding reaction with hydrogen peroxide. In the present study we have examined the reactions of the oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) with the chelated thiolato complex $(en)_2Co(SCH_2CH_2NH_2)^{2+}$ and its sulfenato analogue, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$. The group 6 peroxo complexes are the most reactive we have encountered. The chemistry of the cobalt(III) complexes has been thoroughly established, including a kinetic study of their oxidation by hydrogen peroxide.[17-20] An additional advantage of these complexes for the present study is that the chelated sulfenato and sulfinato products can be readily precipitated. We have therefore examined whether in fact oxygen atom transfer from peroxide to the substrates occurs in the Mo(VI)- and W(VI)-catalyzed reactions by means of oxygen-18 tracer studies.

Experimental Section

Reagents. The preparation and analysis of solutions of molybdenum(VI), tungsten(VI), H_2O_2, and $LiClO_4$ have been described previously.[7,15] The perchlorate salt of (2-aminoethanethiolato-*N*,*S*)bis(1,2-ethanediamine)cobalt(III) was prepared by the method of Nosco and Deutsch.[21]

All other chemicals were of reagent grade and were used as supplied. Deionized water was distilled twice before use; the last distillation was from alkaline permanganate.

Determination of the Hydrolysis Constant for Oxodiperoxotungsten(VI). A significant variation in the absorption spectra of oxodiperoxotungsten(VI) with acidity was observed over the range 0.051–3.00 M H^+. A sufficient excess $[H_2O_2]$ was used in these experiments to ensure >99% complexation of W(VI); corrections for the absorbance due to H_2O_2 were applied. The raw experimental data are summarized in Table S1.[8] By analogy with previous studies on the molybdenum(VI) system, the hydrolysis reaction given in eq 1 was assumed.[7] Coordinated water molecules are omitted in the formulations. The data were analyzed by use of eq 2; calculated values of ϵ_{obsd} from the least-squares-determined values

$$WO(O_2)_2 + H_2O \rightleftarrows WO(OH)(O_2)_2^- + H^+ \quad K_a \qquad (1)$$

$$\epsilon_{obsd} = \{\epsilon_{WO(O_2)_2}[H^+] + \epsilon_{WO(OH)(O_2)_2^-}K_a\}/(K_a + [H^+]) \qquad (2)$$

of K_a and the two extinction coefficients (vide infra) are listed in parentheses in Table S1.[8]

Table I. Experimental Conditions for the Oxygen-18 Tracer Experiments

expt	[thiolato]	$[H_2O_2]$, M	$10^4 \times$ [Mo(VI)], M	$10^5 \times$ [W(VI)], M	$[H^+]$, M	product
1	0.132	0.198	7.00		0.050	sulfenato
2	0.132	0.461	7.00		0.050	sulfinato
3	0.064	0.196	7.00		0.050	sulfenato
4	0.062	0.504	6.76		0.050	sulfinato
5	0.067	0.101		1.77	0.30	sulfenato
6	0.065	0.296		1.73	0.30	sulfinato

Oxygen-18 Tracer Experiments. The source of the oxygen in the $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$ and $(en)_2Co(S\{O\}_2CH_2CH_2NH_2)^{2+}$ products was examined by means of oxygen-18 tracer experiments. Normal H_2O_2 and solvent ca. 4 times enriched in ^{18}O were used. The temperature was ca. 25 °C, and the initial reagent concentrations are summarized in Table I. The reaction times were 3 and 10 min, respectively, for forming principally the sulfenato and sulfinato complexes. These products were precipitated by use of a warm, saturated solution of Reinecke's salt, $NH_4[Cr(SCN)_4(NH_3)_2]\cdot H_2O$. The precipitates were washed with small amounts of cold methanol/ether mixtures and dried overnight under vacuum. The solids were shown to be anhydrous by IR and proton NMR spectroscopy (in deuteriated DMSO solution). The oxygen in the thoroughly dried precipitates was converted to CO_2 (and CO) by reaction with $Hg(CN)_2$ in a break-seal tube at 425 °C. The CO_2 was purified by gas chromatography, and the 46/(44 + 45) mass ratio was determined with a RMS-16 mass spectrometer. Solvent enrichments were measured by similar procedures.

The perchlorate salt of the thiolato complex was used in the first two experiments. Later elemental analysis (Co, Cr, S, and Cl; Galbraith Laboratories, Inc.) revealed some contamination by perchlorate ion in the sulfenato and sulfinato solids precipitated with Reineke's salt. Since the perchlorate oxygens are of normal isotopic abundance, small correlations were necessary in the analysis of the isotopic results. This problem was eliminated in the last four experiments by use of the chloride rather than the perchlorate salt of the thiolato complex.

Kinetic Studies. A Zeiss PMQ-11 spectrophotometer equipped with a rapid-mixing (ca. 1 s), thermostated sample compartment was used for most of the kinetic experiments. The reactions were monitored at 365 nm, an absorption maximum for the sulfenato complex, $(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+}$. The studies with oxodiperoxomolybdenum(VI) were initiated by addition of an aliquot of a H_2O_2 stock solution to a thermally equilibrated solution containing the other desired reagents. The reactions using oxodiperoxotungsten(VI) were initiated by addition of an aliquot of the thiolato complex into a solution prepared by mixing acid, hydrogen peroxide, and then the tungsten solution. The order of addition is important to prevent the decomposition of peroxide that occurs if hydrogen peroxide and tungsten(VI) are mixed or precipitation of hydrous tungsten(VI) oxide if excess acid is added to a tungsten(VI) solution.

