that they were formed by secondary photolysis during the analysis phase of their experiments, which would have been more time consuming than ours.

For the isomers of $[Cr(tn)_2(NH_3)_2]^{3+}$, the chromatographic results gave 4+:3+ product ratios that were in good agreement with the directly measured ratios of tn to NH_3 photoaquation. This assumed that the molar absorptivities of these compounds are all very similar, an assumption that is justified mainly by this concordance, as these compounds now differ pairwise in the number, if not the type, of the ligating atoms. Nevertheless, the agreement gives us some confidence that the measured reaction mode ratios and also those given for the product isomers are not seriously in error.

The stereochemistry predicted for the photoaquations leads to a mixture of products as is shown in Figure 3b for the trans compound and Figure 3c for the cis compound, based on the same procedure as before. For the products arising from tn aquation, in this discussion cis is intended to indicate the relationship of the aquo and monodentate protonated tn ligands to one another; as explained earlier, isomers differing in the cis/trans relationship of the ammonia ligands would not be resolved.

For the trans isomer the prediction is for only cis products to be formed both from loss of ammonia (upper third of Figure 3b) and from the tn mode (lower two-thirds of Figure 3b). This is completely in agreement with experiment and demonstrates that both modes of photoaquation of this compound occur with almost complete stereochemical change in this complex.

For the cis isomer, Figure 3c, the situation is inherently more ambiguous. However the results are consistent with the predictions. For both loss of ammonia (upper third of figure) and of tn (lower two-thirds) the cis and trans products are predicted to be produced in roughly equal amounts; however, as mentioned above, where several different isomers are produced via different edge displacements, the ratio is not predictable with any reliability. Therefore the observed consistency with experiment is as much as can be expected. Again the results for both modes require the partial, if not complete, occurrence of stereochemical change.

The mono-tn compound provides no further insights than already discussed.

Conclusions. In summary it has been found that tn is a much poorer leaving ligand than ammonia, and this in large measure accounts for the lower quantum yield of photoaquation in $[Cr(tn)_3]^{3+}$ without the need to invoke concepts such as the steric blocking of water attack on edges trans to the leaving ligand. Although this blocking can be expected to occur, it seems likely that any free edge will lead to substitution, since potential water ligands are ubiquitous. This therefore does not seem to be as viable an explanation as simply to recognize the stability of the Cr(tn) ring and its consequent slow rate of reaction. This conclusion is strongly supported by our observation of very low tn yields from the mono-tn complex, where steric blocking of the trans edges is nonexistent.

Our results have also demonstrated that ligand loss from the plane of excitation is a competitive process between the ligands on that plane and therefore that a yield can be lower than expected if it is in competition with a more facile process. Also there is evidence that steric enhancement of loss of a ligand can take place, as evidenced by the enhanced ammonia yield found for the *trans*-bis-tn complex.

Finally the results have shown that stereochemical change occurs in some and possibly all of these complexes. It has also been confirmed that the monodentate protonated intermediates in these systems are among the most stable so far reported for Cr complexes, and they invite attempts to isolate them and directly determine their structure and properties.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council and the University of Victoria for financial support. A.M.I. is grateful for the award of a graduate bursary. We thank J. Lilie particularly for the measurements of the doublet lifetimes and the ratio of reaction via the doublet and W. Waltz for helpful advice during these measurements. We are grateful for helpful comments on the work by J. F. Endicott.

Registry No. *trans*-$[Cr(tn)_2(NH_3)_2](ClO_4)_3$, 117178-99-1; *trans*-$[Cr(tn)_2Cl_2]Cl$, 26186-25-4; *cis*-$[Cr(tn)_2(NH_3)_2](ClO_4)_3$, 76295-82-4; *cis*-$[Cr(tn)_2Cl_2]Cl$, 17632-36-9; $[Cr(tn)(NH_3)_4](ClO_4)_3$, 117097-19-5; *cis*-$[Cr(NH_3)_4Cl_2]Cl$, 19706-96-8; $[Cr(tn)_3]^{3+}$, 15276-12-7; *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$, 38985-25-0.

