Kinetics of the Oxidation of $Fe(H_2O)_6^{2+}$ by Polypyridine Complexes of Ruthenium(III). Negative Enthalpies of Activation

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Abstract: Rate constants and activation parameters have been measured for the reactions between $Fe(H_2O)_6^{2+}$ and the ruthenium(III) complexes $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, and $Ru(bipy)_2(py)_2^{3+}$. The net reaction is $Fe(H_2O)_6^{2+} + Ru(III) \rightarrow Fe(H_2O)_6^{3+} + Ru(II)$. Reduction potentials for the Ru(III)–Ru(II) couples are nearly the same (1.23–1.26 V), and the free energies of activation at 25° for the four net reactions are also nearly the same (9.4–9.5 kcal/mol). The calculated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are remarkable. For the oxidants $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, and $Ru(bipy)_2(py)_2^{3+}$ the $\Delta H^{\ddagger}$ values are -2.80 ± 0.50, -1.35 ± 0.33, -0.30 ± 0.05, and $+0.30 \pm 0.05$ kcal/mol, respectively, and for $\Delta S^{\ddagger}$ -41 ± 4, -36 ± 4, -33 ± 3, and -31 ± 3 eu, respectively. It is concluded that the observed activation parameters are indicative of an activation process which differs in detail from the Marcus model for outer-sphere electron transfer.

Various theoretical treatments have been given for outer-sphere electron transfer reactions.[1-4] Direct tests of the various theories have proven difficult because of the unavailability of necessary parameters. However, the treatment given by Marcus has led to the useful "cross reaction" equation (1) which has been

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{1}$$

tested experimentally for a variety of reactions involving metal ions.[5,6] In eq 1 applying to a net reaction like

$$Fe(H_2O)_6^{2+} + Ru(bipy)_3^{3+} \longrightarrow Fe(H_2O)_6^{3+} + Ru(bipy)_3^{2+}$$

k_{12} is the rate constant for the net reaction, k_{11} is the self-exchange rate for the $Fe(H_2O)_6^{3+/2+}$ couple, k_{22} is the corresponding rate for the $Ru(bipy)_3^{3+/2+}$ couple, K_{12} is the equilibrium constant for the net reaction, and

$$\ln f = (\ln K_{12})^2/[4 \ln (k_{11}k_{22}/Z^2)] \tag{2}$$

where Z is the collision frequency between two neutral molecules in solution.

We report here the rates and activation parameters for the reactions between the ruthenium(III) complexes $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, or $Ru(bipy)_2(py)_2^{3+}$ and $Fe(H_2O)_6^{2+}$ (terpy is 2,2′,2′′-terpyridine, phen is 1,10-phenanthroline, bipy is 2,2′-bipyridine, and py is pyridine). Reduction potentials, Ru(III) + e → Ru(II), for all four of the ruthenium complexes have been measured in acid solution and found to be essentially the same, 1.23–1.26 V.[7] The measurement of rates for the four reactions should provide a sensitive test for Marcus theory, since, for the series of reactions, k_{11} is the same and K_{12} is nearly constant. In addition, even small differences in k_{12}, or in its associated activation parameters, may reflect subtle differences in the activated complexes for the four reactions.

Experimental Section

Materials. Water used for the kinetic experiments was deionized and doubly distilled from alkaline permanganate. Perchloric acid (Reagent ACS from G. F. Smith), ceric perchlorate (0.5 *M* Ce(IV) in 6 *M* $HClO_4$ from G. F. Smith), and lead dioxide (Alfa Inorganics) were used without further purification. Ferrous perchlorate (G. F. Smith) was purified by recrystallization from perchloric acid. Stock solutions of $Fe(H_2O)_6^{2+}$ were made up in 0.1 *M* $HClO_4$. The concentrations of iron(II) were determined spectrophotometrically as the $Fe(phen)_3^{2+}$ complex[8] with a maximum absorbance at 510 nm (ϵ 11,100 M^{-1} cm^{-1}).

