Inorg. Chem. **2007**, *46*, 2322–2327

Inorganic Chemistry
Article

Kinetics of Oxidation of Nitroxyl Radicals with Superoxometal Complexes of Chromium and Rhodium

Michael J. Vasbinder and Andreja Bakac*

Ames Laboratory and Chemistry Department, Iowa State University, Ames, Iowa 50011

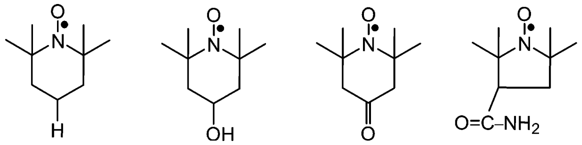
Received October 19, 2006

In acidic aqueous solutions, nitroxyl radicals (X)TEMPO (X = H, 4-OH, and 4-oxo) and 3-carbamoyl-PROXYL readily reduce $Cr_{aq}OO^{2+}$ and $Rh(NH_3)_4(H_2O)OO^{2+}$ to the corresponding hydroperoxo complexes. The kinetics are largely acid independent for $Cr_{aq}OO^{2+}$, but acid catalysis dominates the reactions of the rhodium complex. This emerging trend in oxidations with superoxometal complexes seems to be directly related to the thermodynamics of electron transfer. The weaker the oxidant, the more important the acid-assisted path. The rate constants for the oxidation of (X)TEMPO by $Cr_{aq}OO^{2+}$ are 406 M^{-1} s^{-1} (X = H), 159 (4-OH), and (20. 6 + 77.5 [H^+]) (4-oxo). For the rhodium complex, the values are (40 + 2.20 × 10^3 [H^+]) (X = H), (25 + 1.10 × 10^3 [H^+]) (4-HO), and 2.21 × 10^3 [H^+] (4-oxo). An inverse solvent kinetic isotope effect, $k_H/k_D = 0.8$, was observed in the reaction between (O)TEMPO and $(NH_3)_4(H(D))_2O)RhOO^{2+}$ in 0.10 M $H(D)ClO_4$ in H_2O and D_2O.

Introduction

Stable nitroxyl radicals ($RNO^\bullet$) are versatile reagents that have found applications as oxidation catalysts,[1−4] initiators of free-radical polymerization,[5−8] spin labels,[9,10] radical traps in mechanistic studies,[11−13] probes for reactive oxygen species (ROS) in biology,[14−16] and protective agents against physiological damage by ROS.[17−20] TEMPO, carbamoyl proxyl (CP), and their derivatives, shown in Chart 1, are commonly utilized in many of these areas, although new and more reactive catalysts are being continuously developed.[21]

Chart 1. Nitroxyl Radicals Used in This Work



TEMPO-catalyzed oxidation of alcohols to carbonyl compounds typically requires 2-e oxidants such as hypochlorite (NaOCl), peroxysulfate ($KHSO_5$), hydrogen peroxide, *meta*-chloroperbenzoic acid, oxaziridines, etc.[1,3] The mechanism involves oxidation of $RNO^\bullet$ to RNO^+ (for oxidation

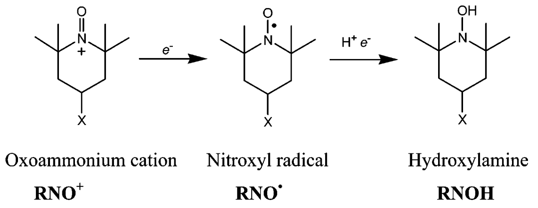
---

* To whom correspondence should be addressed. E-mail: bakac@ameslab.gov.

