and

$$F = [VOL]\alpha_1 + [H^+]\alpha_3 \qquad (16)$$

The α_1, α_2, and α_3 terms were previously defined by eq 8, 9, and 10, respectively. Plots of $1/\tau D$ vs. F/D yielded straight lines with intercepts equal to k_f and slopes equal to k_r with the equalities $K_c = k_1/k_{-1}$ and $K_c/K_{OH} = k'_1/k'_{-1}$, the equilibrium constant $K_c = [VOL][H^+]/[VO^{2+}][HL^-]$ can be calculated from the ratio k_f/k_r.

Registry No. VO^{2+}, 20644-97-7; vanillomandelic acid, 55-10-7; mandelic acid, 90-64-2; thiolactic acid, 79-42-5.

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Reduction of Hydrogen Peroxide by Ruthenium(II) Ammine Complexes: The Surprisingly Identical Mechanism for $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5OH_2^{2+}$, and $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$

FRANK J. KRISTINE, CRAIG R. JOHNSON, STEPHEN O'DONNELL, and REX E. SHEPHERD*

Received October 24, 1979

In phosphate buffer (pH 6.86) the reductions of H_2O_2 by $Ru(NH_3)_6^{2+}$, $Ru(NH_3)_5OH_2^{2+}$, or $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ (1-CH_3imH = 1-methylimidazole) all exhibit a first-order dependence in $[Ru(NH_3)_5L^{2+}]$ and a saturation dependence in $[H_2O_2]$. The activation parameters for the three systems using $Ru(NH_3)_5L^{2+}$ reductants are nearly identical: L = NH_3, $\Delta H^{\ddagger} = 5.87 \pm 1.27$ kcal/mol, $\Delta S^{\ddagger} = -41.9 \pm 4.3$ eu; L = H_2O, $\Delta H^{\ddagger} = 5.32 \pm 0.36$ kcal/mol, $\Delta S^{\ddagger} = -36.8 \pm 1.2$ eu; L = 1-CH_3imH, $\Delta H^{\ddagger} = 5.46 \pm 0.48$ kcal/mol, $\Delta S^{\ddagger} = -50.6 \pm 1.6$ eu. A common two-electron redox mechanism is proposed in which a distorted structure $Ru(NH_3)_5L^{2+*}$, which has a substantial interaction with at least one solvent molecule, adds H_2O_2 as a seventh ligand to promote electron transfer. Comparisons are made to the two-electron pathway for the $Ru(NH_3)_6^{2+}/O_2$ system studied previously by Taube et al. In the range of $[H_3O^+]$ between 0.010 and 0.500 M the rate becomes zero order in $[Ru(NH_3)_5L^{2+}]$ (only L = NH_3 was studied in detail) and the rate proceeds by $[H_3O^+]$-independent and $[H_3O^+]$-dependent paths. Rates in 0.050 M acetate buffer (pH 4.6) are more rapid than predicted by H_3O^+ catalysis alone. The catalysis by H_3O^+ and complexing ligands is attributed to monomeric or labilized Fe(III) complexes. The iron is present at impurity levels from the reagents and electrolytes. The polymeric iron species, present in the phosphate buffer domain, are not catalytic. However, monomerization by H_3O^+ or complexation of the impurities by acetate ion or $edta^{4-}$ converts the iron species into catalytically active forms. The active iron catalysts allow a facile inner-sphere pathway for the reduction of H_2O_2 since the electron transfer between $Ru(NH_3)_5L^{2+}$ and the Fe(III) complexes is rapid. For the noncatalyzed pathway, first order in $Ru(NH_3)_5L^{2+}$, the symmetry advantage of O_2 as an oxidant is compensated by the larger free energy change with H_2O_2 as an oxidant such that at low concentrations of O_2 and H_2O_2, $k_{O_2} \simeq 10^2 k_{H_2O_2}$.

Introduction

The reduction of H_2O_2 by metal centers having labile coordination sites is generally about 10^4 times faster than when H_2O_2 is restricted to an outer-sphere role.[1] The inner-sphere pathway remains the preferred pathway for reduction even when the overall driving force is very large, as for example with $Cr(CN)_6^{4-}$.[2] The reduction of H_2O_2 by simple aquo transition-metal reductants ($Cr(H_2O)_6^{2+}$, $Fe(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$) proceeds predominantly by one-electron paths with hydroxyl radical (HO·) as the initial product.[3-5]

We have begun to examine the mode of reactivity of H_2O_2 with complexes of the iron triad family. The oxidation of $(CN)_5Fe(Him)^{3-}$ (Him = imidazole) by H_2O_2 is much more rapid than for $Fe(CN)_6^{4-}$. Dissociation of the imidazole ligand from $(CN)_5Fe(Him)^{3-}$ followed by substitution of H_2O_2 on the $Fe(CN)_5^{3-}$ center limits the electron-transfer step, generating HO·.[6] It is also known that photodissociation of CN^- from $Fe(CN)_6^{4-}$ accelerates the $H_2O_2/Fe(CN)_6^{4-}$ reaction.[7] The parallels between the spectral properties and chemical reactivities of the $(CN)_5FeL^{3-}$ and $(NH_3)_5RuL^{2+}$ complexes (L = aromatic heterocyclic ligand) have been well documented.[8-10] The question arose as to whether the Ru(II) systems behave the same (via HO·) or whether a two-electron path is used for Ru(II). Pladziewicz, Meyer, Broomhead, and Taube have reported on the oxidation of $Ru(NH_3)_6^{2+}$ by O_2.[11,21] The evidence concerning the $Ru(NH_3)_6^{2+}/O_2$ system

---

(1) (a) L. E. Bennett, *Prog. Inorg. Chem.*, **18**, 1 (1973). (b) References cited in 1a. (c) The outer-sphere pathway has a less favorable driving force of 5.3 kcal/mol if other factors are equal because three particles are being formed outer-sphere instead of two by the inner-sphere path (cf. ref 2).

