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Kinetics and Mechanism of the Reactions of Mononuclear and Binuclear Ruthenium(III) Ammine Complexes with Ascorbic Acid

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Kinetic measurements of the reduction of $Ru_n(NH_3)_{5n}L^{m+}$ complexes (n = 1, L = pyrazine, pyridine, isonicotinamide, m = +3; n = 1, L = methylpyrazinium, m = +4; n = 2, L = pyrazine, m = +5, +6) by ascorbic acid have been carried out at 25 °C, pH 1-3, and ionic strength 0.10 M (maintained with lithium trifluoromethanesulfonate-trifluoromethanesulfonic acid). For each compound the rate law is given by $-d[Ru^{III}]/dt = 2kK_a[Ru^{III}][H_2A]/(K_a + [H^+])$ where $[Ru^{III}]$ is the concentration of the ruthenium(III) complex, $[H_2A]$ is the sum of the concentrations of ascorbic acid and ascorbate monoanion, and K_a is the first acid dissociation constant of ascorbic acid. The rate law is interpreted as a rate-determining reaction between the ruthenium(III) complex and the ascorbate monoanion followed by rapid reaction of the ascorbate radical with the ruthenium(III) complex. With $K_a = 8.3 \times 10^{-5}$, values of k for the complexes in the same order as given above are 3.7×10^4, 3.5×10^2, 4.4×10^3, 1.9×10^8, 4.9×10^3, and 3.5×10^7 M^{-1} s^{-1}. The reaction of $Ru_2(NH_3)_{10}(pyrazine)^{6+}$ produces $Ru_2(NH_3)_5(pyrazine)^{5+}$ as the primary, kinetic product and is, therefore, a one-electron reaction. The reactions are analyzed by means of the Marcus-Sutin treatment of outer-sphere electron-transfer reactions and yield a value of 1×10^6 M^{-1} s^{-1} for the self-exchange rate constant of the ascorbate monoanion/ascorbate radical couple.

We started recently[1-3] a program to study the reactivity of mixed-valence, binuclear complexes. We previously examined the self-exchange reactions of the $Ru_2(NH_3)_{10}pz^{5+/4+}$ and $Ru_2(NH_3)_{10}pz^{6+/5+}$ couples (pz is pyrazine)[2] and the oxidations of $(NC)_5Fe(pz)Ru(NH_3)_5^-$, $Ru_2(NH_3)_5pz^{4+}$, and $Ru_2(NH_3)_{10}pz^{5+}$ by peroxydisulfate.[1,3] In the present paper, we report the results of studies of the reduction of $Ru_2(NH_3)_{10}pz^{6+}$ and of $Ru_2(NH_3)_{10}pz^{5+}$ by the versatile but complicated[4] reducing agent ascorbic acid. We address the question of one- vs two-electron pathways for the $Ru_2(NH_3)_{10}pz^{6+}$-ascorbic acid reaction, and for comparison purposes, we also report the results of studies of the reduction of mononuclear ruthenium(III)ammine complexes.

Experimental Section

Materials. The complex salts $[Ru(NH_3)_5py](PF_6)_2$ (py = pyridine), $[Ru(NH_3)_5pz](PF_6)_2$, $[Ru(NH_3)_5pzCH_3](PF_6)_3$ ($pzCH_3^+$ = methylpyrazinium), $[Ru_2(NH_3)_{10}pz](CF_3SO_3)_5$, and $[Ru_2(NH_3)_{10}pz](CF_3SO_3)_6$ were synthesized for our previous studies.[2] The synthesis of $Ru(NH_3)_5isn^{2+}$ (isn = isonicotinamide) followed the literature procedure[5] except that the complex was isolated as the trifluoromethanesulfonate salt. Trifluoromethanesulfonic acid was purified by two distillations under reduced pressure. Lithium trifluoromethanesulfonate solutions were prepared by mixing stoichiometric amounts of the purified CF_3SO_3H and Li_2CO_3. L-Ascorbic acid (Fisher) was used as received. The purifications of the water and of the nitrogen were described previously.[6]