(1) Sheldon, R. A.; Arends, I. W. C. E. *J. Mol. Catal., A* **2006**, *251*, 200−214.
(2) Arends, I. W. C. E.; Li, Y.-X.; Ausan, R.; Sheldon, R. A. *Tetrahedron* **2006**, *62*, 6659−6665.
(3) Adam, W.; Saha-Moller, C. R.; Ganeshpure, P. A. *Chem. Rev.* **2001**, *101*, 3499 -3548.
(4) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393−427.
(5) Knoop, C. A.; Studer, A. *J. Am. Chem. Soc.* **2003**, *125*, 16327−16333.
(6) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763−10764.
(7) Sessions, L. B.; Miinea, L. A.; Ericson, K. D.; Glueck, D. S.; Grubbs, R. B. *Macromolecules* **2005**, *38*, 2116−2121.
(8) Bricklebank, N.; Pryke, A. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2048−2051.
(9) Borbat, P. P.; Costa-Filho, A. J.; Earle, K. A.; Moscicki, J. K.; Freed, J. H. *Science* **2001**, *291*, 266−269.
(10) Battiste, J. L.; Gross, J. D.; Wagner, G. *Biol. Magn. Reson.* **2003**, *20*, 79−101.
(11) Kelemen, P.; Klumperman, B. *Macromolecules* **2004**, *37*, 9338−9344.
(12) Fleming, P. E.; Daikh, B. E.; Finke, R. G. *J. Inorg. Biochem.* **1998**, *69*, 45−57.
(13) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 5197−5202.
(14) Valgimigli, L.; Pedulli, G. F.; Paolini, M. *Free Rad. Biol. Med.* **2001**, *31*, 708−716.
(15) Skolimowski, J.; Kochman, A.; Gebicka, L.; Metodiewa, D. *Bioorg. Med. Chem. Lett.* **2003**, *11*, 3529−3539.
(16) Herrling, T.; Jung, K.; J., F. *Spectrochim. Acta A* **2006**, *63*, 840−845.
(17) Hu, G.; Lyeth, B. G.; Zhao, X.; Mitchell, J. B.; Watson, J. C. *J. Neurosurgery* **2003**, *98*, 393−396.
(18) Mitchell, J. B.; Krishna, M. C.; Samuni, A.; Russo, A.; Hahn, S. M. In *Reactive Oxygen Species in Biological Systems: An Interdisciplinary Approach*; Gilbert, D. L., Colton, C. A., Eds.; Plenum: New York, 1999; pp 293−313.
(19) Zhang, R.; Shohami, E.; Beit-Yannai, E.; Bass, R.; Trembovler, V.; Samuni, A. *Free Rad. Biol. Med.* **1998**, *24*, 332−340.
(20) Hahn, S. M.; Sullivan, F. J.; De Luca, A. M.; Sprague, M.; Hampshire, V. A.; Krishna, M. C.; Russo, A.; Mitchell, J. B. *Int. J. Oncol.* **1997**, *10*, 119−123.
(21) Shibuya, M.; Tomizawa, M.; Suzuki, I.; Iwabuchi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 8412−8413.

10.1021/ic062010s CCC: $37.00

Scheme 1. Oxidation States of TEMPO Involved in Oxidation Catalysis



Scheme 2

$$2M^{n} + RNOH \rightarrow 2M^{n-1} + RNO^{+} + H^{+}$$

$$RNO^{+} + R_2CHOH \rightarrow R_2CO + RNOH + H^{+}$$

$$M^{n-1} \xrightarrow{O_2} M^{n}$$

states and abbreviations, see Scheme 1), 2-e oxidation of alcohols to carbonyl products with RNO^+, and reoxidation of RNOH to RNO^+. Oxidation with molecular oxygen becomes feasible when nitroxyl is used in combination with metal complexes. The role of the metal cocatalyst (M) is to oxidize either RNOH or $RNO^\bullet$ to a species capable of oxidizing the alcohol. Molecular oxygen then restores the metal cocatalyst to its active state, Scheme 2.

Nitroxyl radicals are also efficient catalysts for the dismutation of superoxide, owing to the rapid oxidation of $RNO^\bullet$ by $HO_2^\bullet$, and reduction of RNO^+ by $O_2^{\bullet-}$.[22] In view of the potential importance of this chemistry for pharmaceutical purposes, as well as its role in the nitroxyl-catalyzed oxidations of alcohols, we thought it would be of interest to explore the possibility that such chemistry takes place with coordinated superoxide as well. Superoxometal complexes L_nMOO^{m+} (L = ligands, M = metal) are often involved as intermediates in both biological and laboratory oxidations with O_2. These species themselves have substantial unpaired spin density on the terminal oxygen, which makes them quite reactive toward radicals. We have shown previously that the initial interaction between $Cr_{aq}OO^{2+}$ and $Br_2^{\bullet-}$, $I_2^{\bullet-}$, $^\bullet NO$, $^\bullet NO_2$, $RC(O)OO^\bullet$, etc. takes place with rate constants in excess of 10^8 M^{-1} s^{-1}.[23-25] Even though the nitroxyls are much less oxidizing or reducing than the radicals examined so far, there is sufficient driving force for the reaction with superoxometal complexes to take place and to generate oxoammonium cations. We have now examined several such reactions. The results are presented herein.

Experimental Section

2,2,6,6-Tetramethylpiperidine-*N*-oxyl radical (TEMPO), 2,2,6,6-tetramethyl-4-hydroxylpiperidine-*N*-oxyl radical ((HO)TEMPO), 2,2,6,6-tetramethyl-4-oxopiperidine-*N*-oxyl radical ((O)TEMPO), and 3-carbamoyl-PROXYL radical (3-CP) were purchased from Aldrich and used without further purification. Acidic aqueous solutions of $Cr_{aq}OO^{2+}$ were prepared from Cr_{aq}^{2+} and O_2 and contained 0.10 M methanol as preservative.[26] Solutions of $Rh(NH_3)_4(H_2O)OO^{2+}$ were prepared by oxidizing $Rh(NH_3)_4(H_2O)OOH^{2+}$ [27] with a slight excess of O_3 followed by removal of the remaining traces of unreacted O_3 with a stream of O_2. The macrocyclic complex $L^2(H_2O)RhOO^{2+}$ (L^2 = Me_6-14[ane]N_4)) was prepared by photolysis of the corresponding rhodium hydride[27] under O_2. The chloride salts of oxoammonium cations (O)TEMPO$^+$ and TEMPO$^+$ were prepared by oxidizing the nitroxyls with chlorine as described in the literature.[28,29] The kinetics were studied under pseudo-first-order conditions, usually with the nitroxyl present in large excess over the superoxo metal complexes. The data were fitted to the first-order rate expression with the program Kaleidagraph 3.6.

