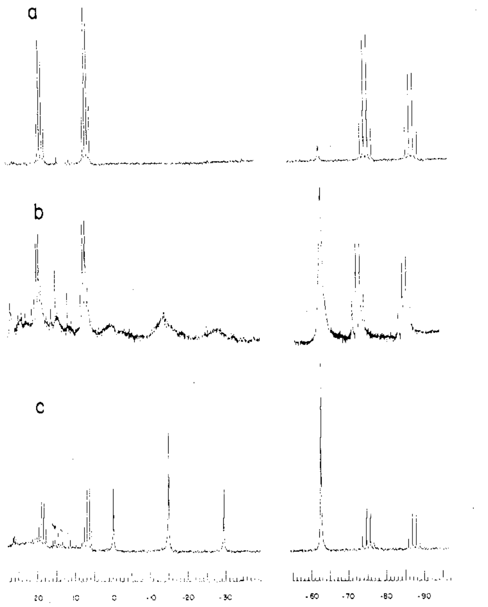

Figure 4. ^{31}P NMR spectra of Me_3PPCF_3 (**1**) in Me_3P/CH_3CN after heating for various times and temperatures: (a) no heating, 30 °C; (b) 1 h, 90 °C; (c) next day, 30 °C.

NMR concentration dependence studies. The experimental concentration dependence studies (Table II) eliminate mechanisms 2 and 3 because, as illustrated in Figure 3, $1/\tau_{PP}$ is dependent upon [P]. The concentration dependence data clearly favor mechanism 1. However, it is important to note that the range of temperatures and concentrations which we could study was severely limited by the thermal instability of **1**. The kinetics are, in fact, complicated by existence of at least one side reaction. Thus, when solutions of **1** containing an excess Me_3P are heated to temperatures in excess of 80 °C the $^{31}P\{^1H\}$ resonance of **1** diminishes in intensity, while that of Me_3P increases and a new set of peaks, a triplet, appears centered at 14.5 ppm (Figure 4). This triplet resonance, $J_{PF} = 533$ Hz, corresponds to that of Me_3PF_2.[24] Inferentially, the Me_3PF_2 is produced by fluorination of Me_3P by the CF_3 groups. Obviously, this fluorination could proceed inter- or intramolecularly. If it were an intramolecular process, the β transfer of two fluorine ligands from carbon to phosphorus would result in equimolar quantities of Me_3PF_2 and $F{-}C{\equiv}P$.[25] However, examination of the integrated areas of the Me_3P and Me_3PF_2 ^{31}P resonances suggests that the thermal decomposition of **1** in CD_3CN solution is more complicated since the overall conversion of **1** to Me_3P and Me_3PF_2 favors the former when a high concentration of Me_3P is already present in solution and the latter when very slight excess Me_3P is present initially.

Finally, equilibria of the general type

$$n\mathrm{Me_3PPCF_3} \rightleftarrows n\mathrm{Me_3P} + (1/n)(\mathrm{CF_3P})_n \quad (n = 4, 5)$$

were considered. However, neither $(CF_3P)_4$ nor $(CF_3P)_5$ was detectable in $^{31}P\{^1H\}$ NMR experiments at 80 °C or below.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE76-10331) and the Robert A. Welch Foundation for generous financial support.

Registry No. 1, 33576-11-3; $(CF_3P)_4$, 393-02-2; $(CF_3P)_5$, 745-23-3; PMe_3, 594-09-2.

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Reduction of Oxygen by Ruthenium(II) Ammines

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The reduction of O_2 to H_2O_2 by a series of ruthenium(II) ammines has been studied in aqueous acidic solution at 25.0 °C and 0.1 M ionic strength in noncomplexing media. The rate law is $-d[Ru(II)]/dt = 2k_1[Ru(II)][O_2]$, with $k_1 = 1.08 \times 10^{-1}$, 1.38×10^{-1}, 3.03×10^{-2}, and 7.73×10^{-3} M^{-1} s^{-1} for $[Ru(NH_3)_5isn]^{2+}$ (isn = isonicotinamide), *cis*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$, and $[Ru(NH_3)_4phen]^{2+}$, respectively. The reaction of $[Ru(NH_3)_5isn]^{2+}$ is inhibited by $[Ru(NH_3)_5isn]^{3+}$, and the inhibition increases with decreasing acidity. These results are accommodated by a mechanism involving outer-sphere formation of O_2^-; the Ru(III)/pH effect arises from a competition between the reaction of O_2^- with Ru(III) and the protonation of O_2^- followed by its reaction with Ru(II). The rate constants are correlated by a linear free-energy relation, (LFER), and they are consistent with the Marcus cross relation. Its application yields a self-exchange rate for the O_2/O_2^- couple of about 1×10^3 M^{-1} s^{-1}. In the presence of Cl^-, the reaction of *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ has two additional terms in the rate law: $-d \ln [Ru(II)]/dt = 2(k_1 + k_5K_{Cl}[Cl^-] + k_6K_{Cl}[Cl^-][H^+])[O_2]$, with $k_5 = 7.84 \times 10^{-1}$ M^{-1} s^{-1}, $k_6 = 1.40 \times 10^2$ M^{-2} s^{-1}, and $K_{Cl} = 0.39$ M^{-1}. The k_5 path fits the LFER when it is treated as the autoxidation of *trans*-$[Ru(NH_3)_4isnCl]^+$, and the k_6 path probably involves direct formation of HO_2 by the reaction of O_2 with $[Ru(NH_3)_4(isn)Cl]^+$.

Introduction

Autoxidation reactions, particularly with metal ions as reducing agents, are currently of much interest.[1] Mechanistic studies of autoxidation of metal ions have emphasized Cu(I) complexes[2] but have also included aquo ions such as V(II),[3] Cr(II),[4] Fe(II),[5] and U(IV)[6] and miscellaneous other complexes such as $Fe(CN)_6^{4-}$ [7] and $Ru(NH_3)_6^{2+}$.[8] Although these investigations have been instructive, little systematic understanding has yet developed, a result due, perhaps, to the variety

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of metal centers considered. Even for Cu(I), for which at least 10 ligand systems have been measured, basic questions such as whether the reactions are inner or outer sphere and whether one- or two-electron transfers occur remain unresolved mainly because of the labile character of the Cu(I) complexes.

In this paper the autoxidation of a series of ruthenium(II) ammines is reported. These complexes are well suited for systematic study because they are well characterized and substitution inert in both oxidation states and span a broad range of reduction potentials. The results herein are significant because (1) they allow a clear generalization of the outer-sphere mechanism, (2) they support an alternate interpretation of prior studies[8] on $Ru(NH_3)_6^{2+}$ and $Ru(en)_3^{2+}$, and (3) they implicate superoxide as a reactive intermediate—a species currently of great biochemical interest.[9]

Experimental Section

Materials. Water was deionized and then distilled from alkaline permanganate. Trifluoromethanesulfonic acid (HTFMS) (3M) was purified by distillation under an inert atmosphere at reduced pressure. NaTFMS was prepared by neutralization of HTFMS with Na_2CO_3; the precipitate was then twice recrystallized from hot water. Lithium trifluoroacetate (LiTFA) was similarly prepared from HTFA (Baker) and Li_2CO_3. Oxygen was scrubbed in a H_2O bubbling tower, and argon used for deaerating was scrubbed in a Cr^{2+} tower followed by a H_2O tower.