Contribution No. 7790 from the Arthur Amos Noyes Laboratories,
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Hydrogen Atom Abstraction from Amine Complexes of Iron(II), Cobalt(II), and Ruthenium(II) by Superoxide. Influence of Driving Force on Rate

Paul Bernhard and Fred C. Anson*

Received June 1, 1988

The unusual chemistry associated with superoxide's acting as an oxidant is examined with several amine complexes of iron(II) and ruthenium(II) as reductants. In each case the reaction is believed to proceed by means of hydrogen atom transfer from the nitrogen atom in the coordinated secondary amine to O_2^-. The metal center participates in the mechanism by stabilizing the ligand radical intermediate involved. The rate of the reaction exhibits a weak but definite dependence on driving force that is consistent with a proposed mechanism.

The superoxide anion radical, O_2^-, and the perhydroxyl radical, HO_2, are intermediates in autoxidation processes.[1,2] Their high kinetic reactivity can control both the stoichiometry and the mechanism of autoxidation processes, as was illustrated in a recent study of the autoxidation of the $Ru(sar)^{2+}$ complex (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane).[3] At pH values above 5, O_2^- generated in the first step of the reaction was found to act as a catalyst for the overall autoxidation process. A key step in the catalytic mechanism was the fast reaction between O_2^- and $Ru(sar)^{2+}$, in which O_2^- acted as an oxidant. Because O_2^- is generally a poor outer-sphere oxidant, our results were interpreted in terms of a hydrogen atom transfer from the ruthenium(II) amine complex to O_2^- with concomitant oxidation of the metal.

The data obtained in the earlier study were not sufficient to permit a rate constant for the unusual hydrogen atom transfer reaction from $Ru(sar)^{2+}$ to O_2^- to be evaluated. The present work was undertaken in an attempt to measure the rate of this reaction directly in stopped-flow experiments at high pH, to explore the generality of the reaction by examining some additional amine

---

(1) Taube, H. *Prog. Inorg. Chem.* **1986**, *34*, 607.
(2) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624.
(3) Bernhard, P.; Sargeson, A. M.; Anson, F. C. *Inorg. Chem.* **1988**, *27*, 2754.

Scheme I

$$\mathrm{Fe(tacn)_2}^{2+} + \mathrm{O_2} \rightleftharpoons \mathrm{Fe(tacn)_2}^{3+} + \mathrm{O_2}^- \qquad k_0, k_{-0} \qquad (1)$$

$$\mathrm{O_2}^- + \mathrm{H}^+ \rightleftharpoons \mathrm{HO_2} \qquad K_{\mathrm{HO_2}}^{-1} \qquad (2)$$

$$\mathrm{Fe(tacn)_2}^{2+} + \mathrm{HO_2} \rightarrow \mathrm{Fe(tacn)_2}^{3+} + \mathrm{HO_2}^- \qquad k_1 \qquad (3)$$

$$\mathrm{Fe(tacn)_2}^{2+} + \mathrm{O_2}^- \rightarrow \mathrm{Fe^{III}(tacn)(tacn(\text{-}H^+))}^{2+} + \mathrm{HO_2}^- \qquad k_2 \qquad (4)$$

$$\mathrm{Fe(tacn)_2}^{3+} \rightleftharpoons \mathrm{Fe^{III}(tacn)(tacn(\text{-}H^+))}^{2+} + \mathrm{H}^+ \qquad K_5 \qquad (5)$$

complexes of iron and ruthenium in aprotic solvents as well as water, and to determine the effect of the driving force on the rates of the reactions.

Experimental Section

Materials. $[\mathrm{Ru(sar)}](\mathrm{CF_3SO_3})_2$,[4] $[\mathrm{Ru(tacn)_2}](\mathrm{CF_3SO_3})_2$ (tacn = 1,4,7-triazacyclononane),[5] and $[\mathrm{Fe(tacn)_2}](\mathrm{CF_3SO_3})_2$[6] were synthesized as described in the cited references (except that precipitation was with $\mathrm{LiCF_3SO_3}$) and dried in vacuo for 3 h. $\mathrm{KO_2}$ (Apache Chemicals) (96.5%) and $\mathrm{NaClO_4}$ (G.F. Smith) were used as received. n-$\mathrm{Bu_4NCF_3SO_3}$ was prepared by neutralizing n-$\mathrm{Bu_4NOH}$ with 2 M $\mathrm{CF_3SO_3H}$ and was recrystallized twice from dichloromethane/ether (1:10) and dried in vacuo at 80 °C overnight. Acetonitrile was of the highest purity (Burdick and Jackson; $\mathrm{H_2O} < 0.004\%$). Deionized water was further purified by passage through a Barnstead Nanopure train. Buffers were prepared from N-morpholineethanesulfonic acid (MES) and N-(2-hydroxyethyl)piperazine-N'-ethanesulfonic acid (HEPES)/NaOH.

