(PPh₃)₂(SiCl₃)₂" caused conversion to Ru(CO)₃(PPh₃)(SiCl₃)₂.

Currently a kinetic study is under way to investigate the cis effect of the ligand L on the rate of substitution by P(OCH₃)₃ of the remaining equatorial carbonyl group in compounds of the type Ru(CO)₃L(SiCl₃)₂.[25] Initial results (and the results here) indicate the rate of substitution increases with the cone angle of L. There are some obvious exceptions (i.e., L = PF₃, CO). Although cis effects appear to be of dominant importance in the substitution reactions of most transition-metal carbonyl compounds, it should not be forgotten that it is the trans effect of the SiCl₃ groups in Ru(CO)₃L(SiCl₃)₂ derivatives which is mainly responsible for the carbonyl lability and this is modulated by the cis effect of the ligand L.

Again, it should be pointed out that there is no indication from the carbonyl stretching frequencies of these or other derivatives reported here of the lability of the carbonyl groups of the respective compound, even though such stretching frequencies are usually taken as being inversely proportional to the metal–carbon bond strength. This, as stated before, is taken to mean that the lability is due to the ease of formation of the intermediate.

At temperatures above 50 °C, Ru(CO)₃(PPh₃)(SiCl₃)₂ reacts with excess P(OCH₃)₃ to give Ru(CO)₂[P(OCH₃)₃]₂⁻(SiCl₃)₂. Also treatment of Ru(CO)₂[P(OCH₃)₃]₂(SiCl₃)₂ in solution with 80 atm of carbon monoxide at 100 °C gives some Ru(CO)₃[P(OCH₃)₃](SiCl₃)₂ on cooling. As in "Ru(CO)₂-(PPh₃)₂(SiCl₃)₂" the increased lability of the Ru–P bond in the bissubstituted derivatives, compared to that in the monosubstituted compounds, is probably due to the mutual cis effect of the two phosphorus ligands.

Phosphorus NMR Data. The ³¹P NMR data for the phosphorus derivatives are reported along with the chemical shift difference between the resonance of the phosphorus in the coordinated and uncomplexed ligand (Δ_{CS}). The factors contributing to Δ_{CS} are not well understood.[28] In these compounds the donor–acceptor properties of the ligand appear to be unimportant in influencing Δ_{CS}. For example, the PF₃ and P(n-C₄H₉)₃ derivatives show very similar downfield chemical shifts on coordination to the ruthenium, yet Tolman[29]

has adjudged these ligands, using CO stretching frequencies, at opposite ends of a scale based on electron donor–acceptor properties. Phosphites which are intermediate on the scale show upfield shifts on coordination except for P(OCH₂)₃C-C₂H₅, which exhibits a downfield shift comparable to phosphines. This last observation adds some support to the suggestion that the changes in the interligand angles on coordination have a marked effect on Δ_{CS}. These changes can be related to the s character in the phosphorus–transition-metal bond.[28]

Registry No. Fe(CO)₄(SiCl₃)₂, 15306-36-2; *cis*-Ru(CO)₄(SiCl₃)₂, 36570-60-2; *cis*-Os(CO)₄(SiCl₃)₂, 36570-61-3; Fe(CO)₃(PPh₃)(SiCl₃)₂, 75030-80-7; Ru(CO)₃(PPh₃)(SiCl₃)₂, 71893-44-2; Os(CO)₃-(PPh₃)(SiCl₃)₂, 75030-81-8; Ru(CO)₃[P(OCH₃)₃](SiCl₃)₂, 75030-82-9; Ru(CO)₃(PF₃)(SiCl₃)₂, 75030-83-0; Ru(CO)₃(ETPB)(SiCl₃)₂, 75030-84-1; Ru(CO)₃[P(OC₂H₅)₃](SiCl₃)₂, 75030-85-2; Ru(CO)₃-[P(OPh)₃](SiCl₃)₂, 75030-86-3; Ru(CO)₃[PPh(CH₃)₂](SiCl₃)₂, 75030-87-4; Ru(CO)₃[PPh₂(CH₃)](SiCl₃)₂, 75045-84-0; Ru(CO)₃-{P[o-C₆H₄(CH₃)]₃}(SiCl₃)₂, 75030-88-5; Ru(CO)₃[P(n-C₄H₉)₃]-(SiCl₃)₂, 75030-89-6; Ru(CO)₃[P(C₆H₄)₃](SiCl₃)₂, 75030-90-9; Ru(CO)₃(AsPh₃)(SiCl₃)₂, 75030-91-0; Ru(CO)₃(SbPh₃)(SiCl₃)₂, 75030-92-1; Ru(CO)₃[CNC(CH₃)₃](SiCl₃)₂, 75030-93-2; Ru(C-O)₂(PF₃)₂(SiCl₃)₂, 75030-94-3; Ru(CO)₂[P(OCH₃)₃]₂(SiCl₃)₂, 75030-95-4; Ru(CO)₂(ETPB)₂(SiCl₃)₂, 75030-96-5; Ru(CO)₂[P(O-C₂H₅)₃]₂(SiCl₃)₂, 75030-97-6; Ru(CO)₂[P(OPh)₃]₂(SiCl₃)₂, 75030-98-7; Ru(CO)₂[PPh(CH₃)₂]₂(SiCl₃)₂, 75030-99-8; Ru(CO)₂[PPh₂-(CH₃)]₂(SiCl₃)₂, 75031-00-4; Ru(CO)₂[P(n-C₄H₉)₃]₂(SiCl₃)₂, 75031-01-5; Ru(CO)₂[P(OCH₃)₃](PPh₃)(SiCl₃)₂, 71852-83-0; Ru-(CO)₂[P(C₆H₁₁)₃]₂(SiCl₃)₂, 75031-02-6; Ru(CO)₂[CNC(CH₃)₃]₂-(SiCl₃)₂, 75031-03-7; Ru₃(CO)₁₂, 15243-33-1; Fe(CO)₅, 13463-40-6; Os₃(CO)₁₂, 15696-40-9; Cl₃SiH, 10025-78-2; *trans*-Os(CO)₄(SiCl₃)₂, 58957-82-7.