The compound $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$ (Matthey Bishop) by a modification of Vogt's procedure.[10] Seven grams of $Ru(NH_3)_6Cl_3$ was dissolved in 75 mL of H_2O, 75 mL of concentrated HCl was added, and the mixture was refluxed for 4 h. After the solution was chilled, the precipitate was filtered and washed with 6 M HCl. The product was then recrystallized from 1 L of 0.1 M HCl at 40 °C.

$[Ru(NH_3)_5H_2O](TFMS)_3$ was prepared by the method of Diamond and Taube.[11] Four grams of $[Ru(NH_3)_5Cl]Cl_2$ was finely ground, added to 200 mL of deaerated H_2O, and stirred for 20 min; 25 mL of deaerated concentrated NH_3 was then added, and the mixture was stirred until dissolution was complete. A deaerated solution of 8.5 g of $Na_2S_2O_6\cdot 2H_2O$ in 40 mL of H_2O was added to the reaction mixture which was allowed to react for 2 h. After the mixture was chilled, the unstable pale yellow solid ($[Ru(NH_3)_5OH]S_2O_6$) which formed was dissolved in a minimum of warm 3 M HTFMS and filtered. An equal volume of 8 M HTFMS was added. On refrigeration, the off-white compound $[Ru(NH_3)_5H_2O](TFMS)_3$ was precipitated.

cis-$[Ru(NH_3)_4Cl_2]Cl$ was prepared from $[Ru(NH_3)_4C_2O_4]_2S_2O_6$ by using the method of Gleu et al.,[12] as outlined in Krentzien's thesis.[10b] The $[Ru(NH_3)_5OH]S_2O_6$, prepared as described above for $[Ru(NH_3)_5H_2O](TFMS)_3$, was isolated and immediately added to a solution of 15 g of oxalic acid in 150 mL of H_2O. After dissolution and filtration, the mixture was heated for 15 min on a steam bath and then allowed to cool to room temperature overnight. The product, $[Ru(NH_3)_4C_2O_4]_2S_2O_6$, was collected and washed with ethanol. This salt was then dissolved in 150 mL of concentrated HCl, the mixture was heated on a steam bath for 15 min and filtered, and the filtrate was added to 150 mL of ethanol. After the solution was cooled to room temperature, the flocculent yellow precipitate was collected and washed with ethanol and ether. This produced 1.5 g of *cis*-$[Ru(NH_3)_4Cl_2]Cl$.

$[Ru(NH_3)_4phen](TFMS)_2\cdot H_2O$ was prepared by a modification of Brown and Sutin's method.[13] One-tenth gram of $[Ru(NH_3)_5H_2O](TFMS)_3$ was added to 5 mL of deaerated methanol in the presence of Zn/Hg and 0.305 g of *o*-phenanthroline monohydrate (phen). The mixture was stirred for 1.5 h in the dark, whereupon 5 mL of H_2O was added, and the mixture was extracted with 150 mL of toluene. The aqueous layer was then rotoevaporated to dryness and the solid was dissolved in 5 mL of methanol. Addition of ether precipitated the crude product as a dark red powder. This powder was recrystallized by dissolving in a minimum volume of H_2O (~6 mL), filtering, and then adding 6 mL of 9 M HTFMS. Refrigeration yielded a mass of glossy black needles, which was washed with ethanol and dried in a vacuum desiccator. Anal. Calcd for $[Ru(NH_3)_4phen](TFMS)_2\cdot H_2O$: C, 25.27; H, 3.33; N, 12.63. Found: C, 25.18; H, 3.05; N, 12.45. Brown and Sutin report the trihydrate, but their crystallization was from a very different medium.

cis-$[Ru(NH_3)_4(isn)Cl]Cl_2$[14] was prepared by the method of Marchant et al. with the modification of using 0.044 g instead of 0.024 g of isonicotinamide (isn).[15]

cis-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ was prepared in situ by reducing *cis*-$[Ru(NH_3)_4(isn)Cl]^{2+}$ with Eu^{2+}.

trans-$[Ru(NH_3)_4isn(H_2O)](PF_6)_2$ was prepared from *trans*-$[Ru(NH_3)_4isn(SO_4)]Cl$ by the method of Stein.[16] *trans*-$[Ru(NH_3)_4isn(SO_4)]Cl$ was prepared by Isied and Taube's method;[17] 0.6 g was reduced with Zn/Hg in 60 mL of 0.1 M HTFMS under argon for 0.5 h. The product, *trans*-$[Ru(NH_3)_4isn(H_2O)](TFMS)_2$, was twice recrystallized by using standard Schlenk techniques from 0.1 M HTFA by adding NH_4PF_6 (300 mg/mL). The resulting solid, *trans*-$[Ru(NH_3)_4isn(H_2O)](PF_6)_2$, was then washed with ethanol and ether. Anal. Calcd: C, 12.02; N, 14.02; H, 3.33. Found: C, 11.96; N, 14.39; H, 3.28.

The compound $[Ru(NH_3)_5isn](ClO_4)_2$ was prepared by a modification of Gaunder's method.[18] One-tenth gram of finely ground $[Ru(NH_3)_5Cl]Cl_2$ was reduced with Zn/Hg under argon in 4 mL of H_2O in a Zwickel flask.[19] The solution was then transferred by argon pressure into a flask containing 0.20 g of argon-flushed dry isonicotinamide. After the mixture was kept 45 min in the dark, 4 mL of deaerated saturated solution of $NaClO_4$ was added. Refrigeration for 3 h yielded dark red crystals; these were recrystallized from $NaClO_4$, washed with ethanol and ether, and air-dried; yield 0.0886 g. Anal. Calcd: C, 14.21; H, 4.17; N, 19.33. Found: C, 13.82; H, 3.86; N, 18.29. *Warning*: *Explosive*!

$[Ru(NH_3)_5isn](TFMS)_3$ was prepared by metathesis of the chloride salt. Three-tenths gram of $[Ru(NH_3)_5Cl]Cl]Cl_2$ was finely ground and reduced with Zn/Hg in 4 mL of H_2O under argon in a Zwickel flask. The solution was then transferred to a flask containing 0.3 g of argon-flushed dry isonicotinamide and allowed to react for 0.5 h in the dark. The solution was then made slightly acidic with HTFMS; 0.080 g of $Na_2S_2O_8$ was added, effecting a change from dark red to a light yellow color. Five milliliters of 6 M HCl was added, and precipitation was induced with ethanol. After the mixture was refrigerated for 3 h, the flocculent pale yellow precipitate was collected, washed with ethanol and ether, and air-dried. The solid was then ground in a mortar while 9 M HTFMS was added dropwise until the liberation of HCl ceased. The resulting yellow solid was washed with ether and air-dried. It was recrystallized by dissolution in a minimum volume of 0.01 M HTFMS, filtration, and precipitation with an equal volume of 9 M HTFMS. The light-sensitive, shiny yellow needles were washed with ether and dried in a vacuum desiccator; yield 0.162 g. Anal. Calcd: C, 14.31; H, 2.80; N, 12.98. Found: C, 14.22; H, 2.83; N, 12.70. The UV/vis spectrum was quite similar to that reported for $[Ru(NH_3)_5isn](ClO_4)_3$,[18] except that we found a shoulder at 335 nm rather than at 355 nm.