Kinetic Measurements. The rate of autoxidation of $\mathrm{Fe(tacn)_2}^{2+}$ was determined by injecting a known amount of a $\mathrm{Fe(tacn)_2}^{2+}$ stock solution into a solution of $\mathrm{O_2}$ and following the course of the reaction spectrophotometrically with an HP8450 spectrophotometer at 250 nm, where $\mathrm{Fe(tacn)_2}^{3+}$ and $\mathrm{Fe(tacn)_2}^{2+}$ have molar absorbances of ~5500 $\mathrm{M^{-1}\,cm^{-1}}$ and ~500 $\mathrm{M^{-1}\,cm^{-1}}$, respectively. Typical half-lives of the reaction were 100 s when the solution was saturated in $\mathrm{O_2}$ (1.1×10^{-3} M).[7] Measurements were performed in triplicate and averaged for each set of reaction conditions in the pH range 4–10. The reaction was followed for at least 5 half-lives, and the data were analyzed numerically by employing a Runge–Kutta–Verner algorithm of the IMSL library on a VAX 11/780 computer. Buffer concentrations were 2×10^{-3} M, the temperature was maintained at 25.0 ± 0.2 °C, and the ionic strength was adjusted to 0.1 M with $\mathrm{NaClO_4}$. The pH was measured with a glass electrode (Orion) calibrated at pH 4, 7, and 10.

The reactions of $\mathrm{O_2}^-$ with $\mathrm{Ru(sar)}^{2+}$ and $\mathrm{Ru(tacn)_2}^{2+}$ were followed in stopped-flow experiments as described by Bradic and Wilkins.[8] The measurements were performed on a Durrum 110 stopped-flow reactor, and the absorbance–time traces were stored on a Tektronix 5223 digital storage oscilloscope and plotted with a Houston X-Y recorder. In a typical experiment a known amount of finely powdered $\mathrm{KO_2}$ was dissolved in a vigorously stirred 0.01 M NaOH solution, which was then rapidly diluted with 0.01 M NaOH/0.001 M $\mathrm{Na_2edta}$ to give a concentration of $\mathrm{O_2}^-$ that was ca. 20% of the concentration of Ru(II) in the second syringe. The diluted solution was then transferred rapidly to one of the syringes of the stopped-flow apparatus, and the kinetic run was carried out immediately. (In preliminary experiments it was determined that ca. 30% of the original $\mathrm{O_2}^-$ survived during the 30 s required for the dilution procedure. This factor was employed in preparing the diluted solutions of $\mathrm{O_2}^-$.) First-order rate constants (k_{obs}) were obtained from fits of the absorbance–time curves to the equation $A(t) = A(\infty) - (A(\infty) - A(0)) - A(0))\exp(-k_{\mathrm{obs}}t)$. The reactions were followed at 430 nm ($\mathrm{Ru(sar)}^{2+}$) and 370 nm ($\mathrm{Ru(tacn)_2}^{2+}$), where the deprotonated Ru(IV) species absorb strongly.

Electrochemistry. Cyclic voltammograms were recorded at 22 °C by employing a BAS 100 electrochemical analyzer. The cell had the conventional three-electrode configuration with a polished (0.3 μm alumina) glassy-carbon disk (0.08 $\mathrm{cm^2}$) as a working electrode and a Pt wire as an auxiliary electrode. A silver wire was used as a quasi-reference electrode. The potentials were calibrated with ferrocene[9] and are quoted vs NHE.