Ozone was generated with an Ozonology L-100 apparatus. Kinetic measurements used a Shimadzu 3101 PC, Applied Photophysics stopped-flow, or OLIS RSM-1000 rapid-scanning stopped-flow spectrophotometer at 25.0 ± 0.2 °C. The progress of the reactions was followed by observing the disappearance of either $Cr_{aq}OO^{2+}$ at 293 nm or $L(H_2O)RhOO^{2+}$ (L = $(NH_3)_4$, L^2) at 270 nm.

Results

The superoxo complexes $Cr_{aq}OO^{2+}$ and $L(H_2O)RhOO^{2+}$ (L = $(NH_3)_4$) are rapidly reduced to the hydroperoxo species by each of the four nitroxyls examined, eq 1. The stoichiometric ratio, $[(X)TEMPO]/[L(H_2O)MOO^{2+}]$ = 1:1, was determined from the associated spectral changes in the UV, where both superoxo and hydroperoxo complexes absorb strongly, Figure S1. The contribution to ΔAbs from the changes in [(X)TEMPO] and [(X)TEMPO$^+$] was negligible at the monitoring wavelengths.

$$(X)TEMPO + L(H_2O)MOO^{2+} (+H^+) \rightarrow (X)TEMPO^+ + L(H_2O)MOOH^{2+} \quad X = H, OH, O \quad (1)$$

The initial products of nitroxyl oxidation, (X)TEMPO$^+$, which typically absorb light around 350 nm, could not be observed directly because their spectral features are too weak in comparison with the strong transitions associated with the superoxo and hydroperoxo complexes. Also, two of the oxoammonium cations, (O)TEMPO$^+$ and (HO)TEMPO$^+$, are known to decompose rapidly[22,30] on the time scale of reaction 1.

Independent experiments showed that there was no reaction between the product hydroperoxo complexes and any of the nitroxyls used in this work or between $Cr_{aq}OO^{2+}$ and the final decomposition products of an authentic sample of (O)TEMPO$^+$.

Under pseudo-first-order conditions with (X)TEMPO present in large excess over the superoxometal ions, the fits to the first-order rate expression were excellent for all the reactions studied. The plots of k_{obs} against the concentration of excess reagent were linear and yielded second-order rate constants for reaction 1, as shown for (HO)TEMPO in Figure

---

[22] Goldstein, S.; Merenyi, G.; Russo, A.; Samuni, A. *J. Am. Chem. Soc.* **2003**, *125*, 789−795.

[23] Bakac, A. *Adv. Inorg. Chem.* **2004**, *55*, 1−59.

[24] Bakac, A.; Shi, C.; Pestovsky, O. *Inorg. Chem.* **2004**, *43*, 5416−5421.

[25] Hung, M.; Bakac, A. *Inorg. Chem.* **2005**, *44*, 9293−9298.

[26] Bakac, A. *J. Am. Chem. Soc.* **2002**, *124*, 9136−9144.

[27] Bakac, A. *J. Am. Chem. Soc.* **2000**, *122*, 1092−1097.

[28] Golubev, V. A.; Zhdanov, R. I.; Rozantsev, E. G. *Izv. Akad. Nauk. SSR, Ser. Khim.* **1970**, 184−185.

[29] Hunter, D. H.; Racok, J. S.; Rey, A. W.; Zea-Ponce, Y. *J. Org. Chem.* **1988**, *53*, 1278−1281.

[30] Goldstein, S.; Samuni, A.; Russo, A. *J. Am. Chem. Soc.* **2003**, *125*, 8364−8370.

Table 1. Kinetic Data for the Oxidation of Nitroxyl Radicals in Aqueous Solution[a]