Methods. Cyclic voltammograms were recorded at room temperature on a PAR electrochemical apparatus, using a carbon paste indicator electrode, a SCE reference electrode, and a Pt wire working electrode. Spectra and kinetics were recorded on Cary 14, Cary 15, and Beckman UV 5270 spectrometers. The spectrometers were equipped with thermostated water baths to maintain the temperature at 25.0 ± 0.2 °C. Measurements of pH were performed on a Brinkmann pH 101 instrument.

The electrochemical determination of the formation constant for *trans*-$[Ru(NH_3)_4isnCl]^+$ was performed with a rotating-disk electrode (1600 rpm) and a Metrohm Polarecord E506. The ratio of *trans*-$[Ru(NH_3)_4isnCl]^+$/*trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ was measured as

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(14) Abbreviations: isn = isonicotinamide; phen = *o*-phenanthroline; TFMS = trifluoromethanesulfonate; TFA = trifluoroacetate; en = ethylenediamine.

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Table I. Visible Spectra and CV of Ru(II) Ammines[a]

complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	medium	$E_{1/2}$,[b] V	E_{p-p}, mV
$[Ru(NH_3)_5isn]^{2+}$	478	1.19×10^4 [c]	0.1 M HCl	0.387	62
trans-$[Ru(NH_3)_4isn(H_2O)]^{2+}$	475	1.20×10^4	0.1 M HTFA	0.437	60
trans-$[Ru(NH_3)_4isnCl]^+$	488	1.15×10^4	5 M LiCl, pH 1	0.279, 0.29[d]	60
cis-$[Ru(NH_3)_4isn(H_2O)]^{2+}$	468[i]	1.19×10^4	0.1 M HTFMS	0.34[e]	
$[Ru(NH_3)_4phen]^{2+}$	471	7.57×10^3	0.1 M HCl	0.533	59
$[Ru(NH_3)_5(4\text{-vinyl-py})]^{2+}$	453[f]	9.91×10^3 [f]	0.1 M HTFA	0.302[f]	80[f]
$[Ru(NH_3)_6]^{2+}$	400[g]	30[g]	0.1 M $NaBF_4$	0.051[h]	
$[Ru(en)_3]^{2+}$	370[g]	120[g]	0.013 M HTFA	0.172[g]	

[a] Results from this work, unless otherwise indicated. [b] $E_{1/2}$ referred to NHE by adding 0.244 V to $E_{1/2}$ vs. SCE. [c] Reference 20. [d] At pH 3, $\mu = 0.2$ M (NaCl); ref 15. [e] Reference 17. [f] Reference 21. [g] Reference 22. [h] Reference 23. [i] Value for λ_{max} in ref 17 is a misprint.

a function of $[Cl^-]$ by using differential pulse polarography and current/voltage curves.

HTFMS was standardized against Titrisol 0.1 M NaOH. NaTFMS was standardized gravimetrically after evaporating the solvent. Solutions of O_2 were prepared by saturation with pure O_2 or air at atmospheric pressure. Ru(II) and Ru(III) solutions were prepared by weighing the solid salts.

Solutions were allowed contact only with glass, Teflon, and platinum and were protected from light. Protection from light was especially important for the reactions with added $[Ru(NH_3)_5isn]^{3+}$.

Spectra and kinetics were run in 1-cm quartz cuvettes which were equipped with Teflon joints to allow manipulations under controlled atmosphere. The usual procedure for the kinetic runs was to flush the dry cell with the appropriate gas and then to transfer 2.8 mL of a solution containing the appropriate gas and ionic medium. After the filled cell was thermostated, 0.20 mL of the Ru(II) solution was injected to initiate the reaction. The Ru(II) solutions were prepared either by dissolving the Ru(II) salt in deaerated water or by adding a slightly less than stoichiometric amount of Eu(II) solution to a deaerated solution of the Ru(III) complex.

The strong charge-transfer bands in the visible spectra of the Ru(II) complexes were used to monitor the Ru(II) concentrations. Because of the large excess of dissolved O_2, these reactions generally showed pseudo-first-order kinetics. The tabulated values of k_{obsd} were obtained as slopes in the semilog plots of $(A_t - A_\infty)$ against time. Values of A_∞ were determined either by waiting for 6 or 7 half-lives or by oxidizing the remaining Ru(II) rapidly with $Na_2S_2O_8$.

Results

Properties of the Reducing Agents. None of the Ru(II) complexes in this study is novel, but since spectra and $E_{1/2}$ values have been reported for conditions differing from ours, they have been measured again in more relevant media; the results are summarized in Table I.

$[Ru(NH_3)_5isn]^{2+}$ as Reductant. Stoichiometry. In all cases, the UV/vis spectra of products in the kinetic studies are consistent with simple one-electron oxidation to the corresponding Ru(III) complexes. The fate of the O_2 is assuredly formation of H_2O_2 as reported earlier for the autoxidations of $[Ru(NH_3)_6]^{2+}$ and $[Ru(en)_3]^{2+}$.[8] Interference by the secondary (catalyzed) reaction of H_2O_2 with the reducing agents we used is more serious than for the systems studied earlier,[8] because in ours the first reaction stages are slower. For $[Ru(NH_3)_5isn]^{2+}$ as reductant, a measurement of the formation of H_2O_2 was attempted. The method was that of Bailey and Boltz;[24] the product solution obtained from a mixture of Ru(II) and O_2 was eluted with water from a strong cation-exchange column and treated with Fe(II) and phen, and the optical density was measured. Under the conditions $[[Ru(NH_3)_5isn]^{2+}]_0 = 1.9 \times 10^{-4}$ M, O_2 saturated, and pH 2 (HTFMS), 2.7 mol of Ru(II) was consumed/mol of H_2O_2 formed, thus indicating some consumption of H_2O_2 during the experiment. Significantly greater departures from the theoretical ratio of 2 were found when less care was taken to clean the glassware and to purify the solutions. The difficulty in obtaining quantitative H_2O_2 formation is consistent with its secondary reduction to H_2O, catalyzed by adventitious Fe(II). That H_2O_2 did accumulate almost quantitatively in some of our systems is demonstrated by the fact (vide infra) that the rate of consumption of Ru(II) nearly doubled when Fe(II) ions were added to catalyze the secondary reaction. It seems clear that, as when $Ru(NH_3)_6{}^{2+}$ is reactant, the primary reaction can be expressed by eq 1.