Table I. Rate Constants for Autoxidation of $\mathrm{Fe(tacn)_2}^{2+}$ [a]

pH	$10^5[\mathrm{Fe(tacn)_2}^{2+}]_0$, M	k_0, $\mathrm{M^{-1}\,s^{-1}}$	k' [b]
4.0	2.3–4.6	8.8 ± 0.8	~0
5.50[c]	6.2–12.0	9.7 ± 1.0	0.02 ± 0.015
5.93[c]	5.2–9.8	8.2 ± 0.5	0.064 ± 0.013
6.04[c]	4.7–9.0	8.0 ± 0.6	0.095 ± 0.015
6.46[c]	6.2–12.0	6.9 ± 0.2	0.23 ± 0.04
6.66[c]	5.2–9.8	6.6 ± 0.3	0.31 ± 0.05
6.94[d]	6.2–12.0	6.4 ± 0.1	0.45 ± 0.02
7.47[d]	6.2–12.0	5.5 ± 0.2	0.43 ± 0.04
7.47[d,e]	6.2	4.7 ± 0.6	0.46 ± 0.08
8.14[d]	5.2–9.8	5.5 ± 0.3	0.48 ± 0.08
8.50[d]	4.7–9.0	5.8 ± 0.2	0.52 ± 0.05
10.0	3.5–9.7	5.9 ± 0.2	0.48 ± 0.02

[a] $T = 25$ °C; $\mu = 0.1$ M ($\mathrm{NaClO_4}$). [b] k' is defined in eq 7. [c] Buffer: MES/NaOH (0.002 M). [d] Buffer: HEPES/NaOH (0.002 M). [e] Excess $\mathrm{Fe(Tacn)_2}^{3+}$ (8.3×10^{-5} M).

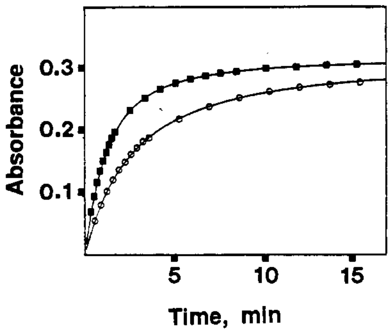

Figure 1. Change in absorbance at 250 nm during autoxidation of $\mathrm{Fe(tacn)_2}^{2+}$ at pH 7.47. The concentration of $\mathrm{O_2}$ was maintained at 1.1 mM. The initial concentration of $\mathrm{Fe(tacn)_2}^{2+}$ was 6.2×10^{-5} M and that of $\mathrm{Fe(tacn)_2}^{3+}$ was 0 (■) or 8.3×10^{-5} M (○). The curves were calculated by using the parameters in Table I.

Results

Autoxidation of $\mathrm{Fe(tacn)_2}^{2+}$. The kinetics of the reaction of $\mathrm{Fe(tacn)_2}^{2+}$ with $\mathrm{O_2}$ exhibited a clear first-order dependence on $[\mathrm{Fe(tacn)_2}^{2+}]$ at pH values below 6, but deviations from first-order behavior appeared at higher pH values, where inhibition by $\mathrm{Fe(tacn)_2}^{3+}$ also became apparent. This behavior is compatible with the mechanism proposed by Stanbury et al.[10] for the autoxidations of a series of ruthenium amine complexes as modified by inclusion of the reaction of unprotonated $\mathrm{O_2}^-$ as an oxidant. The appropriate set of reactions is given in Scheme I, where tacn(-H$^+$) represents the deprotonated tacn ligand.

The application of the steady-state condition for $[\mathrm{HO_2}] + [\mathrm{O_2}^-]$ to Scheme I leads to eq 6 and 7. At sufficiently high concentrations of H^+, eq 6 reduces to a simple pseudo-first-order rate equation that agrees with the pseudo-first-order behavior observed at pH <6. At higher pH values where more complex kinetics were observed, eq 6 was integrated numerically and values of k_0 and k' were estimated by least-squares fitting of the kinetic data. The resulting values (Table I) yielded very good agreement between

$$-\frac{\mathrm{d}[\mathrm{Fe(tacn)_2}^{2+}]}{\mathrm{d}t} = \frac{2k_0[\mathrm{Fe(tacn)_2}^{2+}][\mathrm{O_2}]}{1 + k'\dfrac{[\mathrm{Fe(tacn)_2}^{3+}]}{[\mathrm{Fe(tacn)_2}^{2+}]}} \qquad (6)$$

$$k' = \frac{k_{-0}}{k_1K_{\mathrm{HO_2}}^{-1}[\mathrm{H}^+] + k_2} \qquad (7)$$

---

[4] Bernhard, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1516.

[5] Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122; **1988**, *27*, 2582.

[6] Pohl, K.; Wieghardt, K.; Kaim, W.; Steenken, S. *Inorg. Chem.* **1988**, *27*, 440.