oxidant	RNO	k/M^{-1} s^{-1}	source
$Cr_{aq}OO^{2+}$	TEMPO	406 ± 12	this work
$Cr_{aq}OO^{2+}$	(HO)TEMPO	159 ± 3	this work
$Cr_{aq}OO^{2+}$	(O)TEMPO	$(20.6 \pm 1.0) + (77.5 \pm 1.0)\,[H^+]$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	TEMPO	$(40 \pm 10) + (2.20 \pm 0.20) \times 10^3\,[H^+]$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	(HO)TEMPO	$(25 \pm 5) + (1.10 \pm 0.15) \times 10^3\,[H^+]$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	(O)TEMPO	$(4 \pm 12) + (2.21 \pm 0.20) \times 10^3\,[H^+]$	this work
$L^2(H_2O)RhOO^{2+}$	TEMPO	≤ 1 M^{-1} s^{-1} at 0.020 M H$^+$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	3-CP	$(1.7 \pm 0.2) \times 10^3\,[H^+]$	this work
$HO^•$	TEMPO	$(4.5 \pm 0.4) \times 10^9$	ref 32
$HO^•$	(HO)TEMPO	$(4.5 \pm 0.4) \times 10^9$	ref 32
$HO^•$	(O)TEMPO	$(4.5 \pm 0.4) \times 10^9$	ref 32
$NO_2^•$	TEMPO	$(7.1 \pm 0.2) \times 10^8$	ref 30
$NO_2^•$	(HO)TEMPO	$(8.7 \pm 0.2) \times 10^8$	ref 30
$NO_2^•$	(O)TEMPO	$(7.1 \pm 0.2) \times 10^8$	ref 30
$NO_2^•$	3-CP	$(4.9 \pm 0.2) \times 10^8$	ref 30
$HO_2^•$	TEMPO	$(1.2 \pm 0.1) \times 10^8$	ref 22
$HO_2^•$	3-CP	$(1.2 \pm 0.1) \times 10^8$	ref 22
$Ru(bpy)_3^{3+}$	3-CP	1.4×10^9	ref 33
$C(NO_2)_4$	TEMPO	6.6	ref 34
$C(NO_2)_4$	(HO)TEMPO	0.85	ref 34
$C(NO_2)_4$	(O)TEMPO	0.075	ref 35
I_2	TEMPO	5.3	ref 36
$O_2^{•-}$	TEMPO	$<1 \times 10^3$	ref 22

[a] Conditions: aqueous solutions, 25 °C.

1. In several cases the conditions were reversed, and superoxometal ions were used in excess over nitroxyl radicals. The rate constants obtained under such conditions were identical, within the error, to those obtained with the nitroxyl in excess. For example, the reaction between 1.75×10^{-4} M $Cr_{aq}OO^{2+}$ and 1.0×10^{-5} M (HO)TEMPO in 0.020 M $HClO_4$ yielded a pseudo-first-order rate constant of 0.030 s^{-1}. This translates into $k = 171$ M^{-1} s^{-1}, in good agreement with the value (159 M^{-1} s^{-1}) obtained from the data in Figure 1. This result independently confirms the 1:1 stoichiometry of reaction 1. All the kinetic data are summarized in Table 1.

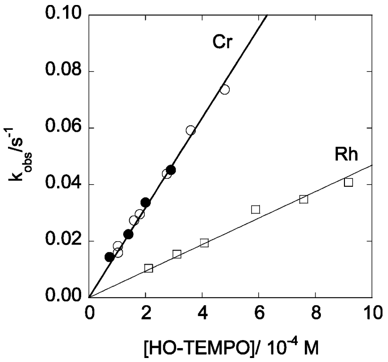


Figure 1. Plots of k_{obs} vs [(HO)TEMPO] for the reactions with $Cr_{aq}OO^{2+}$ (0.008−0.032 mM) in 0.020 M H$^+$ (filled circles) and 0.10 M H$^+$ (open circles), and with $(NH_3)_4(H_2O)RhOO^{2+}$ (0.008−0.032 mM) in 0.020 M H$^+$ (open squares).

The reactions of TEMPO and (HO)TEMPO with $Cr_{aq}OO^{2+}$ exhibited no dependence on [H$^+$] or the ionic strength (maintained with $HClO_4/NaClO_4$) in the range 0.020−0.10 M. The oxidation of (O)TEMPO, on the other hand, is mildly acid-dependent and obeys the rate law of eq 2, where $k_0 = (20.6 \pm 1.0)$ M^{-1} s^{-1} and $k_1 = (77.5 \pm 1.0)$ M^{-2} s^{-1}. The data are displayed in Figures 2 and 3.

$$-d[Cr_{aq}OO^{2+}]/dt = (k_0 + k_1[H^+])[(O)TEMPO][Cr_{aq}OO^{2+}] \quad (2)$$

Acid catalysis is much more pronounced in the reactions of $(NH_3)_4(H_2O)RhOO^{2+}$ as shown in Figure 2 for the reaction with [(O)TEMPO] ($E = 0.91$ V). The second-order rate constants, obtained as slopes of the straight lines in Figure 2, are plotted against [H$^+$] in Figure 3. For the $(NH_3)_4(H_2O)RhOO^{2+}$/(O)TEMPO reaction, the data yielded the rate law in eq 3, where $k_0 = (4 \pm 12)$ M^{-1} s^{-1} and $k_1 = (2.21 \pm$

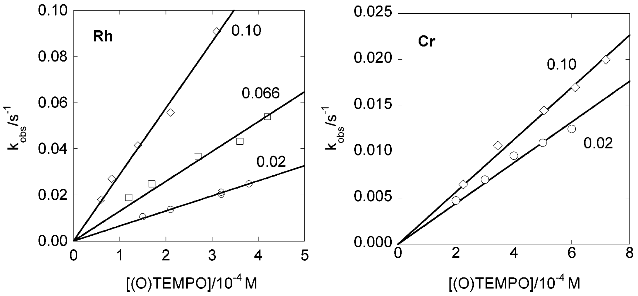


Figure 2. Representative plots of k_{obs} against [(O)TEMPO] for the reaction with $(NH_3)_4(H_2O)RhOO^{2+}$ (0.006−0.085 mM) and with $Cr_{aq}OO^{2+}$ (0.007−0.090 mM) at [H$^+$] = 0.020 M (circles), 0.066 (squares), and 0.10 (diamonds).