Preparations. (A) **Complexes of Ruthenium(II).** The complexes $Ru(terpy)_2^{2+}$, $Ru(phen)_3^{2+}$, and $Ru(bipy)_3^{2+}$ were prepared by heating at reflux a mixture of 1.0 g of $RuCl_3 \cdot nH_2O$ and stoichiometric amounts of the appropriate ligands for *ca.* 3 hr in 50 ml of *N,N*-dimethylformamide (DMF). At the end of 3 hr, the DMF was slowly distilled off, until the solution volume was ~10 ml. The DMF solution which remained was added dropwise to a saturated solution of tetra-*n*-butylammonium chloride in reagent grade acetone, which precipitated the chloride salts, $Ru(terpy)_2Cl_2$, $Ru(phen)_3Cl_2$, or $Ru(bipy)_3Cl_2$. The salts were collected on a frit and dried *in vacuo*. The complex $[Ru(bipy)_2(py)_2](ClO_4)_2$ was prepared according to the literature method.[9] Satisfactory analytical results were obtained for all complexes.

(B) $[Ru(bipy)_2(py)_2](ClO_4)_3 \cdot 2H_2O$. $[Ru(bipy)_2(py)_2][ClO_4]_2$ (0.3 g) was finely ground using a mortar and pestle. Ce(IV) (0.5 *M* in 6 *M* $HClO_4$; 10 ml) was added dropwise with additional grinding. There was an immediate color change, with the suspended red Ru(II) complex giving a deep green solution. The green solution was added dropwise to ~20 ml of cold 0.1 *M* $HClO_4$, which precipitated a green solid. After stirring for 15 min, the precipitate was collected by filtration, washed with three 10-ml portions of cold 0.1 *M* $HClO_4$, and dried *in vacuo*, giving 0.28 g of the green solid $[Ru(bipy)_2(py)_2][ClO_4]_3 \cdot 2H_2O$. *Anal.* Calcd for $RuC_{30}H_{30}N_6Cl_3O_{14}$: C, 39.80; H, 3.75; N, 9.28; Cl, 11.75. Found: C, 39.79; H, 3.86; N, 9.17; Cl, 11.77.

Attempts to isolate the other Ru(III) complexes as perchlorate salts by this method were unsuccessful due to their high solubilities in perchloric acid.

(C) **Solutions of Ru(III) Complexes.** The Ru(III) complexes $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, and $Ru(bipy)_2(py)_2^{3+}$ were generated in aqueous acidic solution by the oxidation of the corresponding Ru(II) complexes using either PbO_2 or Ce(IV). The

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Table I. Ultraviolet–Visible Spectral Data for the Ruthenium Complexes from 550 to 220 nm[a]

Complex	Max, nm[b]			
$Ru(terpy)_2^{3+}$		316 (27,900)	277 (34,500)	253.5 (33,200)
$Ru(terpy)_2^{2+}$	476 (10,600)	307.5 (51,600)	269 (35,000)	
$Ru(phen)_3^{3+}$		356 (~9700)	270 (79,000)	
$Ru(phen)_3^{2+}$	447.5 (18,400)	422 (17,600)	261.8 (112,000)	222 (85,000)
$Ru(bipy)_3^{3+}$	418 (~3000)	313.8 (42,800)	304 (42,300)	243 (34,700)
$Ru(bipy)_3^{2+}$	453 (13,800)	286.5 (79,000)	252.5 (21,800)	243.6 (25,000)
$Ru(bipy)_2(py)_2^{3+}$	418 (~3600)	313.8 (44,200)	304 (44,400)	243 (35,800)
$Ru(bipy)_2(py)_2^{2+}$	452 (13,500)	286 (80,500)		242.6 (25,000)

[a] The values for the Ru(III) complexes were obtained in 1.9 *M* $HClO_4$ and for the Ru(II) complexes in 1.0 *M* $HClO_4$. [b] Molar extinction coefficient values (±5%) are given in parentheses.

ultraviolet–visible spectra of the Ru(III) complexes in solution were identical, regardless of the method used to generate Ru(III)—by Ce(IV) or PbO_2 oxidation of Ru(II) or directly as the Ru(III) salt in the case of $Ru(bipy)_2(py)_2^{3+}$. Oxidation with PbO_2 in 1.9 *M* $HClO_4$ was the most convenient method and was the method used in most of the kinetic runs.