[7] Seidell, A.; Linke, W. F. *Solubilities of Inorganic Compounds*, 4th ed.; Van Nostrand: Princeton, NJ, 1964; p 1228.

[8] Bradic, Z.; Wilkins, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 2236.

[9] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 701.

[10] Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518.

Table II. Rate Constants for the Reaction of Superoxide with $Ru(sar)^{2+}$ and $Ru(tacn)_2^{2+}$ at pH 11.7[a]

$10^5[Ru(II)]_0$, M	k_{obs}, s^{-1}	10^5k_8,[b] M^{-1} s^{-1}
	A. $Ru(sar)^{2+}$	
0.67	24 ± 15	18 ± 10
1.4	26 ± 10	10 ± 4
1.5	23 ± 10	8 ± 4
4.2	~70	~8
5.9	~120	~10
		12 ± 6 (av)
	B. $Ru(tacn)_2^{2+}$	
4.24	17 ± 4	2.0 ± 0.5
13.6	48 ± 8	1.8 ± 0.3
28.2	89 ± 10	1.6 ± 0.2
28.2[c]	95 ± 10	1.7 ± 0.2
		1.8 ± 0.2 (av)

[a] $T \approx 23$ °C; $[Na_2edta] = 0.001$ M; $\mu = 0.01$ M. [b] $k_8 = k_{obs}/(2\cdot[Ru(II)])$. [c] pH 11.0.

calculated kinetic curves and the experimental data, as illustrated in Figure 1.

The values of k_0 obtained were reasonably independent of pH between pH 7.5 and 10 but increased somewhat at lower pH values (Table I). The reason for this trend is not clear, but changes in the buffers employed may be responsible. By the combination of an average value for k_0 of 6.0 ± 1.2 M^{-1} s^{-1} and the equilibrium constant for reaction 1 of $K_0 = 3.9 \times 10^{-5}$, obtained from the formal potentials of the $Fe(tacn)_2^{3+/2+}$ and O_2/O_2^- couples (0.10[6] and −0.16 V (standard state of 1 M O_2[11]), respectively), a value of $(1.5 \pm 0.3) \times 10^5$ M^{-1} s^{-1} can be calculated for k_{-0}.

The pH-dependent values of k' listed in Table I were used in a least-squares fit to eq 7 to obtain the ratios

$$k_{-0}/k_2 = 0.50 \pm 0.03 \qquad k_1/k_2 = 67 \pm 12$$

From these ratios, values of k_1 and k_2 could be calculated:

$$k_1 = (2.4 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$$

$$k_2 = (3.5 \pm 0.8) \times 10^5\ M^{-1}\ s^{-1}$$

The greater reactivity of HO_2 than of O_2^- toward $Fe(tacn)_2^{2+}$ parallels the relative driving forces for the two reactions (note that $E^f_{HO_2/HO_2^-} = 0.72$ V[11]) and matches the order observed recently for reactions with $Ru(sar)^{2+}$.[3]

Reaction of O_2^- with $Ru(sar)^{2+}$ and $Ru(tacn)_2^{2+}$ in Aqueous Solution. Stopped-flow experiments with $Ru(sar)^{2+}$ were more difficult than with $Ru(tacn)_2^{2+}$ because of the great sensitivity of the former to traces of O_2. This factor and the continuous dismutation of O_2^- in aqueous media produced lower precision in the kinetic data obtained. However, it was possible to obtain useful estimates for the two rate constants. Both ruthenium complexes were assumed to follow the mechanism described for the $Ru(sar)^{2+}$ complex in a previous study[3]

$$Ru(sar)^{2+} + O_2^- \rightarrow Ru^{III}(sar(\text{-}H^+))^{2+} + HO_2^- \quad k_8 \tag{8}$$

$$Ru^{III}(sar(\text{-}H^+))^{2+} + O_2^- \rightarrow Ru^{IV}(sar(\text{-}2H^+))^{2+} + HO_2^- \quad k_9 \tag{9}$$

with $k_9/k_8 = 40$–80.[3] Applying the steady-state approximation to $[Ru^{III}(sar(\text{-}H^+))^{2+}]$ leads to eq 10. Values of k_8 were obtained

$$\frac{d[Ru^{IV}(sar(\text{-}2H^+))^{2+}]}{dt} = 2k_8[Ru(sar)^{2+}][O_2^-] \tag{10}$$

from appropriate pseudo-first-order plots for both complexes and are listed in Table II. For $Ru(tacn)_2^{2+}$ the values of k_8 were essentially the same at pH 11.7 and 11.0, illustrating the pH independence of the reaction.