Stopped-flow techniques were used to study the conversion of the thiolato complex to the sulfenato complex by oxodiperoxotungsten(VI). The reactions were monitored at 323 nm, an isosbestic point for the sulfenato and sulfinato complexes, as well as at 365 nm. The kinetic data were collected by use of a Nicolet 3091 digital oscilloscope equipped with a bubble memory that allowed collection of multiple runs.

Results

Hydrolysis Constant for Oxodiperoxotungsten(VI). No spectral variation of oxodiperoxotungsten(VI) with acidity was observed at 256 nm in our previous preliminary study.[7] However, our present study has revealed that 256 nm is an isosbestic point for the species we formulate (with water molecules omitted) as $WO(O_2)_2$ and $WO(OH)(O_2)_2^-$. Spectral variations as a function of acidity were observed at longer wavelengths, as summarized in Table S1. The assumed equilibrium is given in eq 1, and the resulting values of $\epsilon_{WO(O_2)_2}$ (M^{-1} cm^{-1}), $\epsilon_{WO(OH)(O_2)_2^-}$ (M^{-1} cm^{-1}), and K_a (M) as determined by use of eq 2 were respectively 894 ± 18, 558 ± 3, and 0.67 ± 0.08 at 280 nm, 526 ± 13, 234 ± 2, and 0.76 ± 0.07 at 295 nm, and 226 ± 9, 81 ± 1, and 0.79 ± 0.10 at 310 nm in solutions maintained at an ionic strength of 1.0 M.

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(5) Smith, R. H.; Kilford, J. *Int. J. Chem. Kinet.* **1976**, *8*, 1.

(6) (a) Thompson, R. C. *Inorg. Chem.* **1986**, *25*, 184. (b) Lydon, J. D.; Thompson, R. C. *Inorg. Chem.* **1986**, *25*, 3694.

(7) Lydon, J. D.; Schwane, L. M.; Thompson, R. C. *Inorg. Chem.* **1987**, *26*, 2606.

(8) Supplementary material.

(9) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 734.

(10) Bortolini, O.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1982**, *14*, 53.

(11) Di Furia, F.; Modena, G. *Pure Appl. Chem.* **1982**, *54*, 1853.

(12) Di Furia, F.; Modena, G. *Rev. Chem. Intermed.* **1985**, *6*, 51.

(13) Thompson, R. C. *Inorg. Chem.* **1982**, *21*, 859.

(14) Thompson, R. C. *Inorg. Chem.* **1983**, *22*, 584.

(15) Thompson, R. C. *Inorg. Chem.* **1984**, *23*, 1794.

(16) Thompson, R. C. *Inorg. Chem.* **1985**, *24*, 3542.

(17) Lange, B. A.; Libson, K.; Deutsch, E.; Elder, R. C. *Inorg. Chem.* **1976**, *15*, 2985.

(18) Adzamli, I. K.; Libson, K.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303.

(19) Adzamli, I. K.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 1366.

(20) Deutsch, E.; Root, M.; Nosco, D. L. In *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 269.

(21) Nosco, D. L.; Deutsch, E. *Inorg. Synth.* **1982**, *21*, 19.

Table II. Kinetic Results for the Conversion of the (Thiolato)cobalt(III) Complex to the (Sulfenato)cobalt(III) Complex by Oxodiperoxomolybdenum(VI)[a]

$10^6 \times$ [Mo(VI)]$_0$, M	$10^3 \times$ [H_2O_2]$_0$, M	[acid], M	k_{obsd},[b] s^{-1}	$10^{-3}k_{Mo1}$,[c] M^{-1} s^{-1}
		$HClO_4$, $I = 1.0$		
2.10	1.20	1.00	0.0340	14.9
2.10	1.20	0.50	0.0340	15.5
2.10	1.20	0.10	0.0310	13.8
4.21	1.20	0.10	0.0620	14.5
2.10	1.20	0.10	0.0305	13.8
1.05	1.20	0.10	0.0165	14.1
0.526	1.20	0.10	0.00907	13.8
2.10	2.41	0.10	0.0319	13.6
2.10	1.20	0.10	0.0321	14.6
2.10	1.20	0.050	0.0310	14.0
2.10	1.20	0.020	0.0190	8.46
2.10	1.20	0.010	0.0180	7.13
2.10[d]	1.20	0.10	0.0232	10.5
2.10[e]	1.20	0.10	0.0198	9.07
		$HClO_4$, $I = 0.10$ M		
2.10	1.20	0.10	0.0357	16.3
2.10	1.20	0.050	0.0306	14.2
2.10	1.20	0.020	0.0287	13.5
2.10	1.20	0.010	0.0200	9.19
2.10	1.20	0.0050	0.0230	10.6
2.10	1.20	0.0010	0.0077	3.12
10.2	1.20	0.00013	0.0266	2.47
		HNO_3, $I = 0.10$ M		
1.01	1.20	0.10	0.0189	17.2
1.01	1.20	0.050	0.0171	15.2
1.01	1.20	0.020	0.0146	12.9
2.03	1.20	0.010	0.0200	9.28
2.03	1.20	0.0050	0.0182	8.31
2.03	1.20	0.0010	0.00904	3.80
4.09	1.20	0.00050	0.0153	3.42
4.09	1.20	0.00010	0.0113	2.44
4.02[d]	1.20	0.00010	0.0105	2.34
4.02[e]	1.20	0.00010	0.0090	2.12

[a] Monitored at 365 nm. Conditions: [$(en)_2Co(SCH_2CH_2NH_2)^{2+}$]$_0$ = (7.0–7.2) × 10^{-5} M; ionic strength maintained with use of $LiClO_4$; T = 25.0 °C unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Defined by eq 4. [d] T = 17.0 °C. [e] T = 10.0 °C.