Measurements. Ultraviolet–visible spectra were obtained using Cary Model 14, Guilford Model 240 and Unicam Model SP 800 B spectrometers. The stopped-flow spectrometer used for the kinetic studies was similar to that described by Dulz and Sutin[10] but had certain modifications. The drive system used had all-glass stopcocks with Apiezon Ap100 anti-seize grease and silicone O-rings (Southern Rubber Co., Inc.) in both the stop syringe and the eight-jet Teflon mixing chamber. The reservoirs for the reactant solutions were equipped with a gas dispersion tube for degassing purposes, surrounded by a water jacket for constant temperature control, and were positioned above the instrument giving a gravity assist for filling the drive syringes. The solution reservoirs, drive syringes, mixing chamber, and observation tube were thermostated by a Model 2074A Forma Scientific refrigerated constant temperature bath designed to control temperature to ±0.02°.

Techniques for Kinetic Runs. All reactions were carried out under nitrogen using the stopped-flow spectrometer described above. The Ru(III) complexes were prepared immediately before each kinetic run by PbO_2 oxidation of the corresponding Ru(II) complex in 1.9 *M* $HClO_4$. The concentrations of Ru(III) were determined spectrophotometrically using known wavelengths of maximum absorbance and the appropriate extinction coefficients (see Table I in the Results Section). The $Fe(H_2O)_6^{2+}$ reactant solutions were made up in 0.1 *M* $HClO_4$ so that after reaction with the Ru(III) complexes the final mixed solutions were 1.0 *M* in $HClO_4$.

The reactions were first order with respect to each of the reactants. The kinetic runs were carried out under second-order conditions for which the integrated rate law, in terms of absorbance (A), is

$$\log\left[\left(\frac{b}{a}-1\right)\frac{A_M}{A}+1\right] = \frac{(b-a)}{2.303}kT + \log\frac{b}{a} \qquad (3)$$

where $A_M = A_0 - A_\infty$ (or $A_\infty - A_0$) and $A = A_t - A_\infty$ (or $A_\infty - A_t$) and A_t is the absorbance at time t. Plots of $\log[((b/a) - 1)\cdot(A_M/A) + 1]$ *vs.* time were linear for >90% of the reactions.

Stoichiometry. The stoichiometries for the oxidations of $Fe(H_2O)_6^{2+}$ by $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, and $Ru(bipy)_2(py)_2^{3+}$ were determined by a series of mixing experiments in which known concentrations of the Ru(III) complex in 1.9 *M* $HClO_4$ (prepared by either PbO_2 or Ce(IV) oxidation of the corresponding Ru(II) complex) were allowed to react with excess ferrous ion in 0.1 *M* $HClO_4$. After the solutions were mixed, the concentration of the Fe(II) which remained was determined spectrophotometrically. In all experiments it was found that a 1:1 mole ratio existed between the amount of Ru(III) added and the amount of Fe(II) which disappeared, indicating that the stoichiometries are

$$Ru(III) + Fe(H_2O)_6^{2+} \longrightarrow Ru(II) + Fe(H_2O)_6^{3+}$$

It was also shown spectrophotometrically that the Ru(III) complexes were converted quantitatively into the corresponding Ru(II) complexes in the reactions.

Results Section

In Table I are given the wavelengths of maximum absorbance and molar extinction coefficients for the Ru(III) and Ru(II) complexes studied here. Spectra for many of the complexes have been reported previously;[11–14] however, in some cases our values are sufficiently different (in part because of a difference in medium) that we report them here. Assignments for the electronic transitions in these complexes have also been reported.[12,13]