(2) G. Davies, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **92**, 1892 (1970).

(3) (a) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959); (b) A. Samuni, D. Meisel, and G. Czapski, *J. Chem. Soc., Dalton Trans.*, 1273 (1972).

(4) (a) T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965); (b) C. Walling, *Acc. Chem. Res.*, **8**, 125 (1975), and references therein.

(5) (a) W. A. Armstrong, *Can. J. Chem.*, **47**, 3737 (1969); (b) L. J. Csanyi, F. Csek, and F. Szil, *Acta Chim. Acad. Sci. Hung.*, **75**, 1 (1972); cf. *Chem. Abstr.* **78**, 48497*e* (1973); (c) F. J. Kristine and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 132 (1980).

(6) M. L. Bowers, D. Kovacs, and R. E. Shepherd, *J. Am. Chem. Soc.*, **99**, 6555 (1977).

(7) (a) B. Lal, *Curr. Sci.*, **16**, 118 (1947); (b) J. H. Baxendale, *Adv. Catal.*, **4**, 31 (1952); (c) G. Davies and A. R. Garafalo, *Inorg. Chem.*, **15**, 1101 (1976).

(8) (a) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1293 (1973); (b) *ibid.*, **12**, 2080 (1973); (c) H. E. Toma, J. M. Malin, and E. Giesbrecht, *ibid.*, **12**, 2084 (1973); (d) R. C. Koch and J. M. Malin, *ibid.*, **17**, 752 (1978); (e) H. E. Toma and J. M. Malin, *ibid.*, **13**, 1773 (1974).

(9) (a) H. E. Toma and P. S. Santos, *Can. J. Chem.*, **55**, 3549 (1977); (b) H. E. Toma and C. Creutz, *Inorg. Chem.*, **16**, 545 (1977).

(10) R. Ernhoffer and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 859 (1978).

(11) J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, **12**, 639 (1973).

0020-1669/80/1319-2280$01.00/0

supports the interaction of O_2 through the face of the octahedral $Ru(NH_3)_6^{2+}$ complex with the reduction of O_2 proceeding by a two-electron path.[11,21] The two-electron reduction product of O_2 is H_2O_2. The formation of H_2O_2 could have been a troublesome competitive oxidant in the $Ru(NH_3)_6^{2+}/O_2$ study. The Taube group was unsuccessful in attempts to study the intrinsic $Ru(NH_3)_6^{2+}/H_2O_2$ reaction because of catalysis attributed to $\leq 4 \times 10^{-7}$ M iron impurities in the reagents.[11] The catalysis by Fe(II)/Fe(III) cycles imposes zero-order kinetics on the system. We have succeeded in circumventing the catalysis caused by metal ion impurities by studying the H_2O_2 oxidation of $(NH_3)_5RuL^{2+}$ complexes (L = NH_3, H_2O, 1-methylimidazole) in phosphate buffer. Under these conditions a first-order rate with respect to $(NH_3)_5RuL^{2+}$ is obtained. The reduction of H_2O_2 by $(NH_3)_5RuL^{2+}$ complexes apparently proceeds by a two-electron pathway even for $(NH_3)_5RuH_2O^{2+}$, which has a labile position available for substitution by H_2O_2. For $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ the interaction with H_2O_2 must occur at a position other than the primary coordination positions. These interesting studies are the subject of this report. Under conditions comparable to the $Ru(NH_3)_6^{2+}/O_2$ study, a calculated second-order value for $k_{H_2O_2}$ with $Ru(NH_3)_6^{2+}$ (2.0 $M^{-1}\ s^{-1}$) shows that the H_2O_2 reaction would be only a 2% correction to the O_2 studies of Taube's group in agreement with their conclusion that k_{O_2} (126 $M^{-1}\ s^{-1}$) $\gg k_{H_2O_2}$.[21]

Experimental Section

Reagents. $Ru(NH_3)_6Cl_3$, obtained from Matthey-Bishop Co., was purified by the normal recrystallization procedures from HCl after extractions with acetone.[12] Solutions of $Ru(NH_3)_6^{2+}$ were prepared by reduction of $Ru(NH_3)_6^{3+}$ solutions over Zn/Hg.[13] The blanketing gas was Ar, purged of O_2 by passing the Ar through Cr(II) bubblers. Manipulations were carried out by gastight syringe techniques using Pt needles to avoid contact with sources of Fe impurities. $[Ru(NH_3)_5Cl]Cl_2$ was prepared by refluxing the hexaamine complex in HCl.[14] Solutions of $(NH_3)_5RuOH_2^{2+}$ were prepared by the Zn/Hg reduction of $(NH_3)_5RuCl^{2+}$ under Ar. Solutions of $(NH_3)_5Ru(1\text{-}CH_3imH)^{2+}$ were produced by the reaction of $Ru(NH_3)_5OH_2^{2+}$ with a 50-fold excess of 1-methylimidazole (1-CH_3imH). About 2 h was allowed for the removal of $Ru(NH_3)_5OH_2^{2+}$ forming $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$.[15] The H_2O_2 titre was determined by titration of ~1 M H_2O_2 solution with primary standard $Ce(NH_4)_2(SO_4)_3$ in 0.5 M H_2SO_4. Phosphate buffers were prepared from premixed buffer salt packages available from Fisher Scientific. Acetate buffers were prepared from NaOH titration of glacial acetic acid. Ionic strength was maintained with analytically pure NaCl.