Table III. Kinetic Results for the Conversion of the (Sulfenato)cobalt(III) Complex to the (Sulfinato)cobalt(III) Complex by Oxodiperoxomolybdenum(VI)[a]

$10^5 \times$ [Mo(VI)]$_0$, M	$10^3 \times$ [H_2O_2]$_0$, M	[HNO_3], M	$10^3 \times$ k_{obsd},[b] s^{-1}	k_{Mo2},[c] M^{-1} s^{-1}
8.13	2.30	0.10	2.30	28.0
4.07	1.07	0.10	1.15	28.8
2.03	1.07	0.10	0.60	28.8
8.13	1.07	0.10	2.30	27.7
8.13	1.07	0.050	2.09	25.8
8.13	1.07	0.010	1.37	16.9
8.13	1.07	0.0050	1.16	14.3
8.13	1.07	0.0010	0.69	8.52
8.13	1.07	0.00050	0.57	7.04
8.13	1.07	0.00010	0.52	6.43
4.07[d]	1.10	0.10	0.81	19.5
4.07[e]	1.10	0.10	0.50	12.0

[a] Monitored at 365 nm. Conditions: [$(en)_2Co(SCH_2CH_2NH_2)^{2+}$]$_0$ = 7.0 × 10^{-5} M; ionic strength maintained at 0.10 M with use of KNO_3; T = 25.0 °C unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A - A_\infty)$ vs time. [c] Defined by eq 6. [d] T = 17.0 °C. [e] T = 10.0 °C.

In the series with an ionic strength of 3.0 M, the resulting values were respectively 906 ± 8, 543 ± 8, and 0.47 ± 0.05 at 280 nm, 539 ± 4, 232 ± 3, and 0.58 ± 0.03 at 295 nm, and 243 ± 3, 83 ± 2, and 0.66 ± 0.04 at 310 nm. The results at 310 nm are probably the most reliable due to both the larger spectral difference and the smaller contribution of the hydrogen peroxide to the total absorbance.

Kinetic Studies. A large excess of hydrogen peroxide relative to the thiolato complex and the molybdenum(VI) or tungsten(VI) concentrations was used in the kinetic studies. The net reaction shown in eq 3 in the presence of molybdenum(VI) was monitored

$$(en)_2Co(SCH_2CH_2NH_2)^{2+} + H_2O_2 \rightarrow (en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+} + H_2O \quad (3)$$

by measuring the formation of the sulfenato complex at 365 nm. Plots of $-\ln (A_\infty - A)$ vs time were linear for at least 90% of the total reaction. The slopes of these plots, k_{obsd}, and the experimental conditions are summarized in Table II. In these experiments at least 92% and usually greater than 99% of the molybdenum(VI) is complexed as the oxo diperoxo complex, and the rate of formation of the complex from Mo(VI) and H_2O_2 is very large relative to observed reaction rates.[7] The variation of the pseudo-first-order rate constant k_{obsd} with [H_2O_2]$_0$ and [Mo(VI)]$_0$ is adequately correlated by the rate expression shown in eq 4, where

$$d[\text{sulfenato}]/dt = k_{Mo1}[\text{thiolato}][\text{oxodiperoxomolybdenum(VI)}] \quad (4)$$

$k_{Mo1} = (k_{obsd} - \alpha)/[\text{oxodiperoxomolybdenum(VI)}]_0$. A small correction for the reaction of the thiolato complex with free hydrogen peroxide, determined from kinetic experiments performed in the absence of Mo(VI), was applied: $\alpha = k_{H_2O_2}[H_2O_2]_0$. The values of k_{Mo1} generally decreased gradually with a decrease in the acidity, although a limiting value at the highest acidities used is observed.

We have used both lithium perchlorate and potassium nitrate to adjust ionic strength in these studies. The former was normally used for higher ionic strengths, and the latter for lower ionic strengths when low acidities, with added HNO_3, were desired. In general, the results in nitrate and in perchlorate media are virtually identical at a common ionic strength.