The reduction potentials for the $Fe(H_2O)_6^{3+/2+}$ couple and for the various Ru(III)–Ru(II) couples have been measured in aqueous acidic media. For the $Fe(H_2O)_6^{3+/2+}$ couple in 1 *M* perchloric acid $\epsilon = 0.74$ V and for the Ru(III)–Ru(II) couples in 1 *M* sulfuric acid,[7] the values (in volts) are $Ru(terpy)_2^{3+/2+}$, 1.23; $Ru(phen)_3^{3+/2+}$, 1.26; $Ru(bipy)_3^{3+/2+}$, 1.26; and $Ru(bipy)_2(py)_2^{3+/2+}$, 1.25. Although the potentials above are given in two different media, the values for the Ru(III)–Ru(II) couples are known to be relatively insensitive to the nature of the acid at constant acid strengths and so the values in 1 *M* H_2SO_4 were used to calculate overall free energy changes.

Kinetics. The rate law for the oxidation of $Fe(H_2O)_6^{2+}$ by the various Ru(III) complexes was found to be

$$-d[Ru(III)]/dt = k[Fe(H_2O)_6^{2+}][Ru(III)]$$

where Ru(III) is $Ru(terpy)_2^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_3^{3+}$, or $Ru(bipy)_2(py)_2^{3+}$. The rate constants for all four reactions as obtained by stopped-flow kinetic measurements at various temperatures are given in Table II.

The medium used for the kinetic runs (1 *M* $HClO_4$) was chosen for several reasons. Both the reduction potential[15] and the $Fe(H_2O)_6^{3+}$–$Fe(H_2O)_6^{2+}$ self-exchange rate[16] are known in this medium. Although values for both the Ru(III)–Ru(II)[7] and $Fe(H_2O)_6^{3+/2+}$ [17] potentials have been measured in 1 *M* H_2SO_4, in 1 *M* H_2SO_4 the formation of sulfato complexes of iron(II) is known to be important.[18] Also, rate constants for related reactions have been found to be faster in sulfate media than in perchlorate media by factors of up to

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Table II. Rate Constants for the Oxidation of $Fe(H_2O)_6^{2+}$ by the Ruthenium(III) Complexes in 1.0 M $HClO_4$

Oxidant	T, °C[a]	$k \times 10^{-5}$, M^{-1} sec^{-1}	No. of runs
$Ru(terpy)_2^{3+}$	35.0	6.36 ± 0.31	6
	25.0	7.23 ± 0.36	6
	15.0	8.10 ± 0.88	7
$Ru(phen)_3^{3+}$	35.0	7.74 ± 1.33	6
	25.0	8.04 ± 0.50	6
	15.0	8.44 ± 0.43	6
$Ru(bipy)_3^{3+}$	35.0	6.56 ± 0.44	6
	25.0	6.41 ± 0.38	6
	15.0	6.35 ± 0.42	8
$Ru(bipy)_2(py)_2^{3+}$	35.0	6.74 ± 0.56	9
	25.0	6.38 ± 0.44	8
	15.0	6.08 ± 0.32	8

[a] ±0.3°.

9.8.[19,20] Since the reactions reported here are so rapid, rate enhancements of this magnitude would have made the rates difficult to measure.

In all of the kinetic runs, one reactant was present in at least a twofold excess. The observed second-order rate constants were independent of whether $Fe(H_2O)_6^{2+}$ or the Ru(III) complex was the reactant in excess. The reactions were studied using various concentrations of $Fe(H_2O)_6^{2+}$ (2×10^{-6} to 11.90×10^{-5} M) and of Ru(III) (1.06×10^{-5} to 8.70×10^{-5} M) and at various wavelengths where the absorbance changes were maximized. Calculated rate constants for all reactions were found to be independent of the wavelength used in the kinetic runs. The error limits for the k values in Table II are standard deviations calculated from the results of at least six separate kinetic runs. It should be noted that our determination of the rate constant for the oxidation of $Fe(H_2O)_6^{2+}$ by $Ru(bipy)_3^{3+}$ at 25° in 1 M $HClO_4$ ((6.41 ± 0.38) × 10^5 sec^{-1}) compares well with the value obtained by Gordon, Williams, and Sutin[19] (7.2×10^5 M^{-1} sec^{-1}) under similar conditions.