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Superoxide Reactions with (Isonicotinamide)pentaammineruthenium(II) and -(III)

DAVID M. STANBURY, WILLIAM A. MULAC, JAMES C. SULLIVAN,* and HENRY TAUBE*

The reactions of superoxide with [Ru(NH₃)₅isn]²⁺ and [Ru(NH₃)₅isn]³⁺ have been investigated in aqueous solution (μ = 0.1 M (formate buffer) at 23 ± 2 °C with use of pulse radiolysis). The radical HO₂ oxidizes Ru(II) with a rate constant of 9.07 × 10⁶ M⁻¹ s⁻¹, and O₂⁻ reduces Ru(III) with a rate constant of 2.18 × 10⁸ M⁻¹ s⁻¹. These values are in good agreement with those deduced from a study of the reaction of O₂ with [Ru(NH₃)₅isn]²⁺, and this agreement confirms many of the conclusions about the reaction mechanism arrived at from the latter study. Outer-sphere reductions of HO₂ to HO₂⁻ are shown to be anomalous from the perspective of the Marcus theory. Approximate values have also been obtained for the specific rates governing the reactions of Ru(III) with OH, H, e$_{aq}^-$, CO₂⁻, and HC(OH)₂ and of Ru(II) with OH.

Introduction

As a part of a continuing study of the mechanisms of reduction of O₂ in aqueous solution, we recently published a

report of the autoxidation of a series of ruthenium(II) ammines.[1] One conclusion reached in that work was that the mechanism involves outer-sphere reduction of O₂ to O₂⁻ (superoxide); this was supported in part by a good correlation, using Marcus theory, of the rate and equilibrium constants.

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* To whom correspondence should be addressed: J.C.S., Argonne National Laboratory; H.T., Stanford University.

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This correlation has since been exploited in our work to flag anomalous results and to suggest new reducing agents.

In view of the potential utility of the correlation, it seemed important to verify the proposed mechanism. Partial verification was provided by the observation that autoxidation of $[Ru(NH_3)_5isn]^{2+}$ is inhibited by Ru(III),[1,2] but there were two problems which vitiated an unambiguous interpretation. One was an anomaly in the spectra of mixtures of Ru(II) and Ru(III); the other was that the data were too incomplete for us to distinguish between a path for the reduction of HO_2 by Ru(II) first order in each of these reactants and a path also first order in acid. Because of these problems we have resorted to the technique of pulse radiolysis to improve our understanding of the reactions.[3] Pulse radiolysis makes possible the generation of significant concentrations of superoxide so that its reactions with Ru(II) and Ru(III) can then be followed spectroscopically. The results of the pulse radiolytic investigation are described herein.

Experimental Section

Materials. Sodium formate was twice recrystallized from water. Formic acid was purified by distillation. $[Ru(NH_3)_5isn](TFMS)_3$ and $[Ru(NH_3)_5H_2O](TFMS)_3$ were prepared as described previously.[1] $[Ru(NH_3)_5isn](TFMS)_2$ was prepared by reducing 0.20 g of $[Ru(NH_3)_5H_2O](TFMS)_3$ in 5 cm^3 of argon-saturated methanol with zinc amalgam in a Zwickel flask.[4] The solution was then passed into an argon filled flask containing 0.15 g of isn and allowed to react for 0.5 h in the dark. A sample of 9 M HTFMS (1 cm^3) was added, and the mixture was poured into 50 cm^3 of ether. The resulting precipitate was collected and recrystallized by dissolving it in a minimum volume of methanol, filtering the solution, adding 1 mL of 9 M HTFMS and enough ether to the filtrate to initiate crystallization, and refrigerating the mixture. This yielded 0.122 g of dark red microcrystals. The UV–vis spectrum agreed well (±5%) with that reported for $[Ru(NH_3)_5isn](ClO_4)_2$.[5]

Methods. Solutions of Ru(II) were prepared by mixing He-saturated solutions of Ru(II) with O_2-saturated solutions; mixing was performed no more than 20 min before irradiation so as to avoid complications introduced by autoxidation ($t_{1/2} \approx 1.6$ h). Solutions of Ru(III) were prepared by mixing O_2-saturated acidified solutions of Ru(III) with O_2-saturated buffer solutions just before irradiation; this was done to minimize the slow disproportionation of Ru(III) which occurs at pH 4.5.[6]
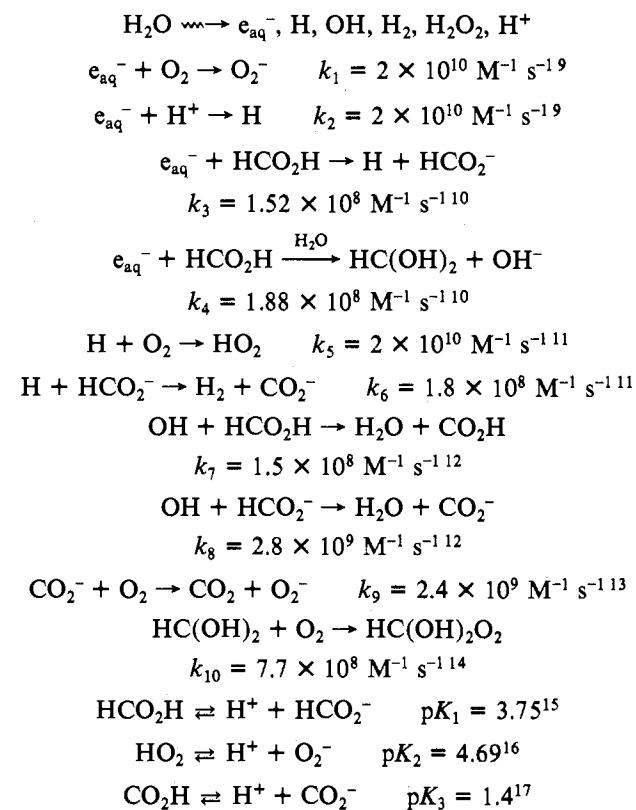
The kinetics were observed in the Ru(II) experiments in a 1-cm cell by monitoring bleaching of the Ru(II) absorbance at 600 nm. The optical density at λ_{max} (480 nm) is too great to be practicable. The Ru(III) experiments were run in 2-cm cells by monitoring the product formation at 480 nm. Appropriate cutoff filters were used in the optical train to minimize photolysis. All runs were performed at room temperature, 23 ± 2 °C.