The subsequent Mo(VI)-catalyzed formation of the sulfinato complex under these conditions, as summarized in eq 5, is very

$$(en)_2Co(S\{O\}CH_2CH_2NH_2)^{2+} + H_2O_2 \rightarrow (en)_2Co(S\{O\}_2CH_2CH_2NH_2)^{2+} + H_2O \quad (5)$$

slow. The kinetics of reaction 5 were conveniently monitored by measuring the disappearance of the sulfenato complex at 365 nm, but with much higher concentrations of molybdenum(VI). Under these conditions the conversion of the thiolato complex to the sulfenato complex is quite rapid, and in effect the sulfenato starting material is prepared in situ. Plots of $-\ln (A - A_\infty)$ vs time were linear for at least 90% of the complete reaction. The slopes of these plots, k_{obsd}, and the experimental conditions are summarized in Table III. The variation of the pseudo-first-order rate constant k_{obsd} with [H_2O_2]$_0$ and [Mo(VI)]$_0$ is adequately correlated by the rate expression shown in eq 6, where $k_{Mo2} = k_{obsd}/[\text{Mo(VI)}]_0$. The

$$d[\text{sulfinato}]/dt = k_{Mo2}[\text{sulfenato}][\text{oxodiperoxomolybdenum(VI)}] \quad (6)$$

rate of reaction of free H_2O_2 with the sulfenato complex, as well as subsequent reactions of the sulfinato complex, is negligibly slow under the experimental conditions used. The variation of k_{Mo2} with acidity is similar to that observed for k_{Mo1}.

The kinetic results and experimental conditions for the conversion of the (thiolato)cobalt(III) complex to the sulfenato complex by oxodiperoxotungsten(VI) are presented in Tables IV and V. Previous efforts to determine either the formation constant or rate of formation of oxodiperoxotungsten(VI) were unsuccessful owing to complexities in the chemistry of free tungsten(VI) in acidic solution.[7] As a result, it was not known what concentrations of excess hydrogen peroxide would be required to continuously and completely (or nearly so) complex the tungsten(VI) during the kinetic experiments. We therefore examined the effect of [H_2O_2] on the kinetic results at various acidities. The values of k_{W1}, calculated as described for the molybdenum(VI) system, reached a limiting value at sufficiently large values of the excess [H_2O_2]. It is interesting to note that, under comparable conditions,

Table IV. Kinetic Results for the Conversion of the (Thiolato)cobalt(III) Complex to the (Sulfenato)cobalt(III) Complex by Oxodiperoxotungsten(VI) in Perchlorate Media[a]

T, °C	$10^2 \times [H_2O_2]_0$, M	$[H^+]$, M	I, M	k_{obsd},[b] s^{-1}	$10^{-4}k_{W1}$,[c] $M^{-1}\ s^{-1}$
25.0[d]	1.00	0.50	1.0	0.683	6.62
25.0[d]	2.00	0.50	1.0	0.919	8.77
25.0[d]	4.00	0.50	1.0	1.15	10.6
25.0[d]	6.00	0.50	1.0	1.14	10.2
25.0[d]	8.00	0.50	1.0	1.16	9.90
25.0[d]	1.00	0.10	1.0	0.266	2.51
25.0[d]	2.00	0.10	1.0	0.497	4.69
25.0[d]	3.00	0.10	1.0	0.495	4.54
25.0[d]	4.00	0.10	1.0	0.492	4.37
25.1[e]	5.00	0.50	0.50	0.719	12.0
25.1	5.00	0.50	0.50	1.29 ± 0.07[g]	11.8 ± 0.8
25.1[f]	5.00	0.50	0.50	2.32	11.0
25.0	5.00	0.40	0.50	1.20	11.0
25.0	5.00	0.30	0.50	0.993	9.07
25.0	3.00	0.10	0.50	0.603 ± 0.006[h]	5.60 ± 0.07
25.0	3.00	0.070	0.50	0.496	4.57
25.0	3.00	0.030	0.50	0.386	3.49
25.0	3.00	0.010	0.50	0.320	2.84
17.6	3.00	0.50	0.50	1.10	10.5
17.6	3.00	0.10	0.50	0.483	4.58
11.2	5.00	0.50	0.50	0.838	7.97
11.2	3.00	0.10	0.50	0.396	3.78
25.2	3.00	0.10	0.10	0.782	7.41
25.2[f]	3.00	0.10	0.10	1.62	7.88

[a] Monitored at 323 nm unless otherwise indicated. Conditions: $[(en)_2Co(SCH_2CH_2NH_2)^{2+}]_0 = 7.0 \times 10^{-5}$ M; $[W(VI)]_0 = 1.00 \times 10^{-5}$ M; ionic strength maintained with use of $LiClO_4$. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Defined as for the Mo(VI) system in eq 4. [d] Monitored at 365 nm. [e] $[W(VI)]_0 = 5.00 \times 10^{-6}$ M. [f] $[W(VI)]_0 = 2.00 \times 10^{-5}$ M. [g] Value listed is average of six independent determinations. [h] Value listed is average of three independent determinations.

Table V. Kinetic Results for the Conversion of the (Thiolato)cobalt(III) Complex to the (Sulfenato)cobalt(III) Complex by Oxodiperoxotungsten(VI) in Nitrate Media[a]