An extraordinary feature of the data in Table II is that for both $Ru(terpy)_2^{3+}$ and $Ru(phen)_3^{3+}$ as the oxidants, the observed rate constants *increase* as the temperature *decreases*. For all four reactions the rate constants are only slightly temperature dependent.

Activation Parameters. The activation parameters for the four reactions were determined from plots of ln k/T *vs.* $1/T$ using the expressions from reaction rate

$$k = (k_BT/h)e^{-\Delta G^{\ddagger}/RT} \qquad \Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

theory. The results are given in Table III. The reaction rate theory expression was used rather than the related expression from Marcus theory[21,22] because of

$$k = Ze^{-\Delta G^*/RT} \qquad \Delta G^{\ddagger} = \Delta G^* + RT \ln (k_BT/hZ)$$

the ease of comparison with earlier data and because of the uncertainty in choosing a value for Z.

Table III. Activation Parameters for the Oxidation of $Fe(H_2O)_6^{2+}$ by the Ruthenium(III) Complexes in 1.0 M $HClO_4$

Oxidant	$\Delta G^{\ddagger}$, kcal/mol (25°)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu (25°)
$Ru(terpy)_2^{3+}$	9.40 ± 1.9	−2.80 ± 0.50	−41 ± 4
$Ru(phen)_3^{3+}$	9.40 ± 1.5	−1.35 ± 0.33	−36 ± 4
$Ru(bipy)_3^{3+}$	9.53 ± 0.9	−0.30 ± 0.05	−33 ± 3
$Ru(bipy)_2(py)_2^{3+}$	9.53 ± 0.9	+0.30 ± 0.05	−31 ± 3

In view of the extraordinary values found for the activation parameters and because of their importance in the later discussion, some mention should be made about the error limits given in Table III. As evidenced by the standard deviations in Table II, the reproducibility in k values was generally good. The standard deviations were used to calculate the uncertainties in the activation parameters by standard methods of error analysis.[23,24] As implied by the error limits given in Table III, we are reasonably certain that, at least for the reactions between $Fe(H_2O)_6^{2+}$ and the oxidants $Ru(terpy)_2^{3+}$ and $Ru(phen)_3^{2+}$, the negative values found for $\Delta H^{\ddagger}$ are real.

The temperature range available for the activation parameter studies was restricted by the insolubility of the Ru(II) complexes as perchlorate salts at low temperatures and by the oxidation of water by the Ru(III) complexes at higher temperatures. Although the temperature range used was small (20°), there is no hint of nonlinearity in plots of ln k/T *vs.* $1/T$ for any of the four reactions.

Discussion

When written in terms of free energies the Marcus cross reaction equation becomes

$$\Delta G_{12}^{\ddagger} = {}^1/_2(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22} + \Delta G°_{12}) - (RT/2) \ln f \quad (4)$$

which can be rearranged giving

$$(\Delta G^{\ddagger}_{12} - {}^1/_2\Delta G^{\ddagger}_{11}) = {}^1/_2\Delta G^{\ddagger}_{22} + {}^1/_2\Delta G°_{12} - (RT/2) \ln f \quad (5)$$

The rates of reduction of $Fe(phen)_3^{3+}$ and of several ligand substituted analogs by $Fe(H_2O)_6^{2+}$ have been studied,[20] *e.g.*

$$Fe(H_2O)_6^{2+} + Fe(phen)_3^{3+} \longrightarrow Fe(H_2O)_6^{3+} + Fe(phen)_3^{2+} \quad (6)$$

as have the rates of oxidation of the corresponding complexes of iron(II) by Ce(IV).[10] By using the rate data to determine the intercepts of plots of $(\Delta G^{\ddagger}_{12} - {}^1/_2\Delta G^{\ddagger}_{11})$ *vs.* $\Delta G°_{12}$, Dulz and Sutin[10] have calculated an "average" rate of self-exchange at 25° for the various iron(III)–iron(II) phenanthroline complexes. The calculated value, 2×10^3 M^{-1} sec^{-1}, is significantly less than the lower limit, 3×10^7 M^{-1} sec^{-1}, established by Larson and Wahl by epr measurements.[25] By using eq 1, the values 3–7 × 10^5 M^{-1} sec^{-1} can be estimated for the Ru(III)–Ru(II) polypyridine self-exchange rates at 25°.[26] In the high ionic strength media (0.5–1.0 M) in which the various reactions were studied, a reason-