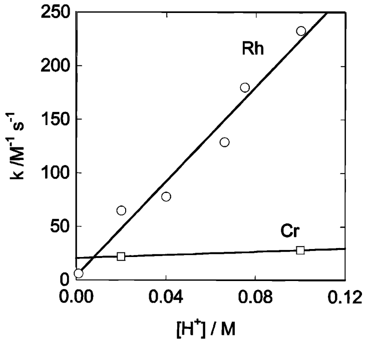


Figure 3. Plot of second-order rate constants against [H$^+$] for the reaction of (O)TEMPO with $(NH_3)_4(H_2O)RhOO^{2+}$ (circles) and $Cr_{aq}OO^{2+}$ (squares).

0.20) × 10^3 M^{-2} s^{-1}. Thus, the reaction proceeds exclusively by the [H^+]-catalyzed path.

$$-d[(NH_3)_4(H_2O)RhOO^{2+}]/dt = (k_0 + k_1[H^+])[(O)TEMPO][(NH_3)_4(H_2O)RhOO^{2+}] \quad (3)$$

The importance of the [H^+]-independent term increases, however, with improved thermodynamics, so that the stronger reductants, (HO)TEMPO ($E = 0.80$ V) and, especially, TEMPO ($E = 0.73$ V), exhibit measurable intercepts in their plots of k_{obs} against [H^+], as shown in Figure 4.

In agreement with the above considerations, the reaction of 3-CP ($E = 0.87$ V) with $(NH_3)_4(H_2O)RhOO^{2+}$ also requires catalysis by H^+, $k = 1.7 \times 10^3$ [H^+]. The 3-CP/$Cr_{aq}OO^{2+}$ reaction was not well behaved, and detailed study was not undertaken.

In accordance with specific acid catalysis,[31] a small inverse solvent kinetic isotope effect (kie) was observed in the reaction of $(NH_3)_4(H_2O)RhOO^{2+}$ with (O)TEMPO. Figure 5 shows the plots of k_{obs} against the concentration of [(O)-TEMPO] in 0.10 M $H(D)ClO_4$ in H_2O and D_2O. The rate constants, obtained from the slopes of the lines in Figure 5 are 237 ± 8 (H_2O) and 288 ± 8 M^{-1} s^{-1} (D_2O), yielding $k_{H_2O}/k_{D_2O} \approx 0.8$.

To find out whether nitroxyls can catalyze the oxidation of alcohols by $Cr_{aq}OO^{2+}$, we carried out a reaction between $Cr_{aq}OO^{2+}$ and TEMPO in the presence of large concentrations of methanol (up to 5 M) and compared the results with those obtained in a similar experiment in 0.1 M methanol. The potential catalytic scheme starts with the oxidation of TEMPO with $Cr_{aq}OO^{2+}$, followed by the known two-electron oxidation of methanol with $TEMPO^+$ ($k = 0.48 \pm 0.02$ M^{-1} s^{-1}), eqs 4 and 5.[22] The regeneration of the catalyst in reaction 6 is the only untested step in the proposed scheme.

$$Cr_{aq}OO^{2+} + TEMPO\ (+H^+) \rightarrow Cr_{aq}OOH^{2+} + TEMPO^+ \quad (4)$$

$$TEMPO^+ + CH_3OH \rightarrow TEMPOH + CH_2O + H^+ \quad (5)$$

$$TEMPOH + Cr_{aq}OO^{2+} \rightarrow Cr_{aq}OOH^{2+} + TEMPO \quad (6)$$

The two experiments yielded identical kinetics and a clean 1:1 [$Cr_{aq}OO^{2+}$]/[TEMPO] stoichiometry. The lack of catalysis is probably caused by the slow kinetics of the catalyst regeneration in step 6, because reactions 4 and 5 are known to be fast under experimental conditions. This interpretation is supported by the results of several qualitative experiments with Et_2NOH and Et_2NO. The oxidation of hydroxylamine with $Cr_{aq}OO^{2+}$ was substantially slower than the oxidation of the nitroxide. The same reactivity order seems to hold for TEMPO/TEMPOH couple. Even if the scheme in reactions 4−6 had worked, it would have no immediate practical use because there is currently no simple way to regenerate $Cr_{aq}OO^{2+}$ under oxidizing conditions.