Kinetic Studies. The Ru(II) oxidations by H_2O_2 were followed in the optical beam of a Durrum D-110 (Dionex) stopped-flow device. The flow path and cell compartment were disassembled and presoaked with HCl followed by 0.10 M H_2edta^{2-} solution for 2 days. After reassembly of the stopped-flow unit, the cell path and barrels were soaked overnight and stored with 0.1 M H_2edta^{2-} solution. The H_2edta^{2-} soaking solution was removed by multiple rinses with Ar-saturated distilled deionized water immediately prior to filling the barrels with $(NH_3)_5RuL^{2+}$ and H_2O_2 reagents. The photomultiplier output was sampled in a digital fashion for storage directly into the memory of a DEC 11/03 minicomputer. Appropriate programs on floppy disks were used for the first-order analysis of absorbance vs. time data. Two runs were averaged per data set. The disappearance of the Ru(II) complex was followed at 300 nm for both the $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$ reductants while the appearance of the Ru(III) complex, $Ru(NH_3)_5(1\text{-}CH_3imH)^{3+}$, was monitored when $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ was the reductant. The agreement in kinetic constants was within ±2% comparing runs made on the same stock solutions. Kinetic runs were made as rapidly as possible, consistent with thermal equilibration of the reagents in the stopped-flow barrels. This was done to minimize the loss of Ru(II) reagents to O_2 which diffuses slowly into the barrel storage and cell system and to minimize accumulation of O_2 via the thermal decomposition of H_2O_2 in the other reactant barrel. Reproducibility was confirmed by several separate preparations of Ru(II) reagents reacted with various H_2O_2 solutions on different days; rate constants determined on different days agreed within a factor of 2. The variance in the data may be related to a minor catalytic component due to fluctuations in the level of Zn^{2+} and therefore indirectly on the amount of free H_2edta^{2-} as described in the catalysis section. The rate uncertainty prompted the determination of activation parameters on several days. The rates of various temperatures under saturation conditions gave comparable values of $\Delta H^\ddagger$; the uncertainties in the values are accumulated largely in the $\Delta S^\ddagger$ term. Activation parameters measured on different days gave values in agreement to 0.6 kcal/mol and ca. 2 eu. Activation rate parameters were obtained by the Eyring rate theory method.

Product Analysis. The amount of $Ru(NH_3)_2OH_2^{2+}$ present in solutions of $Ru(NH_3)_6^{2+}$, generated over Zn/Hg, was checked by sampling the $Ru(NH_3)_6^{2+}$ stock solution and injecting into 2-methylpyrazine (1.0 M). The amount of $Ru(NH_3)_5OH_2^{2+}$ with time was then detected by the formation of the 2-methylpyrazine complex (ϵ 1.34 × 10^4, 472 nm). The amount of $Ru(NH_3)_5OH_2^{2+}$ produced during the time taken to generate the $Ru(NH_3)_6^{2+}$ and to collect all stopped-flow data for the $Ru(NH_3)_6^{2+}$ reductant was less than 4% of the total Ru(II) present in the stock $Ru(NH_3)_6^{2+}$ solution. The product of the $Ru(NH_3)_6^{2+}/H_2O_2$ reaction was shown to be $Ru(NH_3)_6^{3+}$ by the observation that no slower reaction was detected in the range of 350–500 nm for the oxidized solutions. By contrast $Ru(NH_3)_5OH_2^{3+}$ and $Ru(NH_3)_5(1\text{-}CH_3imH)^{3+}$ produced a changing spectrum in this region within 30 min. These absorbance changes are attributable to formation of binuclear Ru^{III} and $Ru^{III}Ru^{IV}$ species. Since no reaction occurs for the $Ru(NH_3)_6^{2+}/H_2O_2$ product, we infer that all coordination positions are retained by NH_3 in the Ru(III) product. The initial Ru(III) product of the $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}/H_2O_2$ was shown to be $Ru(NH_3)_5(1\text{-}CH_3imH)^{3+}$ from its spectrum.[20]

Light Intensity Effect. No apparent photochemical enhancement of the observed rate constants for the $Ru(NH_3)_6^{2+}/H_2O_2$ reaction was detected. Rates were the same within experimental error at 0.30- or 3.0-mm slit width while the lamp intensity through the flow cell is increased approximately a factor of 2 at 3.0 mm over 0.30 mm.

Results and Discussion

$H_2O_2/Ru(NH_3)_6^{2+}$ Reaction. Pladziewicz, Meyer, Broomhead, and Taube previously attempted to study the $Ru(NH_3)_6^{2+}/H_2O_2$ reaction as a supportive study to the $Ru(NH_3)_6^{2+}/O_2$ system which these experimentalists examined in detail.[11] The conclusions for the O_2 reaction with Ru(II)-saturated ammine complexes are useful to understanding our observations with the $Ru(NH_3)_6^{2+}/H_2O_2$ system.