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able limit for the iron and ruthenium self-exchange rates is $k > 10^8\ M^{-1}\ \text{sec}^{-1}$.[28,29] The deviations from the results predicted by eq 1 have been suggested to arise from the failure of nonelectrostatic terms to cancel in the work done in bringing together the various pairs of reactants.[21] It may also be indicative of an activation process which differs in detail from the Marcus and Hush models.

The latter possibility is supported by the activation parameters reported here. For the reactions

$$\mathrm{Fe(H_2O)_6^{2+} + Ru(III) \longrightarrow Fe(H_2O)_6^{3+} + Ru(II)}$$

remarkably low values for $\Delta H^{\ddagger}$ (-2.80 to $+0.30$ kcal/mol) and large negative $\Delta S^{\ddagger}$ values are observed. Because of the negative values for $\Delta H^{\ddagger}$ it is difficult to reconcile all of the mechanistic details of the reactions in terms of the model used by Marcus in deriving eq 4. Important features of the model include the diffusion of the ions in solution to form a collision complex, reorganization of inner and outer coordination spheres, and adiabatic electron transfer between the metal centers. Contributions to the enthalpy of activation from diffusion of the ions[30,31] and from the reorganization of the coordination spheres from their equilibrium positions, as described by Marcus,[21,22] should be positive. Even if the contributions to $\Delta G^{\ddagger}_{12}$ from inner and outer sphere reorganization are small, which is the expected result for reactions like these with large, favorable net free energy changes, it should still be true that $\Delta H^{\ddagger} > 0$, because of the contribution from the diffusion together of the ions in solution. It would appear then that electron transfer between the ruthenium(III)-polypyridine complexes and $\mathrm{Fe(H_2O)_6^{2+}}$ occurs by a "non-Marcus" path in which there is at least one distinctive feature not considered in the Marcus model. The activation parameters for reaction 6, $E_a = 0.8 \pm 0.2$ kcal/mol ($\Delta H^{\ddagger} = 0.2$ kcal/mol) and $\Delta S^{\ddagger} = -37.2$ eu,[32] suggest that the reactions between the analogous polypyridine iron(III) complexes and $\mathrm{Fe(H_2O)_6^{2+}}$ occur by the same path.

The full mechanistic implications of the negative $\Delta H^{\ddagger}$ values which characterize the non-Marcus path are not clear. It is possible that preequilibria involving $\mathrm{Fe(H_2O)_6^{2+}}$ or the reversible protonation of the Ru(III) complexes[14,33,34] could be important. However, the rate of reduction of $\mathrm{Fe(phen)_3^{3+}}$ by $\mathrm{Fe(H_2O)_6^{2+}}$ is relatively insensitive to the concentration of $\mathrm{H_2SO_4}$ in the range 0.05–1.00 M[10] and to the concentration of acid in a perchlorate medium at constant acid strength.[32]

Endicott and his coworkers have found negative $\Delta H^{\ddagger}$ values for inner sphere electron transfer reactions between a series of $\mathrm{Co(en)_2ACl^{2+}}$ complexes (en is ethylenediamine and A a neutral ligand) and $\mathrm{Cr^{2+}}$ and have concluded that the formation and dissociation of chloride-bridged precursor complexes are important features of the reactions.[35] A mechanism in which a ligand is shared in common between normal coordination positions of iron(II) and the ruthenium(III) chelate complexes cannot explain the negative $\Delta H^{\ddagger}$ values since the ruthenium(III) complexes are substitution inert. However, the formation of outer sphere precursor complexes, *e.g.*

$$\mathrm{Fe(H_2O)_6^{2+} + Ru(terpy)_2^{3+} \rightleftharpoons Fe(H_2O)_6^{2+}, Ru(terpy)_2^{3+}} \qquad K$$