Table II. Kinetics of $[Ru(NH_3)_5isn]^{2+} + O_2$[a]

pH	10^5[Fe(II)], M	$10^3[[Ru(NH_3)_5isn]^{3+}]_0$, M	10^4k_{obsd}, s^{-1}
1			2.53
2			2.46
3.15			1.93
1	6.8		4.62
1	1.36		4.68
1	3.16		4.75
2	5		4.70
2	10		0.962[b]
1		2.07	1.89
2		1.81	0.64
3.12		2.07	0.130

[a] $[Ru(II)]_0 \approx 8 \times 10^{-5}$ M; 25.0 °C; $\mu = 0.10$ M (NaTFMS); solutions saturated with O_2 at 1 atm. [b] Saturated with air at 1 atm.

$$2Ru(II) + 2H^+ + O_2 \rightarrow 2Ru(III) + H_2O_2 \qquad (1)$$

Kinetics. The kinetics of the reaction of $[Ru(NH_3)_5isn]^{2+}$ with O_2 were studied in acidic NaTFMS ($\mu = 0.1$ M). With a large excess of O_2, the semilog plots showed downward curvature in the third half-lives and sometimes even in the second half-lives. In Table II are listed k_{obsd} values taken during the initial part of the reaction. In the presence of a small amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, the semilog plots were linear for 3 or 4 half-lives. Reactions at pH 1 and 2 showed no significant pH dependence in either the presence or the absence of Fe(II). At pH 3 the semilog plot showed a slight upward curvature in the second half-life and a slightly lower initial rate than at pH 1 and 2; this result is consistent with the Ru(III)/H^+ effect described below. A series of reactions at pH 1 with variable [Fe(II)] showed only a very weak dependence on [Fe(II)]. The general effect of adding Fe(II) is a doubling of the rate. One experiment was performed with the solution saturated with air instead of O_2; assuming Henry's law for the solubility of O_2 in water and taking air to be 20.95% O_2,[25] we demonstrated a precise first-order dependence on $[O_2]$. These results are accommodated in rate law 2, where

$$-d[Ru(II)]/dt = k[Ru(II)][O_2] \qquad (2)$$

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Table III. Kinetics of *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ (H^+ and Cl^- Effects)[a]

no. of runs	$[H^+]$, M	$[Cl^-]$, M	10^5k_{obsd}, s^{-1}
5	0.100		7.47
2	0.010		7.92
1	0.001		6.83
6	0.100	0.100	138
4	0.100	0.050	64.2
3	0.100	0.025	43.3
1	0.100	0.010	18.3
2	0.100	0.0050	10.3
1	0.100	0.0025	9.67
2	0.010	0.100	28.3
1	0.002	0.100	14.3
2	0.001	0.100	14.8

[a] $\mu = 0.10$ M (LiTFA); 25.0 °C; saturated with 1 atm of O_2; $[Ru(II)]_0 = (2.5–8.3) \times 10^{-5}$ M.

k doubles in the presence of Fe(II). Using 1.1×10^{-3} M as the solubility of $[O_2]$ at one atmosphere[26] gives a value of $k = (2.16 \pm 0.08) \times 10^{-1}$ M^{-1} s^{-1}. This value is based on the runs at pH 1 and 2 which had no added Ru(III).

Some experiments were performed in the presence of a large (~20-fold) excess of Ru(III). These were somewhat complicated by the appearance of a weak absorption centered at about 410 nm; the anomalous absorption could not be attributed to either $[Ru(NH_3)_5isn]^{2+}$ or $[Ru(NH_3)_5isn]^{3+}$, and it was not very reproducible. It was due, presumably, to an impurity at low concentrations in the Ru(III) preparation, which on being reduced by Ru(II) caused a spectral distortion. This problem was sufficiently serious to cause strong upward curvature in some of the semilog plots in the second half-life. As a result, initial rates were used to generate the values of k_{obsd} shown in Table II. In spite of the difficulties acknowledged, the results show that there is strong inhibition by Ru(III) and that this inhibition is enhanced with increasing pH. Since the reduction potential of O_2 to H_2O_2 is 0.695 V,[27] even with added Ru(III) at pH 3 the reaction still should go to completion and so the inhibition should be understood as the effect of a reactive intermediate.

***trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$. Kinetics.** The trans aquo complex reacts with O_2 with pseudo-first-order kinetics; the specific rates are independent of $[H^+]$ in noncomplexing media. As in the reactions of $[Ru(NH_3)_5isn]^{2+}$, the semilog plots showed downward curvature in the latter half-lives. In the presence of Cl^- the reactions were accelerated and showed an acid dependence. Table III summarizes these results. The data were fit with rate law 3 by using a nonlinear least-squares

$$k_{obsd} = k_a + k_b[Cl^-] + k_c[H^+][Cl^-] \qquad (3)$$

computer program. The resulting values are $k_a = (6.67 \pm 0.70) \times 10^{-5}$ s^{-1}, $k_b = (6.73 \pm 1.54) \times 10^{-4}$ M^{-1} s^{-1}, and $k_c = (1.20 \pm 0.05) \times 10^{-1}$ M^{-2} s^{-1}. The relatively large standard deviation for k_b is due to the small contribution of that term at the acidities employed.

As an aid in understanding the effect of Cl^-, an estimate was made of the affinity of *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ for Cl^-. The cyclic voltammogram of *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ developed a second wave with $E_{1/2} = 279$ mV vs. NHE when Cl^- was added. In 5 M Cl^- this was the only visible wave, while in 1 M Cl^- the two waves were of roughly equal area. Thus, K_{Cl}, the formation constant of *trans*-$[Ru(NH_3)_4isnCl]^+$, was estimated to lie between 0.5 and 2 M^{-1}. Because of the high ionic strength (5 M) at which $E_{1/2}$ was measured for the Cl^- complex, Marchant's value of 0.29 V in 0.2 M NaCl is probably more reliable.[15]

Table IV. Kinetics of *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ (ClO_4^- and Fe(II) Effects)[a]

no. of runs	μ, M	$[H^+]$, M	$[Cl^-]$, M	inert salt	$10^3 \times$ [Fe(II)], M	k_{obsd}, s^{-1}
2	0.10	0.010		$LiClO_4$		7.7×10^{-5}
2	0.16	0.010		LiTFA	7	1.7×10^{-4}
1	0.16	0.100		HTFA	7	1.4×10^{-4}
2	0.16	0.010		$LiClO_4$	7	1.5×10^{-4}
1	0.16	0.100	0.015	HTFA	7	3.8×10^{-4}
1	0.16	0.100	0.0075	HTFA	7	2.6×10^{-4}
2	0.13	0.100	0.10	HCl	4	1.5×10^{-3}
1	0.16	0.100	0.10	HCl	7	2.2×10^{-3}
1	0.16	0.100	0.10	HCl	8	2.5×10^{-3}
1	0.23	0.100	0.10	HCl	16	2.6×10^{-3}

[a] 25.0 °C; $[Ru(II)]_0 = (0.8–7.5) \times 10^{-5}$ M; Fe(II) supplied as $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

A more accurate determination of K_{Cl} was made by using a rotating-disk electrode.[28] A series of 24 measurements with $[Cl^-]$ varied between 0.5 M and 5.0 M gave $K_{Cl} = 0.39 \pm 0.08$ M^{-1}.