T, °C	$10^2 \times [H_2O_2]_0$, M	$[H^+]$, M	k_{obsd},[b] s^{-1}	$10^{-4}k_{W1}$,[c] $M^{-1}\ s^{-1}$
24.2[d]	3.00	0.10	0.420	7.58
24.2	3.00	0.10	0.784	7.44
24.2[e]	3.00	0.10	1.54	7.49
24.2[f]	3.00	0.10	3.10	7.64
25.0	3.00	0.10	0.822	7.81
25.2	3.00	0.10	0.818	7.77
17.4	3.00	0.10	0.676	6.51
11.2	3.00	0.10	0.583	5.65
25.0	3.00	0.10	0.826	7.84
25.0	3.00	0.050	0.659	6.21
25.0	3.00	0.020	0.517	4.81
25.0	3.00	0.010	0.436	4.00
25.0	3.00	0.001 0	0.403	3.68
25.1[d]	3.00	0.000 10	0.218	3.55
25.1	3.00	0.000 10	0.422	3.81
25.1[e]	3.00	0.000 10	0.814	3.87
25.0	3.00	0.000 10	0.396	3.61
25.0	0.50	0.000 10	0.269	2.76
25.0	0.75	0.000 10	0.366	3.56
25.0	1.00	0.000 10	0.407	3.94
25.0	2.00	0.000 10	0.394	3.68
25.0	3.00	0.000 10	0.400 ± 0.007[g]	3.59 ± 0.11
25.0[h]	3.00	0.000 10	0.405	3.64
17.6	3.00	0.000 10	0.364	3.38
13.2	3.00	0.000 10	0.313	2.91
11.2	3.00	0.000 10	0.311	2.91
9.4	3.00	0.000 10	0.290	2.71

[a] Monitored at 323 nm unless otherwise indicated. Conditions: $[(en)_2Co(SCH_2CH_2NH_2)^{2+}]_0 = 7.0 \times 10^{-5}$ M; ionic strength maintained at 0.10 M with use of KNO_3. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Defined as for the Mo(VI) system in eq 4. [d] $[W(VI)]_0 = 5.00 \times 10^{-6}$ M. [e] $[W(VI)]_0 = 2 \times 10^{-5}$ M. [f] $[W(VI)]_0 = 4 \times 10^{-5}$ M. [g] Value listed is average of six independent determinations. [h] Monitored at 365 nm.

Table VI. Kinetic Results for the Conversion of the (Sulfenato)cobalt(III) Complex to the (Sulfinato)cobalt(III) Complex by Oxodiperoxotungsten(VI) in Nitrate Media[a]

$10^5[W(VI)]_0$, M	$10^2[H_2O_2]_0$, M	$[HNO_3]$, M	10^3k_{obsd},[b] s^{-1}	k_{W2},[c] $M^{-1}\ s^{-1}$
4.09	1.99	0.10	9.41	230
4.09	1.99	0.050	3.80	186
4.09	1.99	0.020	5.83	143
4.09	1.99	0.010	5.54	135
4.09	1.99	0.0010	5.0	122
4.09	1.99	0.00050	5.10	124
4.09	1.99	0.00010	5.4	132
1.02	1.99	0.00010	1.22	120
2.04	1.99	0.00010	2.44	120
4.09	1.99	0.00010	5.23	128
8.18	1.99	0.00010	10.8	131
8.18	0.992	0.00010	11.3	134
8.18	1.99	0.00010	11.0	134
8.18	3.97	0.00010	11.0	134
8.18	5.96	0.00010	10.0	122
2.04[d]	3.97	0.00010	2.41	118
4.09[e]	2.04	0.00010	3.89	$95._4$
4.09[f]	2.04	0.00010	2.53	$62._7$

[a] Monitored at 365 nm. Conditions: $[(en)_2Co(SCH_2CH_2NH_2)^{2+}]_0 = 7.0 \times 10^{-5}$ M; T = 25.0 °C; ionic strength maintained at 0.10 M with use of KNO_3 unless otherwise indicated. [b] Values are slopes of plots of $-\ln (A_\infty - A)$ vs time. [c] Defined as for the Mo(VI) system in eq 6. [d] Initial $[(en)_2Co(SCH_2CH_2NH_2)^{2+}] = 1.4 \times 10^{-4}$ M. [e] T = 17.0 °C. [f] T = 10.0 °C.

Table VII. Oxygen-18 Tracer Results for the Oxidation of the (Thiolato)cobalt(III) Complex by Oxodiperoxomolybdenum(VI) and Oxodiperoxotungsten(VI)[a]

		enrichment[b]			
expt	catalyst	solvent	sulfenato complex	sulfinato complex	% oxygen from peroxide
1	Mo(VI)	4.288	1.028		98.1–99.1[c]
2	Mo(VI)	4.197		1.137	88.9–91.4[c]
3	Mo(VI)	4.357	1.365		91.1
4	Mo(VI)	4.123		1.324	91.6
5	W(VI)	4.151	1.025		98.7
6	W(VI)	4.220		1.172	94.7

[a] Reaction conditions given in Experimental Section. [b] Enrichment of oxygen of normal composition defined as 1.000. [c] Precipitates contaminated with perchlorate ion.

considerably more hydrogen peroxide is required to achieve these limiting values than was found for the molybdenum(VI) system.

Experiments monitored at 323 nm, an isosbestic point for the sulfenato and sulfinato complexes, yielded rate constants identical with those determined at 365 nm. This feature further illustrates that the sequential reactions are kinetically well separated under our experimental conditions.

The kinetic results for the much slower conversion of the (sulfenato)cobalt(III) complex to the sulfinato complex by oxodiperoxotungsten(VI) are summarized in Table VI. Again, the values of k_{W2} were calculated as previously for the molybdenum(VI) system. The listed values of both k_{W1} and k_{W2} are seen to reach limiting values at low acidities, but not at the higher values examined.