Kinetic Measurements. Solutions of Ru(III) complexes of the desired concentrations were prepared by oxidation of the corresponding Ru(II) complexes with the stoichiometric amount of peroxydisulfate. These solutions, which also contained the desired amounts of $LiCF_3SO_3$ and/or CF_3SO_3H, were deaerated by flushing with nitrogen and then were mixed in a Durrum 110 stopped-flow apparatus with freshly prepared, deaerated solutions of ascorbic acid containing the desired amounts of $LiCF_3SO_3$ and/or CF_3SO_3H. All measurements were carried out at 25 °C and ionic strength 0.10 M with at least a 10-fold excess of ascorbic acid. The absorbance vs time data (at the wavelength for the absorption maximum in the visible region) were stored in a Nicolet Explorer III oscilloscope interfaced with a PDP 11VO3 computer. Observed first-order rate constants k_{obsd} were obtained by nonlinear least-squares fits of absorbance A_t vs time t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t)$. A_0 and A_∞ are the initial and final absorbances, respectively. Some of the rates for reduction of $Ru(NH_3)_5py^{3+}$ were too slow for the stopped-flow apparatus; therefore, absorbance vs time data were obtained on a Cary 118 recording spectrophotometer. The absorbance vs time analog curves were digitized with a 9864A Hewlett-Packard digitizer and rate constants were calculated (9820A Hewlett-Packard calculator with digitizer interfaced) from a linear least-squares fit of $\ln(A_\infty - A_t)$ to t.

Results and Discussion

Spectrophotometric examination of product solutions showed that the stoichiometries of the reactions under consideration obey eq 1, where H_2A is ascorbic acid, A is dehydroascorbic acid, n

$$2Ru_n(NH_3)_{5n}L^{m+} + H_2A = 2Ru_n(NH_3)_{5n}L^{(m-1)+} + A + 2H^+ \quad (1)$$

= 1 for L = py, pz, isn, and CH_3pz^+, and n = 2 for L = pz. It is noteworthy that the 2:1 stoichiometry applies also to $Ru_2(NH_3)_{10}pz^{6+}$, a potentially two-electron oxidant. The pertinent evidence will be presented in detail below.

Plots of $\ln(A_\infty - A_t)$ vs time were linear for at least 3 half-lives under conditions where $[H_2A] > 10[Ru^{III}]$. The observed rate constants k_{obsd} were found to increase linearly with increasing ascorbic acid concentration at constant $[H^+]$. Therefore, at constant $[H^+]$, the rate law is given by eq 2. The second-order

$$-d[Ru^{III}]/dt = k_2[Ru^{III}][H_2A] \quad (2)$$

rate constants k_2 increase with decreasing hydrogen ion concentration. Some representative plots of k_2 vs $1/(K_a + [H^+])$ are presented in Figure 1. K_a is the first ionization constant of ascorbic acid (eq 4), 8.3×10^{-5} M^{-1} at 25 °C and ionic strength 0.10 M.[7] It will be seen that the plots are linear and have zero intercepts. Therefore, the dependence of k_2 upon $[H^+]$ is given by eq 3. The proposed mechanism to account for these observations, eq 4-8, features the rapid acid dissociation of ascorbic

$$k_2 = k_3/(K_a + [H^+]) \quad (3)$$

$$H_2A \rightleftharpoons H^+ + HA^- \quad \text{rapid equilibrium, } K_a \quad (4)$$

$$Ru^{III} + HA^- \rightarrow Ru^{II} + HA \quad \text{rate-determining, } k_5 \quad (5)$$

$$Ru^{III} + HA \rightarrow Ru^{II} + H^+ + A \quad \text{rapid} \quad (6)$$

$$HA \rightleftharpoons H^+ + A^- \quad \text{rapid equilibrium} \quad (7)$$

$$Ru^{III} + A^- \rightarrow Ru^{II} + A \quad \text{rapid} \quad (8)$$

acid, the rate-determining reaction between the Ru(III) complex and the ascorbate monoanion, and the rapid reaction between the Ru(III) complex and the radical HA and/or the rapid dissociation of HA[4] followed by the rapid reaction between the Ru(III) complex and the radical A^-. According to the mechanism given by eq 4-8, the observed rate constants k_{obsd} are given by eq 9.