Dosimetry was performed by using the reading from a Faraday cup which was calibrated with the spectrum of $(SCN)_2^-$ as described in ref 7, and the doses are reported as $[R]_0$, i.e., the initial yield of the sum of OH + H + e_{aq}^- ($G(H) = 0.55$, $G(OH) = 2.75$, $G(e_{aq}^-) = 2.7$).[3] The radiolysis techniques and data treatment have been described elsewhere.[8]
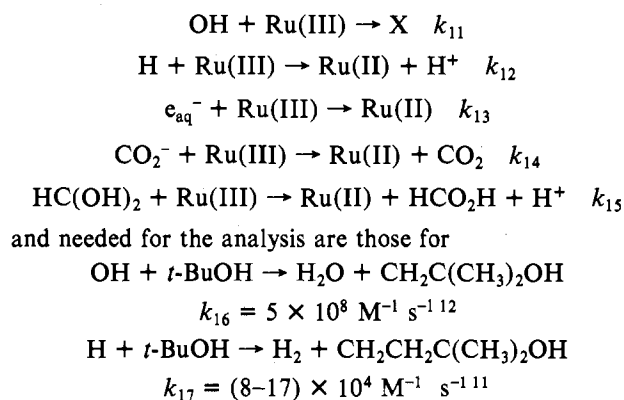
Results

The general method for transient generation of superoxide was the pulse radiolysis of oxygenated solutions of formate buffers. The well-documented reactions in Scheme I describe the process.

Scheme I

$$H_2O \rightsquigarrow e_{aq}^-, H, OH, H_2, H_2O_2, H^+$$

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad k_1 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}{}^{9}$$

$$e_{aq}^- + H^+ \rightarrow H \qquad k_2 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}{}^{9}$$

$$e_{aq}^- + HCO_2H \rightarrow H + HCO_2^-$$
$$k_3 = 1.52 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{10}$$

$$e_{aq}^- + HCO_2H \xrightarrow{H_2O} HC(OH)_2 + OH^-$$
$$k_4 = 1.88 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{10}$$

$$H + O_2 \rightarrow HO_2 \qquad k_5 = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}{}^{11}$$

$$H + HCO_2^- \rightarrow H_2 + CO_2^- \qquad k_6 = 1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{11}$$

$$OH + HCO_2H \rightarrow H_2O + CO_2H$$
$$k_7 = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{12}$$

$$OH + HCO_2^- \rightarrow H_2O + CO_2^-$$
$$k_8 = 2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}{}^{12}$$

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^- \qquad k_9 = 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}{}^{13}$$

$$HC(OH)_2 + O_2 \rightarrow HC(OH)_2O_2$$
$$k_{10} = 7.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{14}$$

$$HCO_2H \rightleftharpoons H^+ + HCO_2^- \qquad pK_1 = 3.75^{15}$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad pK_2 = 4.69^{16}$$

$$CO_2H \rightleftharpoons H^+ + CO_2^- \qquad pK_3 = 1.4^{17}$$

For solutions saturated in O_2 at 0.1 M HCO_2^- and at pH ≥ 3.5, the result is that in less than 1 μs all the primary radicals produced by the electron pulse are converted to superoxide, with the exception of a small fraction which is converted to an O_2 adduct of the formyl radical. A complicating feature of the system is that the primary radicals can also react with the added ruthenium complexes. For one to understand the system over the whole time regime, a brief investigation of the reactions of $[Ru(NH_3)_5isn]^{3+}$ with OH, H, e_{aq}^-, and CO_2^- was also performed. To be determined are rate constants for the reactions

$$OH + Ru(III) \rightarrow X \quad k_{11}$$

$$H + Ru(III) \rightarrow Ru(II) + H^+ \quad k_{12}$$

$$e_{aq}^- + Ru(III) \rightarrow Ru(II) \quad k_{13}$$

$$CO_2^- + Ru(III) \rightarrow Ru(II) + CO_2 \quad k_{14}$$

$$HC(OH)_2 + Ru(III) \rightarrow Ru(II) + HCO_2H + H^+ \quad k_{15}$$

and needed for the analysis are those for

$$OH + t\text{-BuOH} \rightarrow H_2O + CH_2C(CH_3)_2OH$$
$$k_{16} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}{}^{12}$$

$$H + t\text{-BuOH} \rightarrow H_2 + CH_2CH_2C(CH_3)_2OH$$
$$k_{17} = (8-17) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}{}^{11}$$

(2) Abbreviations: isn = isonicotinamide; HTFMS = trifluoromethanesulfonic acid; Ru(III) = $[Ru(NH_3)_5isn]^{3+}$; Ru(II) = $[Ru(NH_3)_5isn]^{2+}$.

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$$e_{aq}^{-} + N_2O \xrightarrow{\text{H}_2\text{O}} OH + N_2 + OH^{-}$$

$$k_{18} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}{}^{9}$$
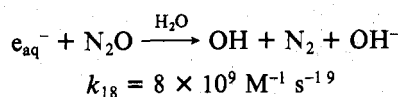
The rate constants we have determined are summarized in Table I; the experimental results and the analyses which lead to the determination of the specific rates are outlined in the following sections.