Taube's study of the O_2 reaction yielded activation parameters of $\Delta H^\ddagger = 11.5 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -10.4 \pm 1.0$ eu for $Ru(NH_3)_6^{2+}$ and 12.1 ± 0.4 kcal/mol and −9.5 ± 1.4 eu for $Ru(en)_3^{2+}$. Taube et al. proposed the mechanism given in Scheme I in which a Ru(IV) species is generated.[11,21]

Scheme I

$$Ru(NH_3)_6^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru^{IV}(NH_3)_6O_2^{2-}]^{2+} \qquad (1)$$

$$[Ru(NH_3)_6O_2]^{2+} + Ru(NH_3)_6^{2+} \xrightarrow[\text{fast}]{2H^+} H_2O_2 + 2Ru(NH_3)_6^{3+} \qquad (2)$$

We undertook the H_2O_2 studies which had troubled the Taube studies. The intrinsic reaction of H_2O_2 and $Ru(NH_3)_6^{2+}$ in pH 6.86 (phosphate) or 7.0 (imidazole) buffers shows a saturation rate dependence in $[H_2O_2]$ and a first-order dependence in $[Ru(NH_3)_6^{2+}]$ (Table I). The stoichiometry requires that k_{obsd} for the disappearance of Ru(II) or for the formation of Ru(III) be divided by 2. The graphical analysis of $1/[k_{obsd}/2]$ vs. $1/[H_2O_2]$ is an excellently straight line of slope 0.486 ± 0.017 Ms and intercept 4.89 ± 1.14 s. A tem-

---

[12] J. N. Armor, "University Microfilms", Ph.D. Thesis, Stanford University, 1970.

[13] R. E. Shepherd, "University Microfilms", Ph.D. Thesis, Stanford University, 1971; cf. ref 15.

[14] L. H. Vogt, J. L. Katz, and S. B. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

[15] R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12**, 1392 (1973).

Table I. Saturation of the $Ru(NH_3)_5L^{2+}/H_2O_2$ Reaction

L	$10^2[H_2O_2]$	10^2k_{obsd}, s^{-1}
NH_3[a]	0.760	2.93
	1.54	5.22
	3.02	9.03
	5.00	14.3
	10.2	24.2
1-CH_3imH[b]	26.2	2.73
	14.2	3.08
	4.34	1.39
	2.17	0.775
	1.18	0.330
H_2O[c]	0.414	127
	0.414	137
	0.840	224
	1.35	331
	2.73	594
	5.05	894

[a] $[Ru(NH_3)]_6^{3+} = 9.35 \times 10^{-4}$; $\mu = 0.105$ (NaCl/phosphate); $T = 25.2$ °C. [b] $[Ru(NH_3)_5(1\text{-}CH_3im^{2+})] = 1.01 \times 10^{-3}$ M; $\mu = 0.100$ (NaCl/phosphate); $T = 25.3$ °C; $[1\text{-}CH_3im] = 5.0 \times 10^{-2}$. [c] $[Ru(NH_3)_5(H_2O)^{2+}] = 1.0 \times 10^{-3}$; $\mu = 0.101$ (NaCl/phosphate); $T = 25.2$ °C.

Table II. Temperature Dependence Data for the $(NH_3)_5RuL^{2+}/H_2O_2$ Reaction under Saturation Conditions in H_2O_2

L	T, °C	$k_{obsd}/2$, s^{-1}	T, °C	$k_{obsd}/2$, s^{-1}
NH_3[a,d]	30.8	0.250	15.2	0.166
	25.3	0.215	10.4	0.109
1-CH_3imH[b]	31.0	0.00660	15.5	0.00361
	25.8	0.00560	10.6	0.00334
	20.7	0.00455		
H_2O[c]	30.5	8.60	20.2	6.25
	25.4	7.60	14.9	5.10

[a] 9.24×10^{-4} M $(NH_3)_5RuL^{2+}$; 0.102 M H_2O_2; $\mu = 0.103$; phosphate buffer. [b] 1.06×10^{-3} M $(NH_3)_5RuL^{2+}$; 0.263 M H_2O_2; $\mu = 0.10$; 1-CH_3imH buffer. [c] 2.04×10^{-4} M $(NH_3)_5RuL^{2+}$; 0.201 M H_2O_2; $\mu = 0.103$; phosphate buffer. [d] Values at half-saturation.

perature-dependent study under near saturation in $[H_2O_2]$ over the range of 10.4 °C to 30.8 °C yields activation parameters of $\Delta H^{\ddagger} = 5.87 \pm 1.27$ kcal/mol and $\Delta S^{\ddagger} = -41.9 \pm 4.3$ eu. Temperature-dependent data for all studies are collected in Table II. The value of k_{obsd} for the $Ru(NH_3)_6^{2+}$ reductant is 10^4 too fast to be accounted for via dissociation of NH_3 and inner-sphere H_2O_2 substitution to allow the HO· pathway.[15] Also if the dissociation of ammonia limited the rate, the product would be $(NH_3)_5RuOH^{2+}$; the observed product is $Ru(NH_3)_6^{3+}$, showing that dissociation does not occur in the activation step (cf. Experimental Section). Furthermore, the activation parameters would have been almost 18 kcal/mol for $\Delta H^{\ddagger}$ with a positive entropy of activation for a substitution limited path, analogous to the $(CN)_5Fe(Him)^{3-}$ system.[1,15,16] The data point toward a similar two-electron mechanism to that of the O_2 reaction. We propose Scheme II to account for the saturation effect in H_2O_2. In Scheme II $Ru(NH_3)_6^{2+}*$ represents a distorted $k_j[H_2O_2]$) different from the ground state. The value of $k_{obsd}/2 = k_3k_4[H_2O_2]/(k_3 + k_4[H_2O_2])$ which tends toward k_3 when $k_{-3} \ll k_4[H_2O_2]$.