Reaction Stoichiometries. The stoichiometry of the oxidation of the thiolato and sulfenato complexes by hydrogen peroxide, as given in eq 3 and 5, has been established previously.[17,18] Our data indicate that the same stoichiometry holds for the Mo(VI)- and W(VI)-catalyzed reactions. The yields of the sulfenato and sulfinato products were 95–100% of the starting thiolato complex. These yields were estimated from the infinite absorbance values measured at 365 and 288 nm, respectively. It was not practical to measure the loss of hydrogen peroxide, since the reagent was present in considerable excess for reasons mentioned earlier.

Tracer Results. The results of the ^{18}O studies are summarized in Table VII and indicate that most, if not all, of the oxygen in the sulfenato and sulfinato products comes from peroxidic oxy-

Table VIII. Summary of Rate Constants and Activation Parameters for the Oxidation of the (Thiolato)- and (Sulfenato)cobalt(III) Complexes at 25 °C and $I = 0.10$ M (KNO_3)

complex	oxidant	k, M^{-1} s^{-1}	ΔH^*, kJ/mol	ΔS^*, J/(mol K)
thiolato	H_2O_2[a]	$1.18 + 1.8[H^+]$	30.4[b]	−133[b]
thiolato	$MoO(OH)(O_2)_2^-$	$(2.4 \pm 0.5) \times 10^3$	4 ± 2	−166 ± 6
thiolato	$MoO(O_2)_2$	$(1.91 \pm 0.02) \times 10^4$	17 ± 3	−106 ± 10
thiolato	$WO(OH)(O_2)_2^-$	$(3.7 \pm 0.7) \times 10^4$	9 ± 1	−126 ± 4
thiolato	$WO(O_2)_2$	$(3.7 \pm 0.1) \times 10^5$	21 ± 4	−70 ± 12
sulfenato	H_2O_2[a]	$3.4 \times 10^{-4} + 5.1 \times 10^{-4}[H^+]$	63[c] 59[d]	−109[c] −109[d]
sulfenato	$MoO(OH)(O_2)_2^-$	6.6 ± 2.0	20 ± 1	−161 ± 1
sulfenato	$MoO(O_2)_2$	30.8 ± 0.1	37 ± 5	−92 ±16
sulfenato	$WO(OH)(O_2)_2^-$	120 ± 20	34 ± 3	−91 ± 9
sulfenato	$WO(O_2)_2$	980 ± 30	*e*	*e*

[a] Values listed are taken from ref 18–20 and refer to an ionic strength of 1.0 M maintained by use of lithium perchlorate. [b] Composite values determined in 1 M $HClO_4$. [c] Vallues are for an acid-independent pathway. [d] Values are for an acid-dependent pathway. [e] Not determined since the protonation constant of the sulfenato complex[18] is similar to the K_a for oxodiperoxotungsten(VI).

gen.[22] Under the experimental conditions employed, virtually all of the oxidation is due to oxodiperoxomolybdenum(VI) rather than free hydrogen peroxide.

Discussion

The kinetic results coupled with the previous equilibrium studies strongly indicate that oxo diperoxo complexes are responsible for the Mo(VI)- and W(VI)-catalyzed oxidation of both the thiolato and sulfenato complexes by hydrogen peroxide. Although the turnover numbers are not large under our experimental conditions, the data suggest that catalysis would persist as long as sufficient hydrogen peroxide is present to maintain the metal ions as the oxo diperoxo complexes.

The rates of both the catalyzed and uncatalyzed reactions tend to increase with increasing acidity. The acid dependence for the uncatalyzed reaction is of the form ($a + b[H^+]$) and is observed in many oxygen-transfer reactions of hydrogen peroxide.[25-27] The hydrogen ion dependent term is generally attributed to protonation of hydrogen peroxide. The origin of the acid dependence is quite different, however, for the catalyzed reactions. The variation of rate constants with acidity for all four systems examined (see Tables II–VI) is satisfactorily correlated by the following scheme (M = Mo(VI) or W(VI)):

$$MO(O_2)_2 + H_2O \rightleftarrows MO(OH)(O_2)_2^- + H^+ \quad K_a \tag{7}$$

$$MO(O_2)_2 + \text{substrate} = \text{products} \quad k_{MO(O_2)_2} \tag{8}$$

$$MO(OH)(O_2)_2^- + \text{substrate} = \text{products} \quad k_{MO(OH)(O_2)_2^-} \tag{9}$$

$$k_{M(1,2)}([H^+] + K_a) = k_{MO(OH)(O_2)_2^-}K_a + k_{MO(O_2)_2}[H^+] \tag{10}$$

Plots of the left-hand side of eq 10 vs $[H^+]$ were linear for all four systems. Values of the rate parameters for the hydrolyzed forms (eq 9) were obtained from the intercepts of such plots for low acid concentration runs with at least a 20% contribution from this pathway by use of the independently determined K_a values. The values for the neutral oxo diperoxo complexes with a given substrate were then obtained as the slope of the same plot by using all the data but with the intercept fixed. The values obtained and the associated activation parameters (as calculated under the assumption that K_a is independent of temperature) are summarized in Table VIII.