H + [Ru(NH₃)₅isn]³⁺. The reaction of H with Ru(III) was measured in He-saturated solution containing 0.5 M *tert*-butyl alcohol, 0.1 M HClO₄, 1.0×10^{-4} M Ru(III), and $[R]_0 = 8.7 \times 10^{-6}$ M. Under these conditions more than 99% of e_{aq}^{-} is scavenged by H⁺ to form H, and on the assumption that $k_{11} = 1.17 \times 10^{10}$ M⁻¹ s⁻¹ (vide infra) then 99% of OH is scavenged by *tert*-butyl alcohol. Since the radical from OH plus *tert*-butyl alcohol is relatively unreactive, the system soon contains only H as the reactive radical. The pseudo-first-order loss of H in our system was observed by the increase in absorbance due to formation of Ru(II) with $k_{obsd} = 9.09 \times 10^4$ s⁻¹ and $A_\infty = 5.73 \times 10^{-2}$. Atomic hydrogen is scavenged by *tert*-butyl alcohol as well as by Ru(III), so that rate law 1 obtains. In view of this competition for H, the yield of Ru(II) obtains.

$$k_{obsd} = k_{12}[\text{Ru(III)}] + k_{17}[t\text{-BuOH}] \qquad (1)$$

(Φ) is given by eq 2. $\Phi = 0.534$ was calculated from A_∞, $[R]_0$,

$$\Phi = \frac{k_{12}[\text{Ru(III)}]}{k_{12}[\text{Ru(III)}] + k_{17}[t\text{-BuOH}]} \qquad (2)$$

$\epsilon = 1.15 \times 10^4$ M⁻¹ cm⁻¹, and $l = 2$ cm. Solving eq 2 for k_{17} and substituting into eq 1 gives eq 3. From eq 3 we obtain

$$k_{obsd} = \frac{k_{12}[\text{Ru(III)}]}{\Phi} \qquad (3)$$

$k_{12} = 4.85 \times 10^8$ M⁻¹ s⁻¹. Using this value in eq 1 we have $k_{17} = 8.5 \times 10^4$ M⁻¹ s⁻¹; this is within the range of values for k_{17} reported by others, but since our data are so limited, we should only give k_{12} as about 5×10^8 M⁻¹ s⁻¹.

e_{aq}^{-} **+ [Ru(NH₃)₅isn]³⁺.** The rate constant for the reaction of e_{aq}^{-} with Ru(III) was obtained by using competition kinetics. A solution saturated in He at $\mu = 0.1$ M (NaTFMS) and pH 3.14 with 0.5 M *tert*-butyl alcohol and 1.0×10^{-4} M Ru(III) was irradiated. The result was a prompt absorbance increase followed by a first-order absorbance increase. The first-order increase had $k_{obsd} = 6.64 \times 10^4$ s⁻¹ and is attributed to the reaction of H with Ru(III) as described above. The prompt initial absorbance increase is due to reaction of e_{aq}^{-} with Ru(III), competitive with the reaction with H⁺; *tert*-butyl alcohol is at a concentration high enough to ensure that OH radicals will be removed before they can react significantly with Ru(III) (see below). This analysis is expressed by eq 4,

$$\Delta A_{\text{prompt}} = \frac{\epsilon l [e_{aq}^{-}]_0 [\text{Ru(III)}] k_{13}}{k_{13}[\text{Ru(III)}] + k_2[\text{H}^+]} \qquad (4)$$

where ϵ is the molar absorptivity of Ru(II) and l is the optical path length. Since $[R]_0 = 4.4 \times 10^{-6}$ M and $\Delta A_{\text{prompt}} = 7.5 \times 10^{-3}$, $k_{13} = (2.8 \pm 0.3) \times 10^{10}$ M⁻¹ s⁻¹ (average of two determinations).

OH + [Ru(NH₃)₅isn]³⁺. The reaction of OH with Ru(III) was observed at pH 3.43 and $\mu = 0.1$ M (NaTFMS) with 3.0×10^{-4} M Ru(III) in an N₂O-saturated solution (0.02 M).[18] Under these conditions about 92% of e_{aq}^{-} is converted to OH, the remainder reacting with H⁺ and Ru(III); thus OH is the predominant radical. A pulse with $[R]_0 = 4.4 \times 10^{-6}$ M resulted in a first-order absorbance increase with $k_{obsd} = 3.52 \times 10^6$ s⁻¹. This was followed by a slow further increase which

we assign to the reactions of the intermediate resulting from the interaction of OH with Ru(III); with our limited data, it could be fit to both first- and second-order kinetics. The first-order fit gave $k'_1 = 2.22 \times 10^3$ s⁻¹, and the second-order fit gave $(k'_2/\epsilon) = 5.78 \times 10^4$ cm s⁻¹.

The rapid initial reaction was that of OH with Ru(III). The pseudo-first-order value of k_{obsd} results in a value for k_{11} of 1.2×10^{10} M⁻¹ s⁻¹, and thus reaction of OH with Ru(III) appears to be diffusion controlled. Using $[R]_0$ and $A_\infty = 8.28 \times 10^{-2}$ for the initial reaction and correcting the absorbance for Ru(II) which arises from scavenging of e_{aq}^{-} by Ru(III) give $\epsilon = 9.95 \times 10^3$ M⁻¹ cm⁻¹ for X, the immediate product of the OH reaction with Ru(III). With this value for ϵ we then have $k'_2 = 5.8 \times 10^8$ M⁻¹ s⁻¹.

The intermediate X, which, from the fact that the absorbance at 480 nm is so strong, is judged to contain Ru(II) rather than Ru(III), may result from OH addition to a 2 or 3 position on the aromatic ring with concomitant reduction of Ru³⁺ to Ru²⁺. If this is the case, the slow subsequent reaction could correspond to proton loss from the carbon to which OH attached itself or to electron transfer between X and excess Ru(III). Regardless of the nature of the intermediate, it is of interest that OH reacts so rapidly with [Ru(NH₃)₅isn]³⁺ compared to free isn (k reported as 1.3×10^9 M⁻¹ s⁻¹)[19] or to [Co(NH₃)₅isn]³⁺ (k reported to be even slower by a factor of 2).[20] The enhanced reactivity of the Ru(III) complex may be due to the operation of a concerted two-electron mechanism long sought in the field of induced electron transfer.[21]