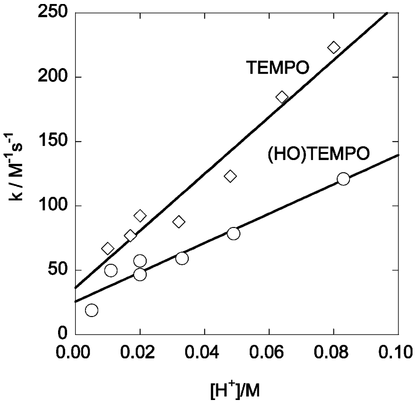


Figure 4. Plots of second-order rate constants against [H^+] for the reaction of $(NH_3)_4(H_2O)RhOO^{2+}$ with TEMPO and with (HO)TEMPO.

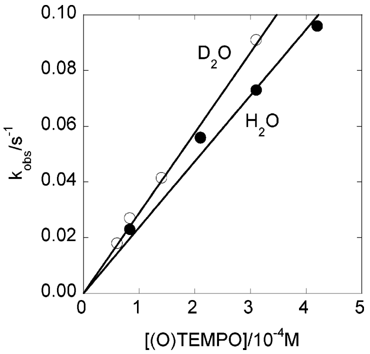


Figure 5. Plot of k_{obs} vs [(O)TEMPO] for the reaction with $(NH_3)_4(H(D))_2O)RhOO^{2+}$ in 0.10 M $H(D)ClO_4$ in H_2O and D_2O.

A brief kinetic study was carried out on the reaction between $Ru(NH_3)_6^{2+}$ and two superoxorhodium complexes under the conditions of excess $Ru(NH_3)_6^{2+}$ (0.2−0.4 mM). These data yielded the second-order rate constants $k = 5 \times 10^5$ M^{-1} s^{-1} for $(NH_3)_4(H_2O)RhOO^{2+}$ and ∼1×10^6 for L^2-$(H_2O)RhOO^{2+}$ at 0.10 M H^+.

Discussion

As expected on thermodynamic grounds, superoxo complexes of Cr(III) (E^0 for $Cr_{aq}OO^{2+},H^+/Cr_{aq}OOH^{2+} = 1.03$ V)[37] and Rh(III) oxidize nitroxyl radicals ($E_{1/2} = 0.73−0.91$ V), although the rate constants are many orders of magnitude lower than those obtained for the reactions of nitroxyls with small inorganic radicals, such as $HO^•$, $HO_2^•$, and $NO_2^•$. In the case of $HO^•$ and $HO_2^•$, the reactions are strongly exoergic and the rates are close to diffusion controlled. The reduction potential for $NO_2^•$ (1.04 V),[38] on the other hand, is comparable[37] to that of $Cr_{aq}OO^{2+}$, but the rate constants for $NO_2^•$ are almost 6 orders of magnitude greater than for the chromium complex. It is not clear whether the greater self-exchange rate constant for the $NO_2^•/NO_2^-$ couple (0.3 M^{-1}

---

(31) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper Collins: New York, 1987; Chapter 2.

(32) Samuni, A.; Goldstein, S.; Russo, A.; Mitchell, J. B.; Krishna, M. C.; Neta, P. *J. Am. Chem. Soc.* **2002**, *124*, 8719−8724.

(33) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem. B* **1997**, *101*, 930−936.

(34) Petrov, A. N.; Kozlov, Y. N. *Zh. Fiz. Khim.* **1986**, *60*, 327−331.

(35) Vorob'eva, T. P.; Durova, E. L.; Kozlov, Y.; Petrov, A. N.; Purmal, A. P. *Zh. Fiz. Khim.* **1986**, *60*, 598−602.

(36) Golubev, V. A.; Kozlov, Y. N.; Petrov, A. N.; Purmal, A. P. *Prog. React. Kinet.* **1991**, *16*, 35−54.

(37) Kang, C.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 2624−2630.

(38) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *33*, 69−138.

s^{-1})[39] can explain the difference because the corresponding parameter is not available for any of the superoxo complexes.

It has been suggested previously[30] that the $NO_2^{\bullet}$/nitroxyl interaction may initially generate an adduct which would allow the reaction to proceed faster than predicted by Marcus theory. Superoxometal complexes utilized here have also been shown to undergo radical coupling, which implies bond formation, with various small radicals.[26] Thus, one might expect that the $LMOO^{2+}$/nitroxyl reactions might also utilize a precursor in the form of an adduct, but the stability constant in this case should be small for steric reasons. At the same time, we note that the rate constants for the reactions of nitroxyls with superoxometal complexes and with $C(NO_2)_4$ are similar. The somewhat smaller values for $C(NO_2)_4$ are consistent with the lower reduction potential (0.93 V)[38] for this oxidant. Since adduct formation between a nitroxyl and a closed-shell species like $C(NO_2)_4$ is unlikely, one might argue against an adduct in the reactions of $L(H_2O)MOO^{2+}$ as well.