The effects of Fe(II) and ClO_4^- were investigated and are given in Table IV. The substitution of ClO_4^- for TFA had an insignificant effect; the direct reaction of Ru(II) with ClO_4^- was negligible in these studies. The addition of Fe(II) at 7×10^{-3} M effected a clean doubling of the rate in the absence of Cl^-. In the presence of 0.1 M Cl^-, the doubling in rate by adding Fe(II) occurred only at higher [Fe(II)].

***cis*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$.** The reactivity of the cis aquo complex was studied only briefly and as a complement to the studies of the trans complex and $[Ru(NH_3)_5isn]^{2+}$. The reaction was observed in an O_2 saturated solution of 0.1 M HTFMS with $[Ru(II)]_0 \approx 3 \times 10^{-5}$ M. The semilog plot was nicely linear for 2 half-lives, and then, as also found for the trans complex and $[Ru(NH_3)_5isn]^{2+}$, downward deviation developed. The initial slope yielded $k_{obsd} = 3.04 \times 10^{-4}$ s^{-1}. Attempts to measure the effect of added *cis*-$[Ru(NH_3)_4isn(H_2O)]^{3+}$ at higher pH failed because of the significant acidity of Ru(III) ($pK_a \approx 4$).

$[Ru(NH_3)_4phen]^{2+}$. This complex was of interest because of its relatively large reduction potential and because of a preliminary study which indicated a surprisingly rapid reaction.[29] Subsequent work showed that the reaction was quite slow, with a half-life of about 12 h, and so an extensive investigation was curtailed. At pH 1 in both 0.1 M HTFMS and 1.0 M LiCl a good isosbestic point occurred at 385 nm for 3 half-lives; the values of k_{obsd} in these different media were 1.70×10^{-5} and 1.65×10^{-5} s^{-1}, respectively. The run in 1.0 M LiCl was performed in an attempt to repeat the preliminary study, in which k_{obsd} was reported as 1.4×10^{-4} s^{-1}. Apparently, there was some unknown catalyst in the original work which produced an acceleration.

Even though $[Ru(NH_3)_4phen]^{2+}$ is a relatively poor reducing agent, a calculation of K_{eq} for the formation of H_2O_2 using the known redox potentials reveals that at pH 1 the reaction should, as observed, have gone to completion.

Discussion

General Mechanism. A mechanism consistent with the data in noncomplexing media follows:

$$Ru(II) + O_2 \rightleftarrows Ru(III) + O_2^- \quad k_1, k_{-1} \qquad (4)$$

$$O_2^- + H^+ \rightleftarrows HO_2 \quad K_a^{-1} \qquad (5)$$

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(26) A. Seidell and W. F. Linke, "Solubilities of Inorganic Compounds", 4th ed., Van Nostrand, Princeton, N.J., 1964, p 1228.

(27) D. M. H. Kern, *J. Am. Chem. Soc.*, **76**, 4208 (1954).

(28) O. Haas, work done at Institute de Chimia Inorganic et Analytique, Universite de Fribourg, CH-1700, Fribourg, Switzerland.

(29) G. M. Brown, unpublished results.

$$\mathrm{Ru(II)} + \mathrm{HO_2} \rightarrow \mathrm{Ru(III)} + \mathrm{HO_2^-} \quad k_3 \qquad (6a)$$

$$\mathrm{H^+} + \mathrm{Ru(II)} + \mathrm{HO_2} \rightarrow \mathrm{Ru(III)} + \mathrm{H_2O_2} \quad k_4 \qquad (6b)$$

Using the steady-state approximation for [O_2^-] and [HO_2] and neglecting k_4 for simplicity, we obtain rate law 7.

$$-\frac{d[\mathrm{Ru(II)}]}{dt} = \frac{2k_1k_3K_a^{-1}[\mathrm{Ru(II)}]^2[\mathrm{H^+}][\mathrm{O_2}]}{k_3K_a^{-1}[\mathrm{Ru(II)}][\mathrm{H^+}] + k_{-1}[\mathrm{Ru(III)}]} \qquad (7)$$

Under the conditions that $k_3K_a^{-1}[\mathrm{Ru(II)}][\mathrm{H^+}] \gg k_{-1}[\mathrm{Ru(III)}]$ the rate law 7 simplifies to that observed: eq 8.

$$-d[\mathrm{Ru(II)}]/dt = 2k_1[\mathrm{Ru(II)}][\mathrm{O_2}] \qquad (8)$$

Equation 6a was used in the derivation of eq 7; if the reaction of Ru(II) with HO_2 involves H^+, k_3 in the rate law would be replaced by $k_4[H^+]$. Our data are not good enough to differentiate between the alternatives. Another complication is the possibility of protonation of HO_2 to form $H_2O_2^+$. The pK_a of $H_2O_2^+$ has been suggested to be 1.2, but its existence is controversial.[30,31] Our data do not rule out this possibility either.

Disproportionation of HO_2 instead of reaction according to eq 6a (or 6b) can be ruled out. Disproportionation would involve a second-order loss of HO_2 which is governed by a rate constant of 7.5×10^5 M^{-1} s^{-1}.[31] In a pulse radiolysis study, the rate of electron transfer between HO_2 and $Fe(CN)_6^{4-}$ was found to be 3×10^4 M^{-1} s^{-1}.[32] Since the Ru(II) complexes we studied have reduction potentials close to that of $Fe(CN)_6^{4-}$, while their self-exchange rates are somewhat larger, a reasonable estimate for k_3 is 10^5 M^{-1} s^{-1}. The steady-state [HO_2] will be very small compared to [Ru(II)]; thus the pseudo-first-order reaction via k_3 is expected to be much faster than the second-order disproportionation.

A value for k_{-1} can be determined by using the principle of microscopic reversibility. The potential for the O_2/O_2^- couple reported as -0.15 ± 0.02 V (1 M O_2 as the standard state)[33] seems reliable. With our data for k_1 and $E°$, k_{-1} is calculated as 1.3×10^8 M^{-1} s^{-1} for $[\mathrm{Ru(NH_3)_5isn}]^{3+}$.

Qualitatively, eq 7 is consistent with the observed acid-dependent inhibition of the $[\mathrm{Ru(NH_3)_5isn}]^{2+}$ reaction by Ru(III). The strongly inhibited reaction at pH 3.12 should, according to eq 7, display pseudo-second-order kinetics. A second-order plot of this run is indeed linear over the first half-life and yields $k_{obsd} = 1.74 \times 10^{-1}$ M^{-1} s^{-1}. With the known value of pK_a = 4.88,[31] the measured k_1, and the calculated k_{-1}, k_3 is calculated as 3.4×10^6 M^{-1} s^{-1} with the assumption that k_4 can be neglected. This value is probably consistent with the estimate based on $Fe(CN)_6^{4-}$ and is also consistent with the approximation used to obtain eq 8.