CO_2^{-} **+ Ru(III).** The reaction of the carboxyl radical with Ru(III) was followed at pH 4.87 (formate buffer) and $\mu = 0.10$ M with 1.0×10^{-4} M Ru(III) in N₂O-saturated solution. Subsequent to a pulse generating $[R]_0 = 5.15 \times 10^{-6}$ M, a first-order absorbance increase was observed with $k_{obsd} = 1.04 \times 10^6$ s⁻¹ and $A_\infty = 0.115$. Under these conditions about 99% of the primary radicals are converted to CO_2^{-}, and so k_{obsd} is the pseudo-first-order rate constant for the reaction of CO_2^{-} with Ru(III). That this reaction gives Ru(II) is confirmed by calculating the effective product extinction coefficient; this gives $\epsilon = 1.12 \times 10^4$ M⁻¹ cm⁻¹ which may be compared to $\epsilon = 1.15 \times 10^4$ M⁻¹ cm⁻¹ for authentic Ru(II). Dividing k_{obsd} by [Ru(III)] gives a value of $(1.04 \pm 0.02) \times 10^{10}$ M⁻¹ s⁻¹ for k_{14} (average of two determinations), and this is a little less than diffusion controlled for this charge type. In general, reductions of metal ions by the strongly reducing carboxyl radical ($E^0 \approx -1.8$)[22] have been little investigated.[23] [Ru(NH₃)₅isn]³⁺ apparently reacts more rapidly with CO_2^{-} than any metal ion yet reported; this is not surprising since Ru(III) is the strongest oxidant yet investigated.

O_2^{-} **+ Ru(III).** The reaction of superoxide with Ru(III) was investigated in O₂-saturated solutions of formate buffer at $\mu = 0.10$ M. The Ru(III) concentration was varied from 1×10^{-4} to 1×10^{-3} M, and the pH was varied from 4.9 to 3.3. Upon irradiation with a pulse of $[R]_0 \approx 4.6 \times 10^{-6}$ M, there was a prompt absorbance increase on the μs time scale; this was followed by a first-order absorbance increase. Qualitatively, the extent of the prompt change was found to increase

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Table I. Derived Rate Constants[a]

$[Ru(NH_3)_5isn]^{3+} + H \rightarrow [Ru(NH_3)_5isn]^{2+} + H^+$	$k_{12} = 5 \times 10^8$
$[Ru(NH_3)_5isn]^{3+} + e^- \rightarrow [Ru(NH_3)_5isn]^{2+}$	$k_{13} = (2.8 \pm 0.3) \times 10^{10}$
$[Ru(NH_3)_5isn]^{3+} + OH \rightarrow X$	$k_{11} = 1.2 \times 10^{10}$
$[Ru(NH_3)_5isn]^{3+} + CO_2^- \rightarrow [Ru(NH_3)_5isn]^{2+} + CO_2$	$k_{14} = (1.04 \pm 0.02) \times 10^{10}$
$[Ru(NH_3)_5isn]^{3+} + HC(OH)_2 \rightarrow [Ru(NH_3)_5isn]^{2+} + HCO_2H + H^+$	$k_{15} \approx 7.5 \times 10^8$
$[Ru(NH_3)_5isn]^{3+} + HO_2 \rightarrow [Ru(NH_3)_5isn]^{2+} + H^+ + O_2$	$k_{20} < 2.0 \times 10^6$
$[Ru(NH_3)_5isn]^{3+} + O_2^- \rightarrow [Ru(NH_3)_5isn]^{2+} + O_2$	$k_{19} = (2.18 \pm 0.19) \times 10^8$
$[Ru(NH_3)_5isn]^{2+} + HO_2 \rightarrow [Ru(NH_3)_5isn]^{3+} + HO_2^-$	$k_{21} = (9.07 \pm 0.54) \times 10^6$
$[Ru(NH_3)_5isn]^{2+} + HO_2 + H^+ \rightarrow [Ru(NH_3)_5isn]^{3+} + H_2O_2$	$k_{22} < 5.7 \times 10^6$ [b]
$[Ru(NH_3)_5isn]^{2+} + OH \rightarrow [Ru(NH_3)_5isn]^{3+} + OH^-$	$k_{23} \approx 1.4 \times 10^{10}$

[a] $\mu = 0.10$ M; room temperature $\approx 23 \pm 2\,^\circ$C. Rate constants are in $M^{-1}\,s^{-1}$. [b] Units are $M^{-2}\,s^{-1}$.

Table II. Rate Data for $[Ru(NH_3)_5isn]^{3+}$ + Superoxide[a]

[Ru(III)], M	pH	$10^6[R]_0$, M	$10^2\Delta A_{prompt}$	$10^2\Delta A_{calcd}$	k_{obsd}, s^{-1}	k_{calcd}, s^{-1}
1.0×10^{-4}	3.84	4.27	1.61	1.73	2.79×10^3	2.59×10^3
6.0×10^{-4}	3.89	4.80	5.70	5.56	1.71×10^4	1.72×10^4
1.0×10^{-3}	3.86	4.71	6.79	6.52	2.84×10^4	2.71×10^4
1.0×10^{-4}	4.86	4.74	1.76	2.08	1.12×10^4	1.29×10^4
3.0×10^{-4}	4.91	4.71	3.56	4.27	3.95×10^4	4.06×10^4
6.0×10^{-4}	4.83	4.55	5.54	5.68	7.97×10^4	7.54×10^4
1.0×10^{-3}	4.87	4.49	6.42	6.69	1.30×10^5	1.30×10^5
3.0×10^{-3}	3.35	4.77	3.71	3.74	2.40×10^3	2.72×10^3
3.0×10^{-3}	4.35	4.71	3.95	4.13	1.84×10^4	2.00×10^4

[a] $\mu = 0.1$ M (formate), $[O_2] = 1.1 \times 10^{-3}$ M, room temperature $\approx 23 \pm 2\,^\circ$C.