Thus, we decided to probe the role of steric effects to gain further insight into the mechanism. To that goal, we examined the reaction of TEMPO with two rhodium complexes, $(NH_3)_4(H_2O)RhOO^{2+}$ and $(L^2)(H_2O)RhOO^{2+}$ (L^2 = Me_6-[14]aneN_4). Even though precise potential data are not available for either complex, we expect the oxidizing power of the two to be similar, but the crowding at the axial sites is much more severe for the macrocyclic complex. Our hypothesis regarding the redox potentials was substantiated by finding that the oxidation of a typical outer-sphere reductant, $Ru(NH_3)_6^{2+}$, was comparable for the two superoxorhodium complexes, $5 \times 10^5\ M^{-1}\ s^{-1}$ ($L = (NH_3)_4$) and $\sim 1 \times 10^6$ ($L = L^2$) in 0.10 M H^+.

As shown in Table 1, the replacement of $(NH_3)_4$ by L^2 has a dramatic inhibiting effect on the reaction with TEMPO. There was no measurable reaction with the L^2 complex which allows us to place an upper limit of $<1\ M^{-1}\ s^{-1}$ at 0.020 M H^+, i.e., about a hundred times less than for $(NH_3)_4(H_2O)RhOO^{2+}$ under identical conditions. These data argue strongly against outer-sphere electron transfer and for adduct involvement in the $L(H_2O)RhOO^{2+}$/nitroxyl reactions and, by inference, also in the $Cr_{aq}OO^{2+}$ reactions. This finding is in full agreement with the known preference of nitroxyl radicals for the oxidation of primary alcohols over the secondary ones,[3] an ordering that clearly underscores the importance of steric effects.

Despite these arguments, the plot of (log *k*) vs the reduction potential for the reaction of nitroxyls with $Cr_{aq}OO^{2+}$ in Figure 6 shows a strong correlation between the kinetics and thermodynamics. To make the data strictly comparable, the point shown for the $Cr_{aq}OO^{2+}$/(O)TEMPO reaction represents the $[H^+]$ independent term, i.e., $k_0 = 20.6\ M^{-1}\ s^{-1}$. A similar trend exists also for the rhodium reactions, but the interpretation is more ambiguous because of the dominant H^+ term in the kinetics.

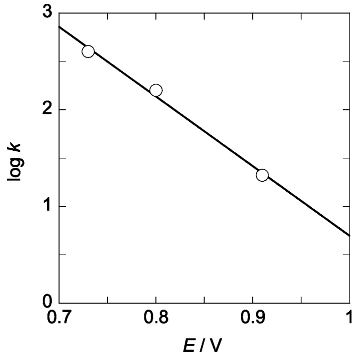


Figure 6. Plot of log *k* vs the reduction potential (vs NHE) of $(X)TEMPO^+/(X)TEMPO$ for the reaction with $Cr_{aq}OO^{2+}$.

The slope of the lines in Figure 6 is −7.4, which is close to the value (−8.4) expected from the Marcus cross-relation of eq 7 for outer-sphere electron transfer. In eq 7, k_{11} and k_{22} are the respective rate constants for the identity reactions for nitroxyls and $Cr_{aq}OO^{2+}$, k_{12} and K_{12} are the rate and equilibrium constants for the cross reaction of eq 1, and *f* is a function of K_{12}, k_{11}, k_{22}, and the collision frequency.[40] As in all correlations of this type, the calculated slope of −8.47 assumes that k_{11} is the same for all three nitroxyls, a reasonable expectation for a series of structurally and electronically closely related compounds.

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{0.5} \qquad (7)$$

If we are correct in concluding that these reactions do not take place by outer-sphere electron transfer but instead involve an intermediate, then the correlation in Figure 6 simply reflects the effect of the reduction potential on the kinetics in a series having constant steric requirements. This condition is fulfilled because the steric bulk around the N−O group of the nitroxide does not change with the change of substituents in the para position, and the counter-reagent, $Cr_{aq}OO^{2+}$, is constant throughout the series. The correlation in Figure 6 is yet another example of the applicability of Marcus cross-relation to reactions taking place by a mechanism other than electron transfer.[27,41−44]

The observed inverse solvent kie is small but consistent with the proposed prior protonation of the superoxometal complexes.[24,31] This path is much more important in the reactions of $(NH_3)_4(H_2O)RhOO^{2+}$ which appears to be a weaker oxidant than $Cr_{aq}OO^{2+}$ and thus more dependent on H^+ catalysis. Table 2 summarizes all the currently available data on the role of $[H^+]$ in the reactions of superoxo complexes of Cr(III) and Rh(III). For each of the two oxidants, reactions with a smaller driving force are more affected by H^+. The reactions of the rhodium and chromium complexes with $(NH_3)_5Rupy^{2+}$ may appear to be anomalous, but the acid concentration used in the $Cr_{aq}OO^{2+}$ study[24] was much higher (up to 1 M) to detect the H^+-catalyzed path,

---

(39) Stanbury, D. M. *Adv. Chem. Ser.* **1997**, *253*, 165−182.

(40) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441−498.

(41) Roth, J. P.; Yoder, J. C.; Won, T. J.; Mayer, J. M. *Science* **2001**, *294*, 2524−2526.

(42) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **2001**, *123*, 7492−7496.