As amply demonstrated for the $[\mathrm{Ru(NH_3)_6}]^{2+}$ reaction with O_2,[8] Fe(II) is an effective catalyst for the reduction of H_2O_2 to H_2O by Ru(II). The zero-order dependence on $[\mathrm{Ru(NH_3)_6}]^{2+}$ for the Fe(II)-catalyzed reduction of H_2O_2 explains the deviation after several half-lives toward zero-order kinetics in our studies with no added Fe(II); H_2O_2 is formed by the pseudo-first-order reaction of Ru(II) with O_2, and then during the latter half-lives the zero-order reduction of H_2O_2 catalyzed by adventitious Fe(II) becomes dominant. This also explains our failure to obtain a full yield of H_2O_2 in the stoichiometry measurements.

Table V. k_1 Values for Ruthenium(II) Ammine Autoxidations[a]

no.	complex	k_1, M^{-1} s^{-1}	medium
1	$[\mathrm{Ru(NH_3)_5isn}]^{2+}$	1.08×10^{-1}	0.1 N HTFMS
2	$[\mathrm{Ru(NH_3)_4phen}]^{2+}$	7.73×10^{-3}	0.1 N HTFMS
3	*trans*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$	3.03×10^{-2}	0.1 N HTFA
4	*cis*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$	1.38×10^{-1}	0.1 N HTFMS
5	*trans*-$[\mathrm{Ru(NH_3)_4isn(Cl)}]^{+}$	7.85×10^{-1} [b]	0.1 N HCl/ LiTFA
6	$[\mathrm{Ru(NH_3)_5(4\text{-}vinyl\text{-}py)}]^{2+}$	5.7×10^{-1} [c]	0.1 N HTFA
7	$[\mathrm{Ru(NH_3)_6}]^{2+}$	6.30×10	1.0 N LiOAC, pH 5.44
8	$[\mathrm{Ru(en)_3}]^{2+}$	3.62×10	1.0 N LiCl, pH 2

[a] k_1 as defined in eq 8, calculated by using $[O_2]_{sat} = 1.1 \times 10^{-3}$ M; 25.0 °C. [b] Assumes $k_1 = k_b/2K_{Cl}[O_2]$ as in eq 3. [c] J. K. Hurst and K. A. Norton, Jr., personal communication; 24.0 °C.

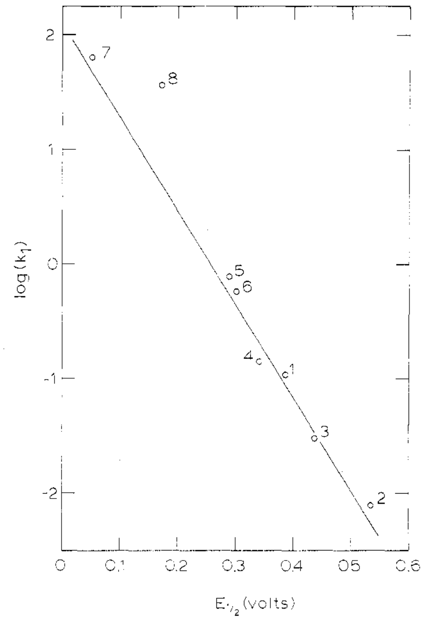

Figure 1. log k_1 vs. $E_{1/2}$ for various ruthenium(II) ammines. Numbering corresponds to numbering in Table V. Line drawn for log k_1 $\propto$ $^1/_2$ log K_{eq}.

The reaction of *trans*-$[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+}$ in Cl^- media shows two paths in addition to the type described above. These two new paths suggest the following steps:

$$trans\text{-}[\mathrm{Ru(NH_3)_4isn(H_2O)}]^{2+} + \mathrm{Cl^-} \rightleftarrows trans\text{-}[\mathrm{Ru(NH_3)_4isnCl}]^{+} \quad K_{Cl}$$

$$trans\text{-}[\mathrm{Ru(NH_3)_4isnCl}]^{+} + \mathrm{O_2} \rightarrow trans\text{-}[\mathrm{Ru(NH_3)_4isnCl}]^{2+} + \mathrm{O_2^-} \quad k_5$$

In the absence of Ru(III) inhibition the rate law is now

$$trans\text{-}[\mathrm{Ru(NH_3)_4isnCl}]^{+} + \mathrm{O_2} + \mathrm{H^+} \rightarrow trans\text{-}[\mathrm{Ru(NH_3)_4isnCl}]^{2+} + \mathrm{HO_2} \quad k_6$$

$$-d[\mathrm{Ru(II)}]/dt = 2(k_1 + k_5K_{Cl}[\mathrm{Cl^-}] + k_6K_{Cl}[\mathrm{Cl^-}][\mathrm{H^+}])[\mathrm{O_2}][\mathrm{Ru(II)}]$$

With the parameters of eq 3 and the measured K_{Cl}, this gives $k_1 = k_a/(2[O_2]) = 3.03 \times 10^{-2}$ M^{-1} s^{-1}, $k_5 = k_b/(2K_{Cl}[O_2]) = 0.784$ M^{-1} s^{-1}, and $k_6 = k_c/(2K_{Cl}[O_2]) = 1.40 \times 10^2$ M^{-2} s^{-1}. The k_5 path is therefore understood as being analogous with the k_1 path. On the other hand, the k_6 path represents a fundamentally different mechanism. The incorporation of H^+ into the activated complex for the k_6 path can be understood on the basis of electrostatics because the Cl^- complex is less positively charged than the H_2O complex. Reviewing the relevant literature, we find no examples among the aut-

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(30) See Discussion in H. N. Po and K. D. Chen, *Inorg. Chim. Acta*, **14**, 173 (1975).

(31) D. Behar, G. Czapski, J. Rabani, L. M. Dorman, and H. A. Schwarz, *J. Phys. Chem.*, **74**, 3209 (1970).

(32) D. Zehavi and J. Rabani, *J. Phys. Chem.*, **76**, 3703 (1972).

(33) (a) Y. A. Ilan, G. Czapski, and D. Meisel, *Biochim. Biophys. Acta*, **430**, 209 (1976); (b) Y. Sawada, T. Iyanugi, and I. Yamazaki, *Biochemistry*, **14**, 3761 (1975).

oxidations of 2+ charged complexes undergoing outer-sphere reaction with a first-order dependence on [H^+]. Most autoxidations of 1+ charged complexes feature Cu(I).[2] These copper complexes occasionally do show a first-order acid dependence but then are not unambiguously outer sphere. Note also that the autoxidations of $CuCl_2^-$ [34] and $Fe(CN)_6^{4-}$ [7] are first order in [H^+]. These few examples indicate a trend for an increasing propensity toward an acid dependence with decreasing positive charge on the reducing agent.