Table III. Rate Data for HO_2 + $[Ru(NH_3)_5isn]^{2+}$ [a]

$10^4[Ru(II)]$, M	[Ru(III)], M	$10^5[R]_0$, M	$10^{-3}k_{obsd}$, s^{-1}	$10^{-3}k_{calcd}$, s^{-1}	A_0	10^2A_∞
1.92	8×10^{-6}	4.02	1.69	1.74	1.58×10^{-3}	-2.55
3.84	1.0×10^{-5}	4.02	3.81	3.48	1.85×10^{-3}	-2.19
3.70	2.5×10^{-5}	3.95	2.89	3.35	-2.35×10^{-4}	-2.15
5.80	2.1×10^{-5}	3.97	4.85	5.26	-6.11×10^{-4}	-2.22
5.60	4.1×10^{-5}	3.92	5.95	5.08	-5.67×10^{-4}	-1.84
3.83[b]	1.2×10^{-5}	7.37	3.09	3.47	4.04×10^{-4}	-4.17

[a] $\mu = 0.1$ M (NaTFMS), $[O_2] = 5.5 \times 10^{-5}$ M, $[H_2CO_2] = 0.1$ M, pH 2.35. [b] $\mu = 0.1$ M (HClO$_4$), pH 1.

with increasing [Ru(III)], and the first-order rate constant, k_{obsd}, in the slower phase increased with increasing [Ru(III)] and increasing pH. These effects reflect prompt scavenging of the primary radicals by Ru(III) followed by pseudo-first-order reduction of Ru(III) by O_2^- to give Ru(II) and O_2.

A detailed computer model of the prompt change was undertaken. It was found that the reaction of Ru(III) with H contributed less than 1% of the absorbance change, and so the remaining function was eq 5. The calculation of ΔA_{prompt} was

$$\Delta A_{prompt} = l[Ru(III)]\left\{\frac{\epsilon_x[OH]_0 k_{11}}{\alpha} + \epsilon_{Ru(II)}\left(\frac{k_{13}[e_{aq}^-]_0}{\beta} + \gamma + \delta\right)\right\} \quad (5)$$

$$\alpha = k_{11}[Ru(III)] + k_8[HCO_2^-] + k_7[HCO_2H]$$

$$\beta = k_1[O_2] + k_2[H^+] + (k_3 + k_4)[HCO_2H] + k_{13}[Ru(III)]$$

$$\gamma = \left(\frac{[OH]_0(k_7[HCO_2H] + k_8[HCO_2^-])}{\alpha} + \frac{[H]_0[HCO_2^-]k_6}{k_6[HCO_2^-] + k_5[O_2]}\right)\frac{k_{14}}{(k_{14}[Ru(III)] + k_9[O_2])}$$

$$\delta = \frac{[e_{aq}^-]_0[HCO_2H]k_4 k_{15}}{\beta(k_{15}[Ru(III)] + k_{10}[O_2])}$$

performed by using known values for all of the parameters except for k_{15}, the reaction of Ru(III) with the formyl radical.

k_{15} was adjusted to give the best fit to the observed values of ΔA_{prompt}, and this occurred at $k_{15} = 7.5 \times 10^8$ M^{-1} s^{-1}. Since the calculations were sensitive to k_{15} only at high [HCO$_2$H], the fit at low [HCO$_2$H] was performed essentially with no adjustable parameters. The results are given in Table II. The model predicts ΔA_{prompt} at worst 20% too high, with an average deviation of 8.2%. The fit was good enough to confirm the general features of eq 4, and therefore it confirms the idea that the prompt rise is due to scavenging of the various radicals other than O_2^-.

The formyl radical has not been studied much, and we are not aware of any measurements, other than our indirect estimate mentioned above, of rates of reaction with metal ions. Since it is also generated by the reactions of e_{aq}^- with CO,[14] OH with H_2CO,[14] and perhaps Ce(IV),[24] Cu(II),[25] and W-(CN)$_8^{3-}$[25] with H_2CO, its general significance in chemistry has probably been underestimated. Our results suggest that the formyl radical is a potent reducing agent.

Given the complex pH and [Ru(III)] dependence of the first-order process in the irradiation of Ru(III), the values of k_{obsd} were fitted to eq 6 by the Los Alamos nonlinear least-

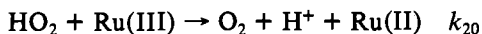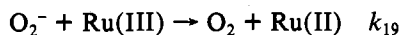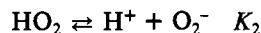$$k_{obsd} = \frac{(k_{19}K_2 + k_{20}[H^+])}{K_2 + [H^+]}[Ru(III)] \quad (6)$$

squares computer program. The optimal fit occurred for $k_{19} = (2.18 \pm 0.19) \times 10^8$ M^{-1} s^{-1}, $k_{20} = -(6.78 \pm 27.6) \times 10^5$

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$M^{-1} s^{-1}$, and $K_2 = (2.01 \pm 0.42) \times 10^{-5}$ M. The negative value and large standard deviation for k_{20} mean that the corresponding path is not statistically defined by this data set; at the 95% confidence level we suggest an upper limit of 5.7×10^6 $M^{-1} s^{-1}$ for k_{20}. Values of k_{obsd} and k_{calcd} are listed in Table III. Rate law 6 is consistent with the following mechanism

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad K_2$$

$$O_2^- + Ru(III) \rightarrow O_2 + Ru(II) \quad k_{19}$$

$$HO_2 + Ru(III) \rightarrow O_2 + H^+ + Ru(II) \quad k_{20}$$

where, in our range of acidity, k_{20} can be neglected.

$HO_2 + Ru(II)$. Oxidation of Ru(II) by perhydroxyl (HO_2) was investigated in 0.1 M formic acid at pH 2.35, $\mu = 0.1$ M (NaTFMS), and $[O_2] = 5.5 \times 10^{-4}$ M. The concentration of Ru(II) was varied from $(2-6) \times 10^{-4}$ M. Under these conditions the generation of HO_2 occurred as in the Ru(III) reactions, with the exception that most of e_{aq}^- reacted with H^+ to form H, which then reacted with O_2 to form HO_2. A series of blanks were run with no added Ru(II) and at 0, 1 $\times 10^{-3}$, 1 $\times 10^{-2}$, and 0.1 M NaTFMS; the absorption at 254 nm due to superoxide showed no dependence on [NaTFMS], and so NaTFMS was assumed to be an inert electrolyte. The experiments in the presence of Ru(II) were of fairly low quality because of photolysis by the analyzing beam and because of noise; noise was a problem because we were observing a small degree of bleaching on top of a rather high absorbance. The results are listed in Table III. With use of the known rates of disproportionation of HO_2,[16] it can be shown that disproportionation was not significant under our conditions. Table III lists concentrations of Ru(II) and Ru(III); these values were calculated from the known rate of autoxidation of Ru(II)[1] and the elapsed time between mixing the solutions and irradiation. Since Ru(III) reacts with superoxide in its deprotonated form, Ru(III) is not expected to affect the values of k_{obsd} at the low prevailing pH.