$$k_{obsd} = 2k_5K_a[H_2A]/(K_a + [H^+]) \quad (9)$$

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Table I. Rate Constants for Reactions of Ru(III) Complexes with Ascorbate Monoanion at 25 °C[a]

complex	k_5, M^{-1} s^{-1}	$E°$,[b] V	k_{22},[b] M^{-1} s^{-1}	10^8r,[b] cm	k_{calcd},[c] M^{-1} s^{-1}
$Ru(NH_3)_5py^{3+}$ [d]	$(3.53 \pm 0.12) \times 10^2$	0.32	1.1×10^5	3.8	1.4×10^2, 3.8×10^2
$Ru(NH_3)_5pz^{3+}$ [e]	$(3.70 \pm 0.05) \times 10^4$	0.53	1.4×10^4	3.8	8.2×10^3, 1.4×10^4
$Ru(NH_3)_5pzCH_3^{4+}$ [f]	$(1.88 \pm 0.04) \times 10^8$	0.92	3.9×10	3.9	6.2×10^6, 2.2×10^7
$Ru(NH_3)_5isn^{3+}$ [g]	$(4.44 \pm 0.10) \times 10^3$	0.38	1.1×10^5	3.9	6.1×10^2, 1.8×10^3
$Ru_2(NH_3)_{10}pz^{5+}$ [h]	$(4.88 \pm 0.15) \times 10^3$	0.40	6.7×10^3	4.7	3.0×10^3, 8.3×10^3
$Ru_2(NH_3)_{10}pz^{6+}$ [i]	$(3.48 \pm 0.11) \times 10^7$	0.81	1.5×10	4.7	1.1×10^7, 3.5×10^7

[a] Ionic strength 0.10 M maintained with $LiCF_3SO_3$–CF_3SO_3H mixtures. [b] From ref 2. [c] Calculated by taking $E° = 0.71$ V for HA/HA^- couple, radius of $HA^- = 3.5 \times 10^{-8}$ cm, from eq 13–16. First entry, $k_{11} = 1 \times 10^5$ M^{-1} s^{-1}; second entry, $k_{11} = 1 \times 10^6$ M^{-1} s^{-1}. [d] $[H^+] = 1.55 \times 10^{-3}$ to 0.10 M; $[H_2A] = 5.0 \times 10^{-5}$ to 1.00×10^{-2} M; [Ru(III)] = $(0.50–1.0) \times 10^{-5}$ M. [e] $[H^+] = 1.55 \times 10^{-3}$ to 0.10 M; $[H_2A] = (0.52–1.9) \times 10^{-4}$ M; [Ru(III)] = 4.3×10^{-6} M. [f] $[H^+] = 0.010–0.10$ M; $[H_2A] = (0.48–4.0) \times 10^{-4}$ M; [Ru(III)] = $(2.3–2.8) \times 10^{-6}$ M. [g] $[H^+] = 7.9 \times 10^{-4}$ to 0.10 M; $[H_2A] = 1.5 \times 10^{-5}$ to 5.0×10^{-3} M; [Ru(III)] = 2.5×10^{-6} M. [h] $[H^+] = 0.050–0.10$ M; $[H_2A] = (0.35–1.0) \times 10^{-2}$ M; [Ru(III)] = 4.4×10^{-6} M. [i] $[H^+] = 0.030–0.10$ M; $[H_2A] = (1.0–5.0) \times 10^{-5}$ M; [Ru(III)] = 2.5×10^{-6} M.