LFER and k_{11}. In Table V are collected the values of k_1 as defined in eq 8. They were obtained by using 1.1×10^{-3} M as the solubility of O_2 at atmospheric pressure. Figure 1 is a plot of log k_1 as a function of $E_{1/2}$ for the various reducing agents; the plot clearly demonstrates a linear free-energy relationship (LFER). The line in the figure has been drawn with a slope corresponding to the $K_{eq}^{1/2}$ dependence which the Marcus cross relationship (eq 9)[35] predicts when k_{22}, k_{11}, and f are constant.

$$\begin{gathered} k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2} \\ \log f = (\log^2 K_{eq})/(4 \log (k_{11}k_{22}/Z^2)) \end{gathered} \tag{9}$$

Equation 9 has been developed for one-electron outer-sphere electron-transfer reactions, where k_{11} and k_{22} are the self-exchange rates of the reactant couples, K_{eq} is the one-electron equilibrium constant defined by the relevant $E°$ values, Z is the collision frequency (10^{11} M^{-1} s^{-1}), and k_{12} is the second-order rate of electron transfer.

The fit to eq 9 suggested by the figure is not surprising since the autoxidations are probably outer sphere, electron transfer is probably the rate-limiting step, and $k_{22}f$ is fairly constant for this series of reactants. With the assumption of the validity of eq 9, an estimate of k_{11}, the self-exchange rate for the O_2/O_2^- couple, can be made by using the quadratic solution to eq 9, eq 10. Good estimates of K_{eq} can be obtained with

$$\begin{gathered} \log k_{11} = 1/2[b - (4 \log (k_{eq}Z/k_{12}) \log (Z/k_{12}))^{1/2}] \\ b = \log (k^2{}_{22}K_{eq}/(Z^2k^2{}_{12})) \end{gathered} \tag{10}$$

our $E_{1/2}$ values for the various reducing agents and with $E°$ for the O_2/O_2^- couple. Reasonable values of k_{22} for the Ru(II) complexes are 4×10^3,[36] 4.7×10^5,[37] and 1.2×10^7 M^{-1} s^{-1} [13] for $[Ru(NH_3)_6]^{2+/3+}$, $[Ru(NH_3)_5isn]^{2+/3+}$, and $[Ru(NH_3)_4phen]^{2+/3+}$, respectively. The values obtained for k_{11} from eq 10 are 9.9×10^3, 1.0×10^3, and 6.0×10^2 M^{-1} s^{-1}. This spread of values for k_{11} is not surprising in light of the square-root dependence on k_{11} in eq 9, and 1×10^3 M^{-1} s^{-1} appears to be a good estimate for the self-exchange rate for the O_2/O_2^- couple.[40] To our knowledge, there has been no prior estimate of k_{11}, and there certainly has been no direct measurement of this intrinsic reactivity parameter.[49]

Woodruff and Margerum have estimated k_{11} for the I_2/I_2^- and Br_2/Br_2^- couples at 8.5×10^4 and 29 M^{-1} s^{-1} by using arguments similar to ours.[38] A significant difference is that they have applied eq 10 to a series of *inner-sphere* reactions. Within the formalism of the Marcus theory, the inner-sphere contributions to k_{11} as calculated by eq 11[35] are 0.94, 1.34,

$$\Delta G_i^{\ddagger} = nf_1f_2(r_1 - r_2)^2/(2(f_1 + f_2)) \tag{11}$$

and 2.33 kcal/mol for the O_2, I_2, and Br_2 couples, respectively.[42] Equation 12 gives the total free energy of activation

$$K = Z \exp(-\Delta G^{\ddagger}/RT) \tag{12}$$

as 10.9, 8.27, and 13.0 kcal/mol. Since $\Delta G^{\ddagger} = \Delta G_i^{\ddagger} + \Delta G_0^{\ddagger}$, we have the outer-sphere reorganizational energies, $\Delta G_0^{\ddagger}$, as 9.96, 6.93, and 10.67 kcal/mol. Thus, contrary to Woodruff and Margerum's estimation, the outer-sphere contributions are dominant. Equation 13 relates $\Delta G_0^{\ddagger}$ to the reactant radii

$$\Delta G_0^{\ddagger} = (\Delta Z)^2(22.7/r_1^{\ddagger}) \tag{13}$$

in the activated complex. This equation shows that for diatomics and other small reactants $\Delta G_0^{\ddagger}$ is very sensitive to the choice of $r_1^{\ddagger}$. Using eq 13 to calculate $r_1^{\ddagger}$ gives radii of 2.28, 3.28, and 2.13 Å for O_2, I_2, and Br_2 in the activated complex. These radii are 0.5–1.0 Å larger than we might have guessed a priori, and they suggest the presence of intervening solvent molecules.

As one example of the utility of our k_{11} value, consider oxygen quenching rates. Excited $Ru(bpy)_3^{2+}$ is quenched by O_2 at a rate of 2×10^9 M^{-1} s^{-1} (corrected for diffusion control).[47] The Marcus cross relation predicts a rate of 7×10^9 M^{-1} s^{-1} for election-transfer quenching. Thus the arguments of Demas et al.[47] in favor of energy-transfer quenching are considerably weakened.[48]

It should be noted that the *cis*- and *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$ reactions do obey the LFER. This shows that although the acidity of the Ru(III) aquo complexes is fairly high ($pK_a \approx 4$), there appears to be no kinetic assistance to form HO_2 with these acidic protons.

The inclusion of the $[Ru(NH_3)_6]^{2+}$ reaction in the LFER and in the calculations of k_{11} calls for special comment in view of the original discussion of that reaction.[8] The failure to observe inhibition by $[Ru(NH_3)_6]^{3+}$ at pH 5.5 was taken as evidence that the reaction does not yield O_2^- in the primary step. This argument was based on a calculation of k_{-1} using an $E°$ of −0.38 V for the O_2/O_2^- couple. Current estimates of $E°$ are quite different, and so the failure to observe inhibition by $[Ru(NH_3)_6]^{3+}$ is reconciled in our current mechanism.

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(34) H. Nord, *Acta Chem. Scand.*, **9**, 430 (1955).

(35) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, 1966, pp 124–37.

(36) T. J. Meyer and H. Taube, quoted in H. Taube, *Adv. Chem. Ser.*, **No. 162**, 127 (1977).

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(38) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **13**, 2578 (1974).

(39) (a) C. Lavallee and D. K. Lavallee, *Inorg. Chem.*, **16**, 2601 (1977); (b) C. Lavallee, D. K. Lavallee, and E. A. Deutsch, *ibid.*, **17**, 2217 (1978).

(40) Sutin and co-workers[41] have shown that for some metal aquo ions, calculation of k_{11} by this method results in low values, the discrepancy increasing with increasing $|\Delta E°|$. While our results show such a trend, an extrapolation to $|\Delta E°| = 0$ is not yet warranted because of the paucity of the data. We would not be surprised if further work showed our estimate of k_{11} to be low by an order of magnitude.

(41) M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).