A least-squares fit of the data in Table III at pH 2.35 to rate law 7 gives $k_{21} = (9.07 \pm 0.54) \times 10^6$ $M^{-1} s^{-1}$. A run

$$k_{obsd} = k_{21}[Ru(II)] \tag{7}$$

performed at pH 1 showed no significant difference in rate; thus we have an upper limit of 2×10^7 $M^{-2} s^{-1}$ for k_{22}, the reaction of HO_2 with H^+ and Ru(II) to give H_2O_2 and Ru(III).

The values of A_∞ in Table III are consistent with $\epsilon = 5.5 \times 10^2$ $M^{-1} cm^{-1}$ at 600 nm, which may be compared with an authentic value of 6.5×10^2 $M^{-1} cm^{-1}$. The slightly low value of ϵ is attributed to a low yield of Ru(III). This can result from the fraction of H which reacts with HCO_2H to give the formyl radical if the formyl radical is a poor oxidant.

Table III also lists values of A_0 calculated from the first-order kinetic fits. A significantly negative value for A_0 would be expected if Ru(II) competed sufficiently with formate and formic acid for OH. Reaction of Ru(III) with CO_2^- would somewhat compensate for this effect. The observed A_0 values are consistent with a value of $(1.4 \pm 0.5) \times 10^{10}$ $M^{-1} s^{-1}$ for k_{23}, the rate constant governing the reaction of OH with Ru(II).

Discussion

The major goal of this work was to test our proposed[1] mechanism for the autoxidation of $[Ru(NH_3)_5isn]^{2+}$ in acidic aqueous solution. From the radiolysis study of the reaction of Ru(III) with O_2^- we have obtained a value of 4.70 ± 0.09 for the pK_a of HO_2, in agreement with Bielski's value of 4.69.[16] Using $E^0 = -0.155$ V for the O_2/O_2^- couple[26] as reported by

(26) Meisel, D.; Czapski, G. *J. Phys. Chem.* **1975**, *79*, 1503.

Table IV. Rate Data for Reductions of HO_2

complex ion	k, $M^{-1} s^{-1}$ [a]	$E°$, V [b]	k_{11}, $M^{-1} s^{-1}$ [c]	k_{22}, $M^{-1} s^{-1}$ [d]
$[Ru(NH_3)_5isn]^{2+}$	9.1×10^6 [e]	0.387 [f]	4.7×10^5 [g]	1.1×10^3
$[Fe(CN)_6]^{4-}$	3×10^4 [h]	0.37 [i]	5×10^3 [j]	5.6×10^{-1}
$[Mo(CN)_8]^{4-}$	5.7×10^4 [k]	0.75 [l]	3×10^4 [m]	2.4×10^5

[a] Rate constant for $HO_2 + M_{red} \rightarrow HO_2^- + M_{ox}$. [b] Reduction potential for M_{ox} vs. NHE; M_{red} is the complex ion listed in the first column. [c] Self-exchange rate for M_{ox}/M_{red}. [d] Self-exchange rate for HO_2/HO_2^- calculated from eq 8. [e] This work. [f] Reference 1. [g] Reference 29. [h] Reference 27. [i] Reference 30. [j] Reference 31. [k] Reference 28. [l] Reference 32. [m] Reference 31a.

Meisel and Czapski and our previously measured value of 1.08×10^{-1} $M^{-1} s^{-1}$ for the reaction of O_2 with Ru(II),[1] we calculate $k = 1.57 \times 10^8$ $M^{-1} s^{-1}$ for the reaction of O_2^- with Ru(III); this may be compared with the rate constant of 2.18×10^8 $M^{-1} s^{-1}$ measured in the present work. Combining the pseudo-second-order rate constant previously obtained for Ru(III) inhibition of the autoxidation of Ru(II) with our rate constant for O_2^- with Ru(III) and the pK_a for HO_2 gives a value of 8.65×10^6 $M^{-1} s^{-1}$ for the rate constant governing reduction of HO_2 by Ru(II); this may be compared with our direct value of 9.07×10^6 $M^{-1} s^{-1}$ for that process. These comparisons constitute good confirmation of the conclusion reached earlier[1] that the first step in the autoxidation of $[Ru(NH_3)_5isn]^{2+}$ is simple bimolecular electron transfer and that in the second step HO_2 is reduced to HO_2^- without involving additional protons in the activated complex.

The potency of superoxide as a reducing agent has been well established, but as an oxidant, its chemistry has been much less explored. Rate constants for the reduction of HO_2 to HO_2^- in an outer-sphere mechanism have been reported for $Fe(CN)_6^{4-}$[27] and $Mo(CN)_8^{4-}$.[28] In Table IV are listed the relevant data. The most striking comparison to be made is that between the $Fe(CN)_6^{4-}$ and $Mo(CN)_8^{4-}$ reactions: the rate constants are almost identical although the redox potentials differ by about 0.4 V. Using eq 8, the cross relation

$$k_{12} = (k_{11}k_{22}K_{eq}f)^{1/2} \qquad \log f = \frac{\log^2 [K_{eq}]}{4 \log (k_{11}k_{22}/Z^2)} \tag{8}$$

of the Marcus theory, we can calculate effective self-exchange rates for the HO_2/HO_2^- couple, k_{22}. These self-exchange rates range over 6 orders of magnitude with the value calculated from the data for the $[Ru(NH_3)_5isn]^{2+}$ reaction intermediate. This departure from the Marcus theory is not understood.[37]

The application of the Marcus theory to reactions of the O_2/O_2^- couple also has some anomalies. In previous work[1] we showed that the theory gave a good description of this couple with a series of Ru(II)/Ru(III) couples using a self-exchange rate of $\sim 10^3$ $M^{-1} s^{-1}$. On the other hand quinone/semiquinone couples suggest[26,34] a much higher self-exchange rate ($\sim 10^8$ $M^{-1} s^{-1}$), and the ferricyanide/ferrocyanide couple implies a much slower self-exchange rate ($\sim 10^{-5}$ $M^{-1} s^{-1}$).[27,35] One may rationalize the rapid quinone

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reactions as involving strong coupling in the activated complex perhaps by direct attack on the ring system, but the slow ferrocyanide reaction seems to imply nonadiabaticity. The autoxidation of $[Co^{II}(sep)]^{2+}$ [36] (sep = sepulchrate) yields a value of 1.3 M^{-1} s^{-1} for the O_2/O_2^- self-exchange rate; this should be interpreted with caution because $Co(sep)^{2+/3+}$ has

not yet been shown generally to obey the Marcus cross relationship.