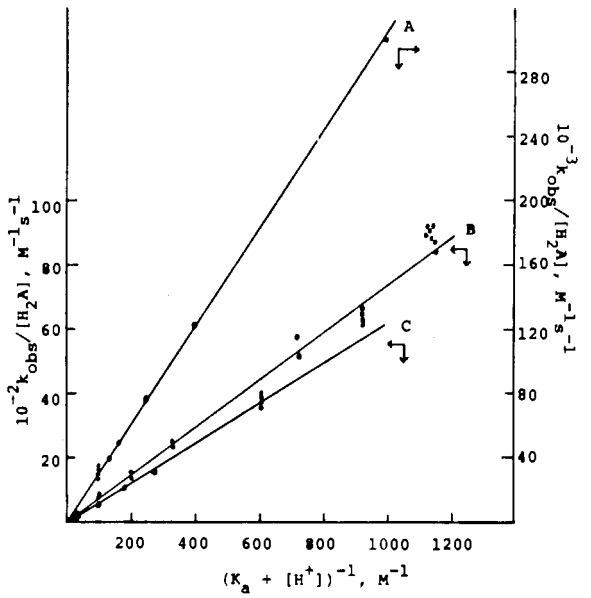

Figure 1. Second-order rate constant versus $1/(K_a + [H^+])$ ($K_a = 8.3 \times 10^{-5}$): (A) $Ru(NH_3)_5pzCH_3^{4+}$; (B) $Ru(NH_3)_5isn^{3+}$; (C) $Ru(NH_3)_5pz^{3+}$. Solid lines were calculated from the parameters given in Table I. Reaction conditions are given in footnotes of Table I.

Measured values of k_{obsd} were fitted to eq 9 by means of a nonlinear least-squares program with $[H^+]$ and $[H_2A]$ taken as independent variables, and k_5 and K_a taken as floating and constant (8.3×10^{-5} M^{-1}) parameters, respectively. The resulting values of k_5 are listed in column 2 of Table I. Reasonable fits are obtained as seen by comparing the experimental points with the theoretical curves in Figure 1.

The reaction between $Ru_2(NH_3)_{10}pz^{6+} + HA^-$ can proceed, in principle, via one- or two-electron mechanisms, eq 10 or 11, re-

$$Ru_2(NH_3)_{10}pz^{6+} + HA^- \rightarrow Ru_2(NH_3)_{10}pz^{5+} + HA \quad (10)$$

$$Ru_2(NH_3)_{10}pz^{6+} + HA^- \rightarrow Ru_2(NH_3)_{10}^{4+} + H^+ + A \quad (11)$$

spectively. The primary reaction products of these pathways are $Ru_2(NH_3)_{10}pz^{5+}$ and $Ru_2(NH_3)_{10}pz^{4+}$, respectively. However, follow-up reactions can produce $Ru_2(NH_3)_4pz^{4+}$ in the one-electron mechanism and $Ru_2(NH_3)_{10}pz^{5+}$ in the two-electron mechanism. These follow-up reactions are the reduction of $Ru_2(NH_3)_{10}pz^{5+}$ by ascorbic acid, eq 12, and the comproportionation reaction, eq

$$Ru_2(NH_3)_{10}pz^{5+} + HA^- \rightarrow Ru_2(NH_3)_{10}pz^{4+} + HA \quad (12)$$

13. Fortunately, the rates of the reactions involved (eq 10 or 11

$$Ru_2(NH_3)_{10}pz^{4+} + Ru_2(NH_3)_{10}pz^{6+} \rightarrow 2Ru_2(NH_3)_{10}pz^{5+} \quad (13)$$