The neutral oxo diperoxo complexes of Mo(VI) and W(VI) are roughly 1 order of magnitude more reactive than the corresponding hydrolyzed forms, and W(VI) is a better catalyst than Mo(VI) for the two substrates examined in this study. The activation of peroxide coordinated to either metal ion relative to hydrogen peroxide is quite impressive. For example, in 3 M acid the ratio $k_{WO(O_2)_2}/k_{H_2O_2}$ is 4×10^4 and 5×10^5 for the thiolato and sulfenato complexes, respectively. Similar values are obtained at pH 4 for the ratio $k_{WO(OH)(O_2)_2^-}/k_{H_2O_2}$. The activation parameters show some interesting features, although we are unable to offer a rationalization. We note that the least reactive oxo diperoxo complex, $MoO(OH)(O_2)_2^-$, has the lowest activation enthalpies. Also, the kinetic advantage of W(VI) over Mo(VI) is entirely due to more favorable activation entropies; the activation enthalpies are actually less favorable.

The oxygen-18 tracer results demonstrate that peroxidic oxygen atom transfer from the oxo diperoxo complexes to the sulfurs of the thiolato and sulfenato complexes is extensive and possibly quantitative. The mechanism of the catalyzed reactions is analogous to that of hydrogen peroxide in the sense that nucleophilic attack by coordinated sulfur at peroxidic oxygen occurs. However, our data cannot resolve the fundamental mechanistic question, Is this nucleophilic attack direct or is there coordination of the sulfur atom at the Mo(VI) or W(VI) center prior to atom transfer? We favor the former, but available data show that either scheme is sterically feasible. For example, reduction of the thiolato complex by chromium(II) has been demonstrated to proceed by inner-sphere attack by the reductant at the coordinated sulfur.[28] A crystal structure of $[Co(en)_2(SCH_2CH_2NH_2)Cu(CH_3CN)_2]_2(ClO_4)_6 \cdot 2H_2O$ shows coordination of two copper ions at the sulfur center (the cation is dimeric).[29]

It is unlikely that a distinction could be made by substitution at sulfur in the thiolato complex. A more promising approach would be to tie up the remaining two coordination sites in the oxo diperoxo complex by use of a chelating ligand and examine the kinetic consequence on the oxygen atom transfer reaction. This type of experiment is easily accomplished in noncoordinating solvents, but in aqueous solution one must prove that the bidentate ligand remains fully coordinated during the reaction. We are presently pursuing this idea with $MoO(O_2)_2(C_2O_4)^{2-}$.

Regardless of which mechanism is dominant, after oxygen atom transfer the d^0 metal ion must rapidly be reconverted to the oxo diperoxo complex. Our previous study demonstrated that entry of the second peroxide is rate determining in the formation of

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(22) While the oxo ligands on Mo(VI) and W(VI) are known to exchange rapidly with solvent oxygen,[23] there is no exchange between the oxo and the peroxo oxygens[24] or between peroxide and solvent oxygen. The exchange rate between the oxygen(s) of the coordinated sulfenato and sulfinato ligands and solvent is not known but was presumed to be negligible for our calculations.

(23) Gamsjager, H.; Murmann, R. K. In *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 349.

(24) Postel, M.; Brevard, C.; Arzoumanian, H.; Reiss, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 4922.

(25) Edwards, J. O. In *Peroxide Reaction Mechanisms*; Edwards, J. O., Ed.; Interscience: New York, 1962.

(26) Edwards, J. O. In *Inorganic Reaction Mechanisms*; Benjamin: New York, 1964; p 77.

(27) Hoffmann, M.; Edwards, J. O. *Inorg. Chem.* **1977**, *16*, 3333.

(28) Kennard, G. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 2225.

(29) Lane, R. H.; Pantaleo, N. S.; Farr, J. K.; Coney, W. M.; Newton, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 1610.

oxodiperoxomolybdenum(VI); the rate is sufficiently rapid under the experimental conditions in this study to maintain virtually all the Mo(VI) in the catalytic form. The corresponding kinetic data for the formation of oxodiperoxotungsten(VI) are not available, but the higher concentrations of hydrogen peroxide required to reach saturation kinetics for the tungsten(VI) systems suggest a slower formation rate.

The value of K_a for oxodiperoxochromium(VI) is apparently about 10^{-4} M.[30-32] Therefore, the acidities of the group 6 oxo diperoxo complexes stand in the order W(VI) > Mo(VI) > Cr(VI). The same ordering holds for the $MO_3(OH)^-$ ions.[33] This trend is opposite to that observed for oxoacids of the main-group elements. We are not aware of a satisfactory explanation for this reversal in periodic properties.

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Supplementary Material Available: Table S1 (variation of the extinction coefficient of oxodiperoxotungsten(VI) with acidity at 25 °C) (1 page). Ordering information is given on any current masthead page.

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(30) Griffith, W. P. *J. Chem. Soc.* **1962**, 3948.
(31) Witt, S. N.; Hayes, D. M. *Inorg. Chem.* **1982**, *21*, 4014.
(32) Bartlett, B. L.; Quane, D. *Inorg. Chem.* **1973**, *12*, 1925.
(33) This comparison is valid since it has been shown that the $MO_3(OH)^-$ ions of group 6 are isostructural. See: (a) Cruywagen, J. J.; Rohwer, E. F. C. H. *Inorg. Chem.* **1975**, *14*, 3136. (b) Brown, P. L.; Shying, M. E.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1987**, 2149.