(42) Our calculations use f_1 and f_2 of 11.77 and 5.22 mdyn/Å for O_2, 1.76 and 0.52 mdyn/Å for I_2, and 2.46 and 0.53 mdyn/Å for Br_2. f_2 values for I_2 and Br_2 were obtained from $\bar{\nu}_0$ reported by Andrews et al.[43] The other f values were tabulated by Nakamoto.[44] We used r_1 and r_2 values of 1.21 and 1.33 Å for O_2, 2.67 and 3.10 Å for I_2, and 2.28 and 2.82 Å for Br_2. r_2 values for $I_2^-\cdot$ and $Br_2^-\cdot$ were estimated by using Badger's rule[45] and Andrews' $\bar{\nu}_0$ data. The other r_1 and r_2 data were obtained from Cotton and Wilkinson.[46]

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(47) J. N. Demas, E. W. Harris and R. P. McBride, *J. Am. Chem. Soc.*, **99**, 3547 (1977).

(48) We wish to thank one of the reviewers for suggesting this example.

(49) Brief consideration of the O_2/O_2^- self-exchange rate is given by R. A. Marcus, *J. Chem. Phys.*, **26**, 872 (1957), and by D. Meisel and R. W. Fessenden, *J. Am. Chem. Soc.*, **98**, 7505 (1976). The latter work implies a very high self-exchange rate (~10^7, 10^8 M^{-1} s^{-1}). Our work, which has recently, been confirmed by pulse radiolysis, raises the possibility that Meisel and Fessenden were not observing a simple outer-sphere electron transfer between O_2 and the semiquinones.

Another point of interest is the deviation of the $[Ru(en)_3]^{2+}$ reaction from the LFER. While there has been no satisfactory direct measurement of k_{22} for the [Ru(en)$_3$] couple, the value has been estimated as being about fivefold greater than for the $[Ru(NH_3)_6]^{2+/3+}$ couple.[39] This difference accounts for about half of the observed deviation in the LFER, and so the reaction is not considered to be anomalous.

In summary, the reduction of O_2 by a series of ruthenium ammines proceeds by one-electron outer-sphere electron transfer. The rates conform to the Marcus theory, and they lead to an estimate of the self-exchange rate for the O_2/O_2^- couple.

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Registry No. $[Ru(NH_3)_4phen](TFMS)_2$, 69799-60-6; *trans*-$[Ru(NH_3)_4isn(H_2O)](PF_6)_2$, 72214-11-0; $[Ru(NH_3)_5isn](ClO_4)_2$, 31279-70-6; $[Ru(NH_3)_5isn](TFMS)_3$, 72214-12-1; *trans*-$[Ru(NH_3)_4isnCl]^+$, 63323-68-2; *cis*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$, 60168-57-2; $[Ru(NH_3)_6]^{2+}$, 19052-44-9; $[Ru(en)_3]^{2+}$, 21393-86-2; O_2, 7782-44-7; $[Ru(NH_3)_5H_2O](TFMS)_3$, 53195-18-9; *trans*-$[Ru(NH_3)_4isn(SO_4)]Cl$, 60209-67-8; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[Ru(NH_3)_5isn]^{2+}$, 19471-53-5; $[Ru(NH_3)_4phen]^{2+}$, 69799-59-3; *trans*-$[Ru(NH_3)_4isn(H_2O)]^{2+}$, 60208-50-6; $[Ru(NH_3)_5(4\text{-vinyl-py})]^{2+}$, 60166-34-9.

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A Kinetic Study of the Oxidation of a Series of *N*-Alkylphenothiazines by Neptunium(VI) in Aqueous Perchlorate Media[1]

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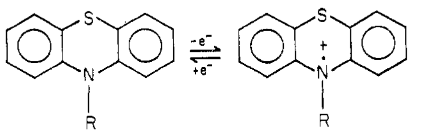
The kinetics of oxidation of a series of *N*-alkylphenothiazines to the corresponding cation radicals by means of neptunium(VI) have been studied by a stopped-flow spectrophotometric technique. The reaction rates are first order in both of the reagents and are independent of acidity. A linear relation between $\Delta G°$ and ΔG^* for the title series of reactions is observed. Values of the rate parameters calculated from the Marcus theory are about 100 times greater than the experimental values. There is also a marked discrepancy between experimental and calculated values of ΔH^* and ΔS^*.

Introduction

In a previous kinetic study of the oxidation of *p*-hydroquinone and *p*-toluhydroquinone by Np(VI) in aqueous perchlorate media[4] an apparent agreement between the experimental values of the rate parameters and those calculated by using the Marcus[5] cross relations was noted. In that study the product of the 1-equiv oxidation of Np(VI) was an unstable intermediate radical species, and there is a consequent ambiguity in the value estimated for the self-exchange parameter required for the Marcus type calculation.

In contrast, the *N*-alkylphenothiazines (PTZ) are oxidized to stable cation radicals through a 1-equiv step[6]



PTZ PTZ$^{+\cdot}$ (1)

By varying the alkyl chain R or the substituents on the aromatic nuclei it is possible to vary the free-energy change of (1). The detailed dynamic studies of the oxidation of a number of such compounds by the aquometal ions Fe(III),[7] Co(III),[8] and $Fe(CN)_6^{3-}$[7] have provided thermodynamic and dynamic data that are useful in analyzing the present results with Np(VI) as the oxidant in terms of the Marcus theory.

Experimental Section

Reagents. The *N*-alkylphenothiazines (Table I) used in this investigation were available from the laboratory reserves of E.P. The purity of these compounds had been verified by elemental analysis as well as by mass spectrometry and NMR spectra. The preparation and standardization of the perchloric acid, lithium perchlorate, and neptunium(VI) perchlorate solutions have been previously described.[9] All solutions were prepared in triply distilled water.

Equipment and Procedures. The computer-interfaced stopped-flow instrumentation, as well as the basic procedures and techniques, has been detailed previously.[10] The observed OD vs. *t* data from individual kinetic experiments were treated by standard nonlinear least-squares techniques in terms of the first-order rate expression

$$OD_t = (OD_0 - OD_\infty) \exp(-k_{obsd}t) + OD_\infty$$

where k_{obsd}, OD_0, and OD_∞ are adjustable parameters. Each kinetic experiment was monitored to at least 90% completion, 800-950 data points being collected during this period. A minimum of seven experimental determinations of k_{obsd} were made for each set of reaction conditions.

The range of initial concentration was chosen to ensure first-order conditions, $[PTZ]_0 = 5.0 \times 10^{-6}$–$1.0 \times 10^{-5}$ M and $[Np(VI)]_0 = 5.0 \times 10^{-5}$–$2.0 \times 10^{-4}$ M. The kinetic experiments were monitored at the wavelength of maximum absorption of the cation radicals, listed in Table I. None of the other species involved in the reaction have an appreciable absorptivity at the chosen wavelengths.

Results

Stoichiometry. For the reactions

$$NpO_2^{2+} + PTZ^+ = NpO_2^+ + PTZ^{2+} \qquad (2)$$

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