Scheme II

$$Ru(NH_3)_6^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Ru(NH_3)_6^{2+}* \qquad (3)$$

$$Ru(NH_3)_6^{2+}* + H_2O_2 \xrightarrow{k_4} [Ru(NH_3)_6(O_2H_2)^{2+}] \qquad (4)$$

$$[Ru(NH_3)_6(O_2H_2)^{2+}] + Ru(NH_3)_6^{2+} \xrightarrow[\text{fast}]{2H^+} 2Ru(NH_3)_6^{3+} + 2H_2O \qquad (5)$$

Under saturation conditions, the limiting rate is step k_3. The activation parameters correspond to the reorganization to form $Ru(NH_3)_6^{2+}*$ which can accept a seventh ligand. This mechanism does not differ essentially from Taube's O_2 system (Scheme I) which is a subset case of Scheme II under certain conditions. In O_2-saturated solutions the $[O_2]$ is still 2 orders of magnitude below the onset of saturation with the H_2O_2 system. If the mechanisms are the same with O_2 replacing H_2O_2 in Scheme II, a different rate step k'_4 exists such that $k_{-3} \gg k'_4[O_2]$ obtains. The activation measurements for the $Ru(NH_3)_6^{2+}/O_2$ reaction are then mixed between the rate constants $(k_3k'_4/k_{-3})$ and not k_3 alone. This might account for the 30 eu more positive value of $\Delta S^{\ddagger}$ attributed to the $Ru(NH_3)_6^{2+}/O_2$ reaction.[21] The differences in $\Delta H^{\ddagger}$ would also contain components from (k'_4/k_{-3}).

$H_2O_2/Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ Reaction. Support for this mechanism was also found from the reaction of H_2O_2 with $(NH_3)_5RuL^{2+}$ (L = 1-methylimidazole). A saturation rate law in $[H_2O_2]$ and first-order $[(NH_3)_5RuL^{2+}]$ dependence was again observed (Table I).

The double-reciprocal plot of $(1/(k/2))$ vs. $1/[H_2O_2]$ has a slope 4.60 ± 0.04 Ms and intercept 43.1 ± 9.5 s. Under saturation conditions in H_2O_2 (0.25 M), we determined the activation parameters from data between 10.6 and 31.0 °C to be $\Delta H^{\ddagger} = 5.46 \pm 0.48$ kcal/mol and $\Delta S^{\ddagger} = -50.6 \pm 1.6$ eu. The values for the activation parameters of the $(NH_3)_5Ru(1\text{-}CH_3im)^{2+}$ reductant are very similar to those of the $Ru(NH_3)_6^{2+}/H_2O_2$ system. The nine entropy unit difference in the $\Delta S^{\ddagger}$ could easily be due to differences in solvation for the parent ions and the strained $Ru(NH_3)_6^{2+*}$ and $Ru(NH_3)_5L^{2+*}$ species.

$H_2O_2/Ru(NH_3)_5OH_2^{2+}$ Reaction. Saturation rate data were also obtained for the $(NH_3)_5RuOH_2^{2+}/H_2O_2$ system as shown in Table I. The substitution reactions on $(NH_3)_5RuOH_2^{2+}$ have been thoroughly studied.[15,16] The exchange of H_2O at the labile position occurs at about 5 s^{-1} at 25 °C. The activation parameters for the dissociation of the H_2O molecule are $\Delta H^{\ddagger} = 18.9 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = 7 \pm 5$ eu. These values are significantly different from those determined for the $Ru(NH_3)_6^{2+}/H_2O_2$ and $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}/H_2O_2$ systems. The higher value of $\Delta H^{\ddagger}$ for substitution processes is due to the essentially complete bond rupture in the transition state. The barrier for dissociation of Ru(II)–NH_3 or Ru(II)–(1-CH_3imH) bonds should be larger in $\Delta H^{\ddagger}$ than for dissociation of H_2O. The dissociative nature is confirmed by the positive value of $\Delta S^{\ddagger}$ for loss of H_2O. If $(NH_3)_5RuH_2O^{2+}$ were to react with H_2O_2 with a substitution limited rate, these activation parameters should be observed. Also for the known substitution reactions of $(NH_3)_5RuOH_2^{2+}$ saturation in the substituting ligand has not been observed with ligand concentrations as high as 2 M for CH_3CN.[13,15] The $(NH_3)_5RuOH_2^{2+}/H_2O_2$ system exhibits saturation effects at 100-fold lower levels of H_2O_2.

The plot of $1/(k/2)$ vs. $1/[H_2O_2]$ is again linear with slope of $(5.72 \pm 0.26) \times 10^{-3}$ Ms and intercept 0.149 ± 0.040 s. The intercept is the reciprocal of the rate constant for the rate-limiting step at saturation. The value 6.7 s^{-1} from the intercept is very close to the H_2O-exchange value and could be taken as support for the involvement of H_2O exchange in the redox process. But a substitution reaction with $[H_2O_2] = 5.05 \times 10^{-2}$ M, the highest concentration shown in Table I, should exhibit a $k_{obsd} \approx 5 \times 10^{-3}$ s^{-1} compared to the 10^3 larger constant for the redox process. The value of the limiting rate constant (6.7 s^{-1}) appears to be fortuitously comparable to the first-order water-exchange rate. The activation parameters from 10.5 to 30.5 °C are $\Delta H^{\ddagger} = 5.32 \pm 0.36$ kcal/mol and $\Delta S^{\ddagger} = -36.8 \pm 1.2$ eu. The comparable activation parameters indicate a common redox mechanism for $(NH_3)_5Ru(1$-

---

(16) R. J. Allen and P. C. Ford, *Inorg. Chem.*, **11**, 679 (1972).