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(37) Although electrostatic effects render the comparison with Ru(II) dubious, the Fe(II)/Mo(IV) comparison does not suffer from this problem.

Affinity of Aquopentaammineruthenium(II) and -(III) for Esters of Amino Acids

ANDREW YEH and HENRY TAUBE*

The paper is concerned with the change in affinity for amines of $Ru(NH_3)_5H_2O^{2+}$ and $Ru(NH_3)_5H_2O^{3+}$ when hydrogen on NH_3 is progressively replaced by alkyl groups. A kinetic method was used to determine the association quotients for Ru(II), and electrochemical measurements then fix those for Ru(III). The equilibrium quotient at 25 °C for the association of Ru(II) with the ligands NH_3, ethyl glycinate, methylamine, and methyl sarcosinate are 3.5 × 10⁴ (earlier work, corrected for the statistical factor), 3.2 × 10³, 3.5 × 10³, and 50 ± 10 M^{-1}, respectively, and for Ru(III) are 3.6 × 10⁵, 5.5 × 10², 3.5 × 10³, and 2.0 M^{-1}. The decrease in affinity for Ru(II) registered when H on ammonia is replaced by an alkyl group is in marked contrast to the effect of the same change when sulfur is the donor atom.

Qualitative observations made by a number of different investigators working in these and perhaps other laboratories have suggested that the affinity of an amine for $Ru(NH_3)_5^{2+}$ decreases when hydrogen in ammonia is replaced by an alkyl group, but no equilibrium quotients have been reported except for NH_3.[1,2] In view of the importance of the polar group NH_2–R in polypeptide and protein chemisty, we felt it to be worthwhile to extend the studies on rates and affinities to primary and other amines.

Experimental Section

Chemicals and Reagents. Distilled water used for kinetic runs was purified by distillation from alkaline permanganate before use. Isonicotinamide (Aldrich) was purified by recrystallizing it twice from hot water. Glycine ethyl ester hydrochloride and sarcosine methyl ester hydrochloride were purchased from Aldrich Chemical Co. and United States Biochemical Corp., respectively. They were used without further purification. $[Ru(NH_3)_5Cl]Cl_2$ was prepared according to the method described by Vogt et al.[3] All other chemicals were reagent grade and were used as received.

Preparation of Pentaammineruthenium(II) Complexes. $[Ru(NH_3)_5NH_2CH_2CO_2C_2H_5](PF_6)_2$[4] and $[Ru(NH_3)_5NH_2CH_3](PF_6)_2$[5] were prepared according to the cited literature methods.

Electrochemical Measurement. Reduction potentials of the complexes were measured on a Princeton Applied Research Model 173 potentiostat and Model 175 Universal Programmer system. Platinum was used in the working and counter electrodes; the saturated calomel was used as a reference electrode. The concentration of the complexes was kept at ∼ 1 × 10⁻³ M, and the ionic strength was maintained at μ = 0.10 (LiCl). Reversible behavior was observed in all cases at a scan rate of 100 mV s^{-1}.

Kinetic Measurements. All the kinetic runs were followed by using a Beckman Acta MVII recording spectrophotometer. Temperatures

Table I. Reaction of Ethyl Glycinate with $Ru(NH_3)_5OH_2^{2+}$ [a]

pH	10^2[isn], M	10^2[EG],[b] M	10^3k_{obsd}, s^{-1}
9.48	0.983	0.605	1.69
9.73	1.10	0.818	1.87
9.57	1.12	1.06	2.14
9.61	1.02	1.23	2.33

[a] $[Ru(NH_3)_5OH_2^{2+}]$ = (1.0–1.5) × 10⁻⁴ M, μ = 0.10 (LiCl), T = 25 °C. [b] EG = ethyl glycinate ester.

of the experiments were controlled by a Haake FK2 temperature bath. $Ru(NH_3)_5OH_2^{2+}$ solutions were prepared by dissolving $Ru(NH_3)_5Cl^{2+}$ in water and then reducing with zinc amalgam under argon for 20 min. In measuring the rate constants for the formation of amino acid complexes, the competition method[2] was adopted, using isonicotinamide as the competitor ligand. The pH of the solution was adjusted to between 9 and 10 with 4 M NaOH and the ionic strength maintained at μ = 0.10 with lithium chloride. The resulting solution was monitored at λ = 478 nm, the band maximum of isonicotinamide complex, until no further change in absorbance was observed. Isonicotinamide was chosen as scavenger also in the aquation experiments, and the rates were obtained by measuring the formation of isonicotinamide complex. Because of the slow rate of aquation, side reactions interfere toward the end of the reaction, and accordingly the calculated value of A_∞, based on the measured extinction of 11.9 × 10³ M^{-1} cm^{-1} [1] at λ = 478 nm, was used in the analysis of the data on the aquation of ethyl glycinate and methylamine complexes.

The reactions for these systems are very sensitive to oxygen. The oxygen problem becomes even more serious in the study of kinetics of formation because of the instability of the amineruthenium complexes in the basic solution[6] required for the formation reactions. To minimize interference by oxygen, we used the Zwickel reaction flask[7] and syringe technique[8] for transfers throughout in the reactions. Small amounts of ascorbic acid[9] were added to the reaction mixtures

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