and eq 12 and 13) are such that conditions could be chosen for the follow-up reactions (eq 12 and 13) to be too slow to interfere with the quantitative identification of the primary reaction products generated via each mechanism. We chose the following conditions: $[H^+] = 0.010$ M; $[H_2A] = 0.020$ M; $[Ru_2(NH_3)_{10}pz^{6+}] = 2.78 \times 10^{-6}$ M. When the solutions were mixed in the stopped-flow apparatus (measurements at 545 nm, the absorption maximum for $Ru_2(NH_3)_{10}pz^{4+}$; molar absorbance = 3.21×10^4 M^{-1} cm^{-1}), the initial absorbance per cm was measured as 0.0668 and then the absorbance was found to increase according to a first-order process with a k_{obsd} value of 1.84 s^{-1}. In a comparison experiment with $[Ru_2(NH_3)_{10}pz^{5+}] = 2.88 \times 10^{-6}$M, $[H^+] = 0.010$ M, and $[H_2A] = 0.020$ M, the initial absorbance was 0.0674 and the subsequent absorbance increase was governed by a first-order rate constant equal to 1.79 s^{-1}. The initial absorbance values correspond to molar absorbances of 2.40×10^4 and 2.34×10^4 M^{-1} cm^{-1} for the $Ru_2(NH_3)_{10}pz^{6+}$ and $Ru_2(NH_3)_{10}pz^{5+}$ experiments, respectively. (The molar absorbances of $Ru_2(NH_3)_{10}pz^{5+}$ and $Ru_2(NH_3)_{10}pz^{4+}$ are 2.16×10^4 and 3.21×10^4 M^{-1} cm^{-1}, respectively.) At the concentrations of H_2A and H^+ utilized in the above experiments, the half-lives of the $Ru_2(NH_3)_{10}pz^{6+}$–H_2A and $Ru_2(NH_3)_{10}pz^{5+}$–H_2A reactions are $\sim 7 \times 10^{-5}$ and ~ 0.4 s, respectively. Therefore (regardless of mechanism), the $Ru_2(NH_3)_{10}pz^{6+}$–H_2A reaction is effectively complete in the mixing chamber of the stopped-flow apparatus, and the measured initial absorbance corresponds to the first observable product of the reaction. Evidently, the above experiments show that $Ru_2(NH_3)_{10}pz^{5+}$ is produced in essentially quantitative yield in the $Ru_2(NH_3)_{10}pz^{6+}$–H_2A reaction within the 2×10^{-3} s mixing time of the stopped-flow apparatus. The only question left is whether $Ru_2(NH_3)_{10}pz^{5+}$ is the primary reaction product, (e.g., the one-electron mechanism is operative) or a secondary reaction product formed by the comproportionation reaction (eq 13) of the $Ru_2(NH_3)_{10}pz^{4+}$ produced in the two-electron mechanism (eq 11) with unreacted $Ru_2(NH_3)_{10}pz^{6+}$. The latter alternative can be ruled out by comparing the rate of comproportionation with the rate of the $Ru_2(NH_3)_{10}pz^{6+}$–H_2A reaction. As already indicated, under the conditions utilized, the half-life for the $Ru_2(NH_3)_{10}pz^{6+}$–H_2A reaction is $\sim 7 \times 10^{-5}$ s^{-1}. The rate constant for the reaction given by eq 13 is 4.8×10^6 M^{-1} s^{-1}.[2] Therefore, the minimum half-life of the comproportionation reaction (at $[Ru_2(NH_3)_{10}pz^{4+}] = [Ru_2(NH_3)_{10}pz^{6+}] = {}^1/_2[Ru_2(NH_3)_{10}pz^{6+}]_0$) is 0.15 s. Evidently, the comproportionation reaction is too slow to account for any $Ru_2(NH_3)_{10}pz^{5+}$ produced, and we conclude that the $Ru_2(NH_3)_{10}pz^{6+}$–HA^- reaction proceeds via the one-electron mechanism, eq 10. Since the $Ru_2(NH_3)_{10}pz^{5+}$–HA pair produced in eq 10 is most likely generated in a solvent cage, we further conclude that cage separation and/or proton dissociation of HA[4] followed by cage separation are faster than cage recombination. This conclusion is reasonable in view of the low pK_a of HA and the large barrier for self-exchange in the A/A^- couple.[4]