$$\mathrm{Fe(H_2O)_6^{2+}, Ru(terpy)_2^{3+} \longrightarrow Fe(H_2O)_6^{3+} + Ru(terpy)_2^{2+}} \qquad k$$

may be important.[35,36] Although the reacting ions are of like charge, in the high ionic strength media in which the reactions were studied, coulombic repulsion is expected to be small.[37] The origin of a negative heat of interaction for the preequilibrium (K) could then lie in charge fluctuation forces in an outer sphere complex in which the electrical charges on the ions are largely neutralized by the surrounding ion atmosphere.[38] Because of the intimately close distances needed for a significantly attractive interaction of this kind, it is probably necessary that in the precursor complex the iron(II) ion would have to penetrate somewhat between the chelate rings of the ruthenium(III) chelate complexes. For the reactions between iron(III) polypyridine complexes and $\mathrm{Fe(H_2O)_6^{2+}}$, Sutin and coworkers have suggested a nearly equivalent mechanism in which it is necessary for $\mathrm{Fe(H_2O)_6^{2+}}$ to penetrate into the space between the chelating ligands in the activated complex.[19,20] Alternately, the distinctive mechanistic feature of the non-Marcus path may be the occurrence of an extensive and energetically favorable ordering of solvent and/or ion atmosphere in the activated complex.

For the reactions between $\mathrm{Fe(H_2O)_6^{2+}}$ and the Fe(III) and Ru(III) chelate complexes, it is interesting to speculate that a more or less "normal" Marcus–Hush path distinctly different from the path observed here should exist, characterized by positive, but possibly small $\Delta H^{\ddagger}$ values. Equation 4 should hold for such a path, and if so, it would have a lower free energy of activation (~6.5 kcal/mol at 25° using $\Delta G^{\ddagger}_{22} = 6.5$ kcal/mol ($k_{22} = 10^8\ M^{-1}\ \text{sec}^{-1}$)) than for the path observed here ($\Delta G^{\ddagger}_{12} = 9.4$ kcal/mol). Since the non-Marcus path dominates, the free energy of activation for a Marcus–Hush path must be significantly greater (>9.4 kcal/mol) than the calculated value of 6.5 kcal/mol. A Marcus–Hush path is not observed here and the reason for its unexpected slowness may lie in a significant nonadiabatic contribution to electron transfer.[39] In terms of electronic configurations the net reactions

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(28) J. C. Solenberger, Ph.D. Thesis, Washington University, St. Louis, Mo., June 1969.

(29) J. B. DeRoos, mentioned in ref 28.

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(36) We have recorded the ultraviolet spectra of solutions of $\mathrm{Ru(bipy)_3^{3+}}$ ($7 \times 10^{-4}\ M$) in the presence of high concentrations of $\mathrm{Co(H_2O)_6^{2+}}$ (up to 0.5 M) in order to search for outer sphere complex formation. $\mathrm{Co(H_2O)_6^{2+}}$ is not oxidized by the ruthenium(III) complexes and, because of its similarities with $\mathrm{Fe(H_2O)_6^{2+}}$, it should be a good model for $\mathrm{Fe(H_2O)_6^{2+}}$. The ruthenium(III) complexes have intense $\pi \rightarrow \pi^*$ transitions in the ultraviolet which should be somewhat sensitive to complex formation.[11,12] The spectra that we have obtained are essentially the superimposed spectra of the two ions. From these data we estimate that if precursor complex formation is important K must be less than 0.5.

(37) Reference 3, p 123.

(38) H. Jehle, *Ann. N. Y. Acad. Sci.*, **158**, 240 (1969).