Reaction of O_2^- with $Ru(sar)^{2+}$, $Ru(tacn)_2^{2+}$, and $Fe(tacn)_2^{2+}$ in Acetonitrile. In acetonitrile there is no apparent reaction between the title complexes and O_2, and the reaction rate is also reduced considerably in dimethyl sulfoxide. This diminished reactivity permitted cyclic voltammetry to be conducted with solutions containing both O_2 and the complex so that the effects of possible reactions between electrogenerated O_2^- and the complexes could be observed. In air-saturated ($[O_2] = 1.7 \times 10^{-3}$ M[12]), anhydrous acetonitrile the O_2/O_2^- couple exhibits a reversible wave at −0.76 V vs NHE (Figure 2D). In the absence of O_2 the complexes $Ru(tacn)_2^{2+}$, $Ru(sar)^{2+}$, and $Fe(tacn)_2^{2+}$ are reversibly oxidized and reduced at +0.42, +0.36, and +0.25 V vs NHE, respectively (Figure 2A–C). The voltammetric responses for solutions containing both O_2 and the metal complexes are shown in Figure 2E–F. The reduction of O_2 becomes irreversible, and the waves for the amine complexes, unaffected by O_2 in the first scan toward more positive potentials (solid line in Figure 2E–G), are much depressed in the second scan (dashed line in Figure 2E–G), implying that O_2^- reacts with the M(II) complexes. Analogous behavior was observed in dimethyl sulfoxide, and it seems very likely that the electrogenerated O_2^- is consumed by reaction 8 for the $Ru(sar)^{2+}$ complex and by corresponding reactions for the other complexes. The equilibrium constants for reaction 8, and the corresponding reactions for the other two complexes, are much larger than unity in aqueous media (see Discussion). The same is expected to be true in nonaqueous solvents. Furthermore, the deprotonated Ru(III) complexes, which are more easily oxidized than the original Ru(II) complexes, will react rapidly with a second O_2^- radical to produce O_2H^- and doubly deprotonated Ru(IV) complexes. These doubly deprotonated Ru(IV) complexes are apparently not reducible under the conditions employed to record Figure 2 because the cathodic peak currents at potentials in the vicinity of the O_2/O_2^- wave are decreased, not enhanced, by addition of the metal complexes. The difficulty in reducing the Ru(IV) complexes may be associated with the lack of a suitable source of protons. The reason for the

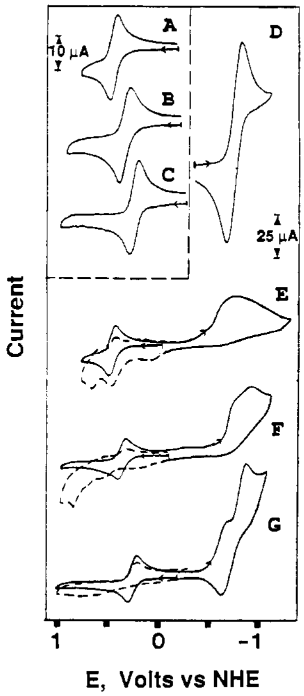

Figure 2. Effect of O_2 and O_2^- on the cyclic voltammetry of metal amine complexes in acetonitrile. Solution composition: (A) 1.0 mM $Ru(tacn)_2^{2+}$ (current scale is 11.8 instead of 10 μA); (B) 0.85 mM $Ru(sar)^{2+}$; (C) 1.0 mM $Fe(tacn)_2^{2+}$; (D) air-saturated solution, $[O_2] = 1.7$ mM; (E) solutions A + D; (F) solutions B + D; (G) solutions C + D. The supporting electrolyte was 0.1 M $n\text{-}Bu_4NCF_3SO_3$. A glassy-carbon electrode (0.08 cm^2) was used. Scan rate = 0.1 V s^{-1}.

---

(11) Ylan, Y. A.; Czapski, G.; Meisel, D. *Biochim. Biophys. Acta* **1976**, *430*, 209. Sawada, Y.; Iyanugi, T.; Yamazaki, I. *Biochemistry* **1975**, *14*, 376.

(12) Sawyer, D. T.; Chiericato, G.; Angelis, C. T.; Nanni, E. J.; Tsuchiya, T. *Anal. Chem.* **1982**, *54*, 1720.