Inverse acid pathways have been prominently featured in most kinetic studies[7-14] of reactions of ascorbic acid with transition metal

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complexes. Such pathways implicate HA^- as a reactive species (cf. eq 5 and 10). Most complexes utilized are substitution-inert and therefore the oxidations of HA are viewed as outer-sphere electron-transfer reactions that obey eq 14–17,[2,14] where k_{11} and

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (14)$$

$$\ln f_{12} = \frac{(\ln K_{12} + (w_{12} - w_{21})/RT)^{1/2}}{4(\ln (k_{11}k_{22}/10^{22}) + (w_{11} + w_{22})/RT)} \quad (15)$$

$$W_{12} = \exp(-(w_{12} + w_{21} - w_{11} - w_{22})/RT) \quad (16)$$

$$w_{ij} = Z_iZ_je^2/D_sa_{ij}(1 + \beta a_{ij}\mu)^{1/2} \quad (17)$$

k_{22} are the self-exchange rate constants for the ascorbic acid and transition metal complex couples, respectively; k_{12} and K_{12} are the rate constant and the equilibrium constant for the cross-reaction, Z_i and Z_j are the charges of the reacting species; a_{ij} is their separation distance, which is taken to be the sum of the appropriate ionic radii, β is equal to $(8Ne^2/1000D_skT)^{1/2}$ and D_s is the static dielectric constant. By utilizing the values $E° = 0.71$ V and $k_{11} = 1 \times 10^5$ M^{-1} s^{-1} for the HA/HA^- couple, Macartney and Sutin[14] obtained good agreement between the measured rate constants for a wide variety of cross-reactions and rate constants calculated with the aid of eq 14–17. For the reactions studied here, as well as for those studied by Williams and Yandell,[13] a value of $k_{11} = 10^6$ M^{-1} s^{-1} gives a somewhat better agreement than a value of 10^5 M^{-1} s^{-1} (compare first and second values in column 6 of Table I with the value in column 2). However, estimates of self-exchange rate constants from measurements of cross-reactions yield only an order of magnitude for the desired quantity; therefore, values falling in the range 10^5–10^6 M^{-1} s^{-1} should be regarded as being in reasonable agreement with each other.

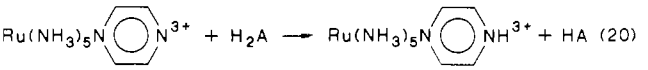
It is noteworthy that, in contrast with findings in other studies,[9,12,14] the complexes studied in the present work do not exhibit, at least up to $[H^+] = 0.10$ M, a detectable contribution of an acid-independent pathway in their reactions with ascorbic acid. For a mechanism where both H_2A and HA^- are reactive species, the rate law is given by eq 18 where k_0 and k_{-1} are the rate

$$\text{rate} = \frac{k_0[H^+] + k_{-1}K_a}{K_a + [H^+]}[\text{oxidant}][H_2A] \quad (18)$$