Table III. Acceleration of the Zero-Order Path by Protons[a]

$[H_3O^+]$, M	10^6k_{obsd}, Ms^{-1}	$10^4[Ru(NH_3)_6^{2+}]$, M
0.010	4.16	10.3
0.100	4.31	10.3
0.500	5.54	10.3
2.51×10^{-5} [b]	6.55	7.0

[a] HCl; $\mu = 1.0$ (NaCl/HCl); $T = 25.2$ °C; $[H_2O_2] = 0.105$ M. [b] $[HC_2H_3O_2] + [C_2H_3O_2^-] = 0.050$ M; $\mu = 0.10$ ($NaCl/NaC_2H_3O_2$); $[H_2O_2] = 0.103$ M.

$CH_3imH)^{2+}$, $Ru(NH_3)_6^{2+}$, and $(NH_3)_5RuH_2O^{2+}$. The distortion that limits the redox activation step occurs at ca. 0.30 s^{-1} for $Ru(NH_3)_6^{2+}$, 0.023 s^{-1} for $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$, and 6.7 s^{-1} for $Ru(NH_3)_5OH_2^{2+}$. Differences in these numbers are in the order of our intuitive understanding of the abilities of these complexes to undergo bond rupture. The dissociative process is also a crude measure of the ease in reorganizing the structure of the complexes. Since the activation parameters do not match those of ligand dissociation and the observed rate constants are not in agreement with dissociation of either NH_3 or 1-methylimidazole for the $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$ cases, an interaction at the open facial position of the pseudooctahedral Ru(II) complexes is indicated in order to allow for an efficient inner-sphere-like pathway. Reasons to account for the large negative value of ΔS^* are given in a later section.

The slopes of the saturation plots of $1/(k/2)$ vs. $1/[H_2O_2]$ can be used to calculate the ratio k_4/k_{-3}, which reflects the competition of the distorted structure for oxidation by H_2O_2 compared to reversion to the ground-state octahedral complex. The values obtained for k_4/k_{-3} are as follows: H_2O, 26.3 M^{-1}; NH_3, 6.9 M^{-1}; $1\text{-}CH_3imH$, 9.5 M^{-1}. Therefore in the range of $[H_2O_2]$ close to 0.10 M, $k_4[H_2O_2] \approx k_{-3}$, and at saturation $k_{-3} < k_4[H_2O_2]$.

Catalysis Studies. The $Ru(NH_3)_6^{2+}/H_2O_2$ reaction was examined under conditions similar to the Taube group's experiments. In the presence of 0.050 M $C_2H_3O_2^-$/0.050 M $HC_2H_3O_2$ buffer the order of the reaction changed to a zero-order dependence on $[Ru(NH_3)_6^{2+}]$. The amount of iron impurity responsible for the catalysis was not determined. However a marked enhancement occurred upon addition of 1.0×10^{-5} M Fe(II), solubilized as $Fe(edta)^{2-}$, in acetate buffer. The amount of impurity without added $Fe(edta)^{2-}$ is assumed to be much less than 1×10^{-5} M, and the true value is probably comparable to the 10^{-6} M level in the Taube study. The rate provided by the intrinsic impurity level was examined in the range of $[H_3O^+]$ from 0.010 to 0.500 M (HCl). The rate increased linearly with $[H_3O^+]$ according to eq 6 (cf.

$$k_{obsd} = a + b[H_3O^+] \qquad (6)$$

Table III). The values of the coefficients were found to be $a = (4.08 \pm 0.06) \times 10^{-6}$ Ms^{-1} and $b = (2.89 \pm 0.22) \times 10^{-6}$ s^{-1} at $[H_2O_2] = 0.103$ M. Acetate buffer is more efficient as a catalyzing system. At pH 4.6 under comparable conditions, $k_{obsd} = 6.55 \times 10^{-5}$ Ms^{-1} instead of the 4.08×10^{-6} Ms^{-1} calculated from eq 6. This shows that acetate ion has a second effect in addition to the catalysis provided by the $[H_3O^+]$ in acetate buffer. In phosphate buffer the rate could also be enhanced by the addition of H_2edta^{2-} in excess of the amount needed to chelate Zn^{2+} produced during the generation of $Ru(NH_3)_6^{2+}$. The dominant process remains a first-order decay in $[Ru(NH_3)_6]^{2+}$; the catalysis introduces a parallel zero-order path. The effect of chelating ligands and complexing anions (H_2edta^{2-} and $C_2H_3O_2^-$) and the increased effectiveness of higher concentrations of H_3O^+ suggest that monomeric Fe(III) or Fe(II) species are more efficient in the zero-order catalysis of the $Ru(NH_3)_6^{2+}/H_2O_2$ reactions than are the polymeric complexes present in 5×10^{-3} M phosphate buffer or imidazole buffer.