(43) Murdoch, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 2159−2164.

(44) Dodd, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 5356−5357.

(45) Lemma, K.; Ellern, A.; Bakac, A. *Dalton Trans.* **2006**, 58−63.

which becomes negligible under the conditions used in this study (≤ 0.10 M H^+).

Another parameter that must play a role in determining the importance of acid catalysis is the effect of the metal and ligands on the basicity of coordinated superoxide and thus on the concentration of the protonated form. Unfortunately, we do not currently have the data, or means to obtain them, to address this point separately.

The individual steps in the $LMOO^{2+}/R_2NO$ reactions and the associated rate laws presented in eqs 8−13 are consistent with all the observations. Entities inside the square brackets represent intermediates formed by prior association of the reactants, probably by an interaction between the superoxo and N−O moieties. Equation 13 reduces to the observed form for $K_{a2} \gg [H^+]$.

$$LMOO^{2+} + R_2NO \overset{K}{\rightleftarrows} [LMOO^{2+},R_2NO] \xrightarrow{k} LMOO^{+} + R_2NO^{+} \quad (8)$$

$$LMOO^{+} + H^{+} \rightleftarrows LMOOH^{2+} \quad \text{fast} \quad (9)$$

$$k_{obs} = K_8 k_8 \quad (10)$$

$$LMOO^{2+} + H^{+} \rightleftarrows LMOOH^{3+} \quad 1/K_a \quad (11)$$

$$LMOOH^{3+} + R_2NO \overset{K}{\rightleftarrows} [LMOOH^{3+},R_2NO] \xrightarrow{k} LMOOH^{2+} + R_2NO^{+} \quad (12)$$

$$k_{obs} = \frac{k_{12}K_{12}[H^+]}{K_a + [H^+]} \quad (13)$$

Table 2. Acid Dependence in Oxidations with Superoxo Complexes of Chromium and Rhodium[a]

oxidant	reductant	$k/M^{-1}\ s^{-1}$	source
$Cr_{aq}OO^{2+}$	I^-	$93.7\ [H^+]$	ref 24
$Cr_{aq}OO^{2+}$	$(NH_3)_5Rupy^{2+}$	$7 \times 10^4 + 1.8 \times 10^5\ [H^+]$	ref 20
$L^1(H_2O)CrOO^{2+}$	I^-	$402\ [H^+]$	ref 20
$L^2(H_2O)CrOO^{2+}$	I^-	$729\ [H^+]$	ref 45
$L^2(H_2O)CrOO^{2+}$	$ABTS^{2-}$	$3.56 \times 10^6\ [H^+]$	ref 45
$(NH_3)_4(H_2O)RhOO^{2+}$	I^-	$888\ [H^+]$	ref 24
$L^2(H_2O)RhOO^{2+}$	$(NH_3)_5Rupy^{2+}$	5.0×10^5	ref 24
$(NH_3)_4(H_2O)RhOO^{2+}$	O-TEMPO	$4 + 2.21 \times 10^3\ [H^+]$	this work
$Cr_{aq}OO^{2+}$	O-TEMPO	$20.6 + 77.5\ [H^+]$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	TEMPO	$40 + 2.2 \times 10^3\ [H^+]$	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	HO-TEMPO	$25 + 1.1 \times 10^3\ [H^+]$	this work
$Cr_{aq}OO^{2+}$	TEMPO	406	this work
$Cr_{aq}OO^{2+}$	HO-TEMPO	159	this work
$(NH_3)_4(H_2O)RhOO^{2+}$	3-CP	$1.7 \times 10^3\ [H^+]$	this work

[a] $L^1 = 14[ane]N_4$; $L^2 = Me_6\text{-}[14]aneN_4$.

Conclusions

Superoxide coordinated to chromium(III) and rhodium(III) efficiently oxidizes nitroxyl radicals to the corresponding oxoammonium cations. These reactions are much slower than the oxidation by free $HO_2^{\bullet}$, consistent with both higher reduction potential and smaller steric requirements for $HO_2^{\bullet}$. Unlike free superoxide, the complexes $LMOO^{2+}$ are not subject to nitroxyl-catalyzed disproportionation. This chemistry is ruled out by the thermodynamics: the reduction potential of the nitroxyl radicals is too low to oxidize $LMOO^{2+}$ (which requires >1 V in the case of $Cr_{aq}OO^{2+}$).[37] At the same time, $LMOO^{2+}$ (unlike $HO_2^{\bullet}$) lacks an easily dissociable proton which would provide access to a more reducing form. Catalytic oxidation of alcohols with $Cr_{aq}OO^{2+}$ was not observed, most likely because the oxidation of hydroxylamine to nitroxyl by $Cr_{aq}OO^{2+}$ is slow.

Acknowledgment. This manuscript has been authored by Iowa State University under Contract No. DE-AC02-07CH11358 with the U.S. Department of Energy.

Supporting Information Available: UV−vis spectra of reactants and reaction mixtures, and kinetic traces, Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

IC062010S