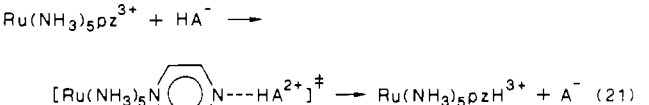
constants for the reactions of the oxidant with H_2A and HA^-, respectively. It has been found invariably[9,12,16] that k_0 is smaller than k_{-1}. Two factors account for the decreased reactivity of H_2A as compared to HA^-, an intrinsic factor—the rate constants for the self-exchange reactions of the H_2A^+/H_2A and HA/HA^- couples are 1×10^5–1×10^6 M^{-1} s^{-1} and 2.5×10^3 M^{-1} s^{-1},[14] respectively—and a thermodynamic factor—the reduction potentials of the H_2A^+/H_2A and HA/HA^- couples are 1.17 and 0.71 V, respectively. These factors, when introduced in eq 14 (with $f = 1$), would yield a reactivity ratio $k_0/k_{-1} \sim 10^{-4}$. The ratio of the contributions to the overall disappearance of the reactants via the acid-independent path and the inverse-acid path is $k_0[H^+]/k_{-1}K_a$. At $[H^+] = 0.10$ M, the maximum concentration utilized in the present work, the acid-independent path would be expected to contribute 12% to the measured rate. We believe that such contribution would have been detected. However, several of the complexes studied here are mild oxidants, and inclusion of the f_{12} factor results in reactivity ratios k_0/k_{-1} considerably less than 10^{-4}. The calculated (eq 14–17) reactivity ratios for the complexes in the same order as given in Table I are 1×10^{-7}, 4×10^{-7}, 2×10^{-6}, 5×10^{-6}, 2×10^{-8}, and 2×10^{-4}. Except for the last value, the reactivity ratios would result in undetectable contributions of the acid-independent path. The above analysis is general, and we predict that the reactions of ascorbic with mild oxidants would not exhibit acid-independent pathways.

Finally, we consider the $Ru(NH_3)_5pz^{3+}$–ascorbic acid reaction. We note, with disappointment, that this system does not exhibit an acid-independent pathway. Here, in addition to the ordinary outer-sphere electron-transfer mechanism of HA^- discussed above, a hydrogen atom transfer mechanism (electron–proton-transfer pathway) from H_2A to $Ru(NH_3)_5pz^{3+}$ represents an attractive mechanistic possibility. Upon reaction, the oxidant becomes a stronger base (the pK_a values of $Ru(NH_3)_5pzH^{4+}$ and $Ru(NH_3)_5pzH^{3+}$ and <0 are 2.5, respectively)[15] and the reductant becomes a stronger acid (the pK_a values of H_2A and H_2A^+ are 4.07 and −4, respectively).[14] Under such circumstances, a hydrogen atom transfer mechanism[16] becomes feasible and, sometimes, favorable. Indeed, such mechanism is prominently featured in the $Ru(bpy)_2(py)O^{2+}$–$Ru(bpy)_2(py)OH_2^{2+}$ comproportionation reaction[17] and in the one-electron oxidation of H_2O_2 by $Ru(bpy)_2(py)O^{2+}$ or $Ru(bpy)_2(py)OH^{2+}$ to produce the radical HO_2 and the corresponding protonated, reduced ruthenium complex.[18] Reaction 19 is entirely analogous to the postulated reaction, eq 20. In both cases, reduction of the metal complex results in a

$$Ru(bpy)_2(py)O^{2+} + H_2O_2 \rightarrow Ru(bpy)_2(py)OH^{2+} + HO_2 \quad (19)$$



considerable increase in its basicity, and oxidation of the substrate results in a considerable increase in its acidity. Unfortunately, the inverse-acid pathway dominates the $Ru(NH_3)_5pz^{3+}$–H_2A reaction even at the higher acidities utilized. In this context, it must be noted that the $Ru(NH_3)_5pz^{3+}$–HA^- pathway, which has been interpreted on the basis of an outer-sphere electron-transfer mechanism, could proceed by a hydrogen atom transfer mechanism, eq 21. (The pK_a values of HA^- and of HA are 11.2 and



−0.45, respectively.[14]) Although we cannot categorically rule out this mechanism, we tend to discard it because no pathway implicating a reactive H_2A species was detected and the calculated rate constant on the basis of an outer-sphere mechanism agrees very well with the measured rate constant (see column 2 and second entry in column 5 of Table I).

Registry No. $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5pz^{3+}$, 38139-16-1; $Ru(NH_3)_5pzCH_3^{4+}$, 48135-77-9; $Ru(NH_3)_5isn^{3+}$, 103258-88-4; $Ru_2(NH_3)_{10}pz^{5+}$, 35599-57-6; $Ru_2(NH_3)_{10}pz^{6+}$, 38900-60-6; ascorbic acid, 50-81-7; ascorbate, 299-36-5.

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