Several experiments were carried out to determine the effect of Ru(III) complexes, $Ru(NH_3)_5L^{3+}$, on the rates. Addition of 1.17×10^{-4} M $Ru(NH_3)_6^{3+}$ to the 1.02×10^{-3} M $Ru(NH_3)_6^{2+}$ reagent caused no effect on the rate within the reproducibility of these experiments. A reversible step between Ru(II) and Ru(III) is eliminated as a mechanistic possibility. Also the back-reaction between Ru(III) with radical intermediates such as $HO_2\cdot$ is an unlikely possibility on these grounds, consistent with the absence of a radical-forming path.[11,17,21] $HO_2\cdot$ is formed by the reaction of $HO\cdot$ and H_2O_2. The reaction of $HO_2\cdot$ with Ru(III) would produce O_2. The absence of evidence for any back-reaction process argues against $HO\cdot$ as being formed in the original reduction step and supports the proposed two-electron path.

Summary of the Mechanisms. Several alternate mechanisms to Scheme II have been considered to explain the behavior of H_2O_2 reductions by $(NH_3)_5RuL^{2+}$ species.[21] Most of these are rejectable on the requirement that the observed rate constant saturates in $[H_2O_2]$. The simple mechanism type of Scheme I would not saturate in H_2O_2. The values for ΔH^* and ΔS^* (under saturation conditions) for the three Ru(II) complexes of this study are ca. 5.5 kcal/mol and ca. −43 eu, respectively. These parameters reflect the activation step k_3 of Scheme II. The large negative values for ΔS^* requires a rather highly organized structure for the distorted species $(NH_3)_5RuL^{2+*}$ (L = NH_3 as a special case in Scheme II). Since this distorted species reacts in the next step with H_2O_2, it is reasonable to assume that H_2O_2 replaces a solvent molecule, forming the seven-coordinate species with H_2O_2 in the first coordination sphere. This interchange of H_2O_2 for H_2O implies that a molecule of solvent in the normal solvation shell is rather strongly bound in the activation process. H_2O_2 would have an advantage over O_2 in the interchange process due to similar H bonding to that of H_2O in the second solvation shell. The loss of rotational and translational entropy for a water molecule originally in the second coordination sphere of the ground-state $(NH_3)_5RuL^{2+}$ complex would contribute ca. −15 eu to the negative value of ΔS^*. The remainder must come from distortion of the complex ($\Delta S^* \approx -30$ eu). In this sense the distortion process is associative in nature, with water serving as a replaceable center for H_2O_2. The modest value for ΔH^* is in keeping with an associative process in which bond making to solvent helps to compensate for the costs of distortion compatible with seven-coordination.

Applying Scheme II with provisos $k_{-3} \gg k'_4[O_2]$ and $k_{-3} \lesssim k_4[H_2O_2]$ below saturation levels in the oxidant species implies $k_{O_2} = k_3k'_4/k_{-3}$ and $k_{H_2O_2} = k_3k_4/(k_{-3} + k_4[H_2O_2])$. The experimental observation that $k_{O_2} \gg k_{H_2O_2}$ with $Ru(NH_3)_6^{2+}$ requires $k'_4/k_{-3} \gg k_4/(k_{-3} + k_4[H_2O_2])$. This suggests that $k'_4 \gtrsim k_4$; e.g., O_2 is the intrinsically more rapid oxidant.

The oxidation mechanism of $Ru(NH_3)_6^{2+}$ by O_2 is understood with the Ru(II) center as a π base with a filled t_{2g}^6 configuration and O_2 as a π acid acceptor. The first empty orbital of H_2O_2 has σ^* symmetry.[18] Therefore the interaction between Ru(II) and π^* levels of O_2 is likely to be stronger than between Ru(II) and the higher energy σ^* level of H_2O_2. Since the Ru(II) reducing center is a π reductant, the rate of reduction of H_2O_2 might be anticipated to be slower under conditions below the saturation limit than for the equivalent concentration of O_2. This prediction is in agreement with the

---

(17) (a) This argument has been presented in ref 11 for O_2^- with $Ru(NH_3)_6^{3+}$ in the O_2 reaction. (b) L. M. Dorman and G. E. Adams, *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*), **NSRDA-NBS 46** (1973).

(18) W. L. Jorgensen and L. Salem, "The Organic Chemists' Book of Orbitals", Academic Press, New York, 1973, p 112.

experimental results even though the predictive tools are based primarily on one-electron-transfer reactions between dissimilar metal centers.[19] At pH 7 the reduction potential of O_2 to H_2O_2 is 0.27 V while the reduction potential of H_2O_2 to H_2O is 1.27 V. The additional driving force for the H_2O_2 reduction must compensate for the symmetry advantage of O_2 as the electron acceptor. The advantage of electron transfer between symmetry matched orbitals is ca. 10^9 between separated metal centers.[19] Only about 0.5 V of driving force in favor of H_2O_2 is needed to compensate for a 10^9 kinetic advantage. Since the electron-transfer step is a two-electron process and therefore non-Marcus in nature, the utilization of only about 50% of the overall 1.0-V advantage of the driving force for H_2O_2 relative to O_2 seems a realistic estimate to bring the observed rates for O_2 and H_2O_2 at equal concentration to within a factor of 10^2.

It is also interesting to note that although the oxidation of $Fe(CN)_6^{4-}$ by H_2O_2 is only about 0.3 V less favorable than $Ru(NH_3)_6^{2+}$ by H_2O_2, the $Fe(CN)_6^{4-}$ reductant fails to utilize the Fe(IV) pathway. Models show that the $M(CN)_6$ moiety is about equally crowded on the face as the $M(NH_3)_6$ unit. The effective availability of the t_{2g}^6 electrons is reduced both by smaller radial extension of the 3d vs. 4d level and by the CN^- ligands. The CN^- ligands compete for the t_{2g}^6 electrons much more than the saturated NH_3 ligands. Distortion to achieve a seven-coordinate structure would be much more costly for CN^- than for NH_3 ligands because of the additional change experienced for the π bonding of CN^- to the metal center. This raises the interesting possibility of finding a coordination sphere for Fe(II) strong enough to cause spin pairing but weak enough to allow for the Fe(IV) pathway in its oxidations by two-electron acceptors.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation through Grant CHE-76-21290 for these studies.