(13) *Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1975–76; p F-224 ff.

Table III. Rate Constants and Driving Forces for Hydrogen Atom Transfer Reactions between Superoxide and Amine Complexes of Fe(II), Co(II), Ru(II), and Ru(III)

metal complex	E^f vs NHE, V	pK_a[a]	E^f_{11},[b] V	k_{11}, $M^{-1}\ s^{-1}$
$Co(sep)^{3+/2+}$	−0.26[c]	12–13[d]	0.5–0.55	$(4.7 \pm 1.0) \times 10^7$[c]
$Fe(tacn)_2^{3+/2+}$	+0.10[e]	11.4[e]	0.23	$(3.5 \pm 0.5) \times 10^5$[f]
$Ru(sar)^{3+/2+}$	+0.29[h]	6.3[i]	0.34	$(1.2 \pm 0.6) \times 10^6$[f]
$Ru(tacn)_2^{3+/2+}$	+0.37[g]	9–11[g]	0–0.1	$(1.8 \pm 0.2) \times 10^5$[f]
$Ru(sar(\text{-}H^+))^{3+/2+}$	+0.05[i]	4–6[j]	0.6–0.7	$\approx(4–8) \times 10^7$[k]

[a] Acid dissociation constant for the secondary amine coordinated to the tripositive metal complex. [b] Driving force for reaction 11 calculated from eq 5. The ranges listed reflect the uncertainties in pK_a values. [c] Reference 2. [d] Sargeson, A. Personal communication. [e] Reference 6. [f] This work. [g] Reference 5. [h] Reference 4. [i] Reference 3. [j] Reference 18. [k] Derived by using the rate constant for $Ru(sar)^{2+}$ and the experimental ratio k_5/k_2 in ref 3.

decreased peak currents is not clear, but the filming of the electrode that was observed during repetitive cycling between 1.0 and −1.0 V in solutions containing $Fe(tacn)_2^{2+}$ and O_2 and the appearance of prewaves near the O_2 reduction potential in the presence of the complexes indicate that the overall electrode processes in solutions of O_2 and the complexes probably involve reactions in addition to those depicted in (8) and (9).

Discussion

The rate constants in Tables I and II together with the value reported for the reaction between O_2^- and $Co(sep)^{2+}$[2] represent the only presently available data on reactions in which O_2^- engages in hydrogen atom transfer reactions with transition-metal complexes. The general reaction under consideration can be written as

$$(M^{II}\text{–}NH)^{2+} + O_2^- \rightarrow (M^{III}\text{–}N^-)^{2+} + HO_2^- \quad k_{11} \qquad (11)$$

The free energy change for the reactions can be calculated from the difference in the formal potentials for the corresponding half-reactions:

$$O_2^- + H^+ + e^- \rightleftharpoons HO_2^- \quad E^f_{O_2^-/HO_2^-} \qquad (12)$$

$$(M^{III}\text{–}N^-)^{2+} + H^+ + e^- \rightleftharpoons (M^{II}\text{–}NH)^{2+} \quad E^f_{M^{III}\text{–}N^-/M^{II}\text{–}NH} \qquad (13)$$

At pH 0, E^f for the O_2^-/HO_2^- couple is 1.0 V.[11] The formal potential for half-reaction 13 at pH 0 is given by eq 14, where

$$E^f_{14} = E^f_{M(III)/M(II)} + 0.059pK_a^{M(III)} \qquad (14)$$

$E^f_{M(III)/M(II)}$ is the formal potential of the M(III)/M(II) complex at pH values where the ligand is fully protonated in both oxidation states and $K_a^{M(III)}$ is the acid dissociation constant for the ligand coordinated to the metal in oxidation state III. Thus the (pH-independent) formal potential for reaction 11 is

$$E^f_{11} = 1.0 - E^f_{M(III)/M(II)} - 0.059pK_a^{M(III)} \qquad (15)$$

pK_a values for the complexes of interest that have been measured or estimated are listed in Table III together with the calculated values of E^f_{11} and the experimental rate constants, k_{11}. A plot of log k_{11} versus E^f_{11} (Figure 3) exhibits a clear tendency for k_{11} to increase with the driving force of the reaction. The slope of the plot corresponds to a Brønsted coefficient of ≃0.28 ± 0.06, which indicates that the reaction is less sensitive to changes in driving force than is, for instance, the outer-sphere reduction of O_2 (to O_2^-) by a series of ruthenium(II) amine complexes.[10] This result is in qualitative agreement with our interpretation of reaction 11 as a hydrogen atom transfer. However, the meagerness of the presently available data leaves unsettled the issue of the nature of the transition state involved.