Notes

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Formation of Chlorine–Fluorine and Nitrogen–Fluorine Bonds Using Carbonyl Difluoride as the Fluorinating Agent

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Previous studies by Shreeve and her co-workers have shown that carbonyl difluoride (COF_2) is a useful reagent for displacing either hydrogen by fluorine from P–H, N–H, and C–H bonds[1] or oxygen by fluorine from the oxides of V, Nb, Ta, Cr, Mo, W, B, Si, Ge, Sn, P, Se, Te, I, and U.[2] The latter study prompted us to examine whether COF_2 could also be used for the formation of Cl–F and N–F bonds from their oxides. The formation of Cl–F[3] and N–F[4] bonds usually requires relatively powerful fluorinating agents and previously has not been achieved with a fluorinating agent as mild as COF_2. Thermochemical calculations that were carried out by us revealed the feasibility of reaction 1 for M = Li and Na. It increases with decreasing atomic weight of M and

$$\begin{gathered} MNO_3 + COF_2 \rightarrow MF + FNO_2 + CO_2 \\ M = Li, Na, K, Rb, Cs \end{gathered} \tag{1}$$

for M = Li and Na results in ΔH values of −9.5 and −4.5 kcal mol^{-1}, respectively. Reaction 2 was found to be thermochemically feasible by comparable amounts with ΔH values of −20.6 and −11.2 kcal mol^{-1} for M = Li and Na, respectively.

$$\begin{gathered} MClO_3 + COF_2 \rightarrow MF + FClO_2 + CO_2 \\ M = Li, Na, K, Rb, Cs \end{gathered} \tag{2}$$

In view of the thermochemical results, reactions 1 and 2 were experimentally studied. It was found that $LiNO_3$, when heated with a slight excess of COF_2 in a steel cylinder at 45–90 °C, formed CO_2, N_2O_4, and O_2 in high yield. These products are best explained by reaction 3, followed by the attack of the steel cylinder

$$LiNO_3 + COF_2 \rightarrow LiF + FNO_2 + CO_2 \tag{3}$$

by FNO_2. Since HF generally promotes the attack of steel by oxidizers such as FNO_2, small amounts of CsF were added to the reaction as an HF getter (see reaction 4). In this manner, FNO_2

$$CsF + HF \rightarrow CsHF_2 \tag{4}$$

was isolable in essentially quantitative yield according to (3), with 12 mol % of CsF as an additive at 85 °C. For $NaNO_3$ with CsF addition, an 85% yield of FNO_2 was obtained under comparable conditions. For $CsNO_3$, either with or without CsF, no reaction was observed with COF_2, in agreement with the above thermochemical predictions.

The postulate that CsF serves only as an HF getter and not as a catalyst was confirmed by carrying out reaction 3 in an all-Teflon reactor. In such a reactor, high yields of FNO_2 were obtainable without CsF addition.

For the reaction of $NaClO_3$ with COF_2, reaction conditions similar to those used for $NaNO_3$, i.e. 85 °C and CsF catalysis, were required. The best yield obtained for $FClO_2$ was about 44% based on the limiting reagent $NaClO_3$, but no systematic effort was undertaken to maximize this yield.

Attempts failed to prepare $FClO_3$ from $LiClO_4$ and COF_2. Although this reaction is thermochemically favored by 14.8 kcal mol^{-1}, no reaction was observed up to 120 °C. At 160 °C, a 30% conversion of $LiClO_4$ to LiF was obtained, but even in the presence of CsF only chlorine and oxygen and no $FClO_3$ were isolated.

In summary, the successful formation of N–F and Cl–F bonds from the corresponding oxides by the very mild fluorinating agent COF_2 was quite unexpected and significantly expands the utility of this fluorinating agent.

Experimental Section

Materials and Apparatus. $LiNO_3$ (J. T. Baker, 99.7%) and $NaNO_3$ (J. T. Baker, 99.5%) were dried in a vacuum oven at 120 °C for 1 day prior to their use. The $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. The CsF was dried by fusion in a platinum crucible, followed by immediate transfer of the hot clinker to the dry N_2 atmosphere of a glovebox. The $NaClO_3$ and $LiClO_4$ (Baker, Analyzed reagents) were used as received. The COF_2 (PCR Inc.) was used without further purification after removal of any volatile material at −196 °C.

Volatile materials were handled in a stainless steel–Teflon FEP vacuum line[5] and solids in the dry N_2 atmosphere of a glovebox.

Synthesis of FNO_2. In a typical experiment, $LiNO_3$ (2.10 mmol) and CsF (0.25 mmol) were loaded in the drybox into prepassivated (with ClF_3) 30-mL stainless steel cylinder, which was closed by a valve. On the vacuum line, COF_2 (2.38 mmol) was added to the cylinder at −196 °C. The cylinder was kept in an oven at 85 °C for 16 h and was then cooled again to −196 °C. It did not contain any significant amount of gas noncondensable at −196 °C. The material volatile at 25 °C was

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(1) Gupta, O. D.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 416 and references therein. Williamson, S. M.; Gupta, O. D.; Shreeve, J. M. *Inorg. Synth.* **1986**, *24*, 62.
(2) Mallela, S. P.; Gupta, O. D.; Shreeve, J. M. *Inorg. Chem.* **1988**, *27*, 208.
(3) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 319.
(4) *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, FRG, 1987; Fluorine Supplement Vol. 5, Compounds with N.
(5) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.