(39) There are other possibilities. The $\mathrm{Fe(H_2O)_6^{3+}}$–$\mathrm{Fe(H_2O)_6^{2+}}$ self-exchange rate used in the calculation is the measured value[16] and the mechanism may be inner sphere. If so, the true outer sphere rate constant which should be used in the calculation, may be considerably less which would increase the calculated value for $\Delta G^{\ddagger}$. Also, eq 4 may not hold for reactions, like the reactions studied here, for which the overall ΔH change is large and negative.[40]

(40) P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

are, for example

$$Fe(H_2O)_6^{2+}\ (t_{2g}^4e_g^2) + Ru(bipy)_3^{3+}\ (t_{2g}^5) \longrightarrow Fe(H_2O)_6^{3+}\ (t_{2g}^3e_g^2) + Ru(bipy)_3^{2+}\ (t_{2g}^6)$$

The metal π orbitals of d origin are labeled as t_{2g}, even though the symmetries of the chelated complexes are lower than octahedral. The molecular radii of the chelated complexes are large (6–8 Å).[28] If in the activated complex for electron transfer $Fe(H_2O)_6^{2+}$ is constrained to remain on the periphery of the chelate complex, overlap between d orbitals on the two metal centers may be weak leading to nonadiabatic electron transfer.

It has been suggested that polypyridine ligands may be good "conducting ligands" for electron transfer[41] since their metal complexes characteristically undergo rapid electron transfer. However, as Linck has pointed out[5] rapid electron transfer may occur because ligands like the polypyridines tend to make the two valence states involved in electron transfer more alike by π bonding and not because they provide a low-lying path for electron conduction between metal centers. π and π^* orbitals, basically ligand in character but extensively mixed with metal π-type orbitals, do exist on the peripheries of the complexes;[42,43] however, these orbitals may not provide a useful path for electron transfer into the metal center. Evidence on this point comes from the chemi- and photoluminescence properties of $Ru(bipy)_3^{2+}$ in solution.[44–46] Emission is observed from the lowest charge transfer triplet state ($^3d-\pi^*$) at ~17.8 kK, essentially independent of the exciting wave length.[46] The observed phosphorescence can be viewed as accompanying intramolecular electron transfer where the phosphorescence lifetime (~0.7

$$^3d-\pi^*(t_{2g}^5\pi^*) \longrightarrow {}^1d-d(t_{2g}^6) + h\nu$$

μsec in room temperature aqueous solution[45]) gives an upper limit on the rate of electron transfer. The same excited state can be reached chemically by reducing $Ru(bipy)_3^{3+}$ with hydrazine in aqueous solution[47] or by $Ru(bipy)_3^{+}$ in acetonitrile.[48] Conceptually the chemiluminescent reactions are very similar to oxidation–reduction reactions involving pentaamminecobalt(III) where ligand-reduced radical anion intermediates have been postulated.[49,50] It is important to note that in the chemiluminescent reactions, electron transfer occurs to ligand π^* orbitals and not through them to metal d orbitals, even though reduction at the metal is far more favorable thermodynamically. For a reductant like $Fe(H_2O)_6^{2+}$, where net reduction of the ligand is not possible thermodynamically, it may also be true that overlap with a π^* (ligand) orbital does not lead to efficient electron transfer to the metal d orbitals in the lifetime of a collision complex. Direct overlap between d orbitals may be a necessary feature of such reactions. The importance of specific chemical interactions with t_{2g} orbitals in the chemistry of ruthenium–ammine complexes has been suggested by Ford and Taube.[51]

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Eliminating Solvation Contributions to the Enthalpy of Adduct Formation in Weakly Polar, Acidic Solvents

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Abstract: A previously reported procedure for eliminating solvation contributions to measured enthalpies in basic solvents has been successfully extended to several adducts in the weakly acidic solvent methylene chloride, CH_2Cl_2. For the donor *N,N*-dimethylacetamide, DMA, and the series of Lewis acids reported here, the enthalpy measured in CH_2Cl_2 differs from that in poorly solvating media by a constant amount, 2.0 ± 0.2 kcal mol^{-1}. The origin of this constant difference has been investigated by measuring the transfer energies of the acids, the base, and the adducts from CCl_4 to CH_2Cl_2.

The extension of our studies of donor–acceptor interactions[1] to a broader range of compounds has been limited by solubility considerations and has made it necessary to employ polar solvents as a reaction medium. Solvents of this nature are no longer "poorly solvating" and, in general, do not produce enthalpies

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