These results show that the metal center plays a crucial role in inducing the atom-transfer process because abstraction of a hydrogen atom by O_2^- from a simple aliphatic amine has no precedent to the best of our knowledge. The strength of N–H bonds in aliphatic amines is considerably larger than that reported for the H–O bond in HO_2^- ($H\text{–}N(CH_3)_2$ 400 kJ mol^{-1};[13] $H\text{–}O_2^-$ 265 kJ mol^{-1} [14]) so that direct hydrogen atom transfer is not favored. Results by Hussey et al.[15] and Nanni et al.[16] imply that such a pathway exists in the case of aromatic amines, for which the bond strengths are generally smaller ($H\text{–}N(CH_3)(C_6H_5)$ 310 kJ mol^{-1} [13]) because of delocalization of the radical character into the π system. Aliphatic amines that are coordinated to oxidizable metals may resemble such aromatic systems because of the ability of the metal center to accept the unpaired electron resulting from loss of a hydrogen atom. This ability is apparently influential in stabilizing the transition state for the reaction.

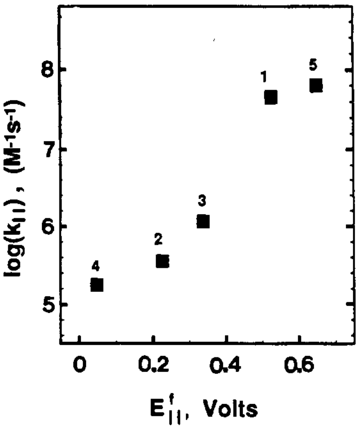

Figure 3. Rate versus driving force for hydrogen atom transfer to O_2^- by the metal(II) amine complexes of Table II: (1) $Co(sep)^{2+}$; (2) $Fe(tacn)_2^{2+}$; (3) $Ru(sar)^{2+}$; (4) $Ru(tacn)_2^{2+}$; (5) $Ru^{III}(sar(\text{-}H^+))^{2+}$.

One consequence of this interpretation is that hydrogen atom transfer reactions should proceed slowly, if at all, in cases where the amine is coordinated to metal centers that are not oxidizable at moderate potentials. An example is $Co(sepulchrate)^{3+}$, which is unreactive toward O_2^-.[2] Similarly, addition of the difficultly oxidized $Ni(tacn)_2^{2+}$ complex had no effect on the cyclic voltammetry of the O_2/O_2^- couple in nonaqueous solvents. The $Ni^{III/II}$ potential (measured as 0.95 V vs NHE[17]) is apparently too high to produce a sufficient stabilization of the transition state to facilitate the hydrogen atom transfer reaction to O_2^-.

Conclusions

Rate constants for the fast (10^5–10^8 $M^{-1}\ s^{-1}$) oxidation of coordinatively saturated amine complexes of Fe(II) and Ru(II) by O_2^- have been measured. These oxidations and that of the $Co(sepulchrate)^{2+}$ complex[2] proceed by hydrogen atom transfer, and the reaction rate exhibits a distinct dependence upon the driving force. The important role played by the metal centers in these oxidations appears to be based on their ease of oxidation and corresponding ability to stabilize the (formal) ligand radical in the transition state. It seems likely that the reaction pathway identified may be accessible to additional complexes of transition-metal ions that may be oxidized at moderate potentials. This oxidative chemistry of O_2^- seems worth pursuing with other metals and ligands in view of its possible relevance to the reactivity of O_2^- in biological contexts.

Acknowledgment. This work was supported by the National Science Foundation. Prof. J.-M. Savéant was a source of helpful commentary.

---

(14) *The Chemistry of Peroxides*; Palai, S., Ed.; Wiley: New York, 1983; p 432.
(15) Hussey, C. C.; Laker, T. M.; Achord, J. M. *J. Electrochem. Soc.* **1980**, *127*, 1865.
(16) Nanni, E. J.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 7591.
(17) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Kuppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953.
(18) Bernhard, P. Unpublished experiments.