Registry No. H_2O_2, 7722-84-1; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_5OH_2^{2+}$, 21393-88-4; $Ru(NH_3)_5(1\text{-}CH_3imH)^{2+}$, 73697-79-7.

---

[19] (a) S. S. Isied and C. G. Kuehn, *J. Am. Chem. Soc.*, **100**, 6754 (1978); (b) H. Fischer, G. M. Tom, and H. Taube, *ibid.*, **98**, 5512 (1976).

[20] R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).

[21] In the time interval required to publish this manuscript Taube offered an alternative explanation to his earlier data (D. M. Stanbury, O. Haas, and H. Taube, *Inorg. Chem.*, **19**, 518 (1980)). A one-electron path is suggested utilizing O_2^- as an intermediate in the oxidation of RuL_6^{2+}/O_2 and $Ru(en)_3^{2+}/O_2$ reactions reflect the primary outer-sphere electron transfer reaction forming Ru(III) and O_2^- in the first step. We have attempted to derive expressions which involve a similar one-electron transfer from $Ru(NH_3)_6^{2+}$ to H_2O_2 that would account for the saturation dependence in $[H_2O_2]$ reported here. No simple expression that utilized HO· as an intermediate, scavenged competitively by Ru(II) and H_2O_2, was obtained that predicted a rate law other than a simple power in $[H_2O_2]$. It appears that if O_2^- is the proper intermediate in the RuL_6^{2+}/O_2 reactions, as recently supported by new data, the reactivities of O_2 and H_2O_2 with these species are divergent in nature. This is consistent with strikingly different activation parameters, particularly $\Delta S^\ddagger$, as reported here.

Contribution from the Chemistry Department, Faculty of Science,
Tohoku University, Aoba, Aramaki, Sendai, 980, Japan

Kinetic Studies of the Anation and Related Reactions of Aqua(nitrilotriacetato)oxovanadate(IV) in Aqueous Solution

MASATO NISHIZAWA and KAZUO SAITO*

Received October 5, 1979

Nitrilotriacetate (nta^{3-}) gives blue complexes of composition $M[V^{IV}O(nta)H_2O]$ (M = K, Na, and $^1/_2$Ba), which seem to have the tertiary amine trans to the oxo. The aqua ligand is replaced by thiocyanate and azide.

$$[V^{IV}O(nta)H_2O]^- + X^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [V^{IV}O(nta)X]^{2-} + H_2O$$

The kinetic parameters (k_f and k_b for NCS^- and N_3^- are 0.62 and 4.1 $M^{-1}\,s^{-1}$ and 0.17 and 0.48 s^{-1} at 25 °C, respectively, and the corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are 40.5, 53.5, 69.4, and 52.7 kJ mol^{-1} and −112, −52, −25, and −75 J $K^{-1}\,mol^{-1}$, respectively) are very similar to those of the corresponding substitution reactions of the complex $[V^{IV}O(pmida)H_2O]$ ($pmida^{2-}$ = (2-pyridylmethyl)iminodiacetate), and the substitution seems to correspond to the direct basal S_N2 substitution. Nitrite oxidizes the complex to $[V^VO_2(nta)]^{2-}$ through substitution at the basal site for coordinated water and subsequent electron transfer. This vanadium(V) complex replaces the aqua ligand of $[V^{IV}O(nta)H_2O]^-$ to give a deep blue binuclear complex, which has two vanadium ions in 4+ and 5+ oxidation states. Kinetic studies suggest that the same kind of S_N2 substitution with $X^{2-} = [V^VO_2(nta)]^{2-}$ is involved in the formation of the mixed-valence complex.

Introduction

Substitution reactions of oxovanadium(IV) complexes give various rates depending on the site at which the substitution takes place. We have studied the substitution for the aqua ligand in aquaoxo[(2-pyridylmethyl)iminodiacetato]vanadium(IV), $[VO(pmida)H_2O]$, in aqueous solution and found that the direct substitution at the basal site gives very small rate constants ($\simeq 10^{-1}\,s^{-1}$ at 25 °C).[1] The hitherto claimed basal substitution reactions involving unidentate ligands were considered to reflect the rate of a process involving intramolecular rearrangement of the ligand from the apical to basal site of VO^{2+} complexes. With aims of clarifying the reaction further, we have synthesized a new complex $M[V^{IV}O(nta)H_2O]$ (M = Na, K, and $^1/_2$Ba) and studied the replacement of the aqua ligand by $X^- = NCS^-, N_3^-$, and NO_2^-.

$$[VO(nta)H_2O]^- + X^- \rightleftharpoons [VO(nta)X]^{2-} + H_2O \qquad (1)$$

Nitrite ions oxidized the vanadium(IV) to vanadium(V), and the resulting $[V^VO_2(nta)]^{2-}$ also underwent similar substitution for the aqua ligand to give a very characteristic deep blue binuclear complex of the composition $[V_2O_3(nta)_2]^{3-}$. This

---

[1] Nishizawa, M.; Saito, K. *Inorg. Chem.* **1978**, *17*, 3676.

0020-1669/80/1319-2284$01.00/0