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A Comparison of the Rates of Electron Exchange Reactions of Ammine Complexes of Ruthenium(II) and -(III) with the Predictions of Adiabatic, Outer-Sphere Electron Transfer Models

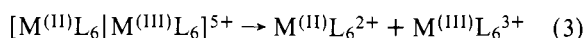
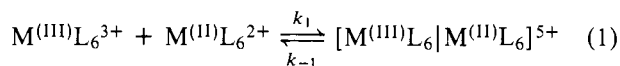
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Abstract: The rate constants for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$, and $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$ electron exchange reactions have been measured by a technique involving subtle modifications of the ligands. The rate constants ($\text{M}^{-1} \text{s}^{-1}$, medium) at 25 °C are 3.2×10^3 , 0.1 M $\text{CF}_3\text{SO}_3\text{H}$, for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ exchange; 7.7×10^5 , 0.1 M $\text{CF}_3\text{SO}_3\text{H}$, and 2.2×10^6 , 0.1 M HClO_4 , for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange; 8.4×10^7 , 0.1 M HClO_4 , for the $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$ exchange. The rate constants and activation parameters for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction were determined as a function of ionic strength ($k = 4.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 4.0 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -24 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at zero ionic strength and 25 °C). The rate constants determined in this work together with those for the analogous $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ and $\text{Ru}(\text{bpy})_3^{3+/2+}$ exchange reactions are compared with the predictions of theoretical models. Good linearity was found for a plot of $\log k_{\text{ex}}$ vs. $1/\bar{r}$, where \bar{r} is the mean separation of the ruthenium centers in the activated complex. The Marcus model derived on the basis of a reactive collision formulation gives better agreement with the observed rate constants and activation parameters at zero ionic strength than the conventional ion-pair preequilibrium model. Contrary to prediction, the increase in exchange rate with increasing ionic strength is reflected primarily in a decreased enthalpy of activation.

Introduction

Outer-sphere electron exchange reactions constitute the simplest class of electron transfer reactions.¹ The rates and activation energetics of such reactions are therefore of considerable interest. The currently accepted model for bimolecular electron exchange between $\text{M}^{(\text{III})}\text{L}_6^{3+}$ and $\text{M}^{(\text{II})}\text{L}_6^{2+}$ involves the reaction sequence²



In this scheme the reactants first form a precursor complex (eq 1). The electron transfer takes place within this complex to form a successor complex (eq 2). Dissociation of the successor complex yields the observed electron transfer products (eq 3). In this paper we treat the case in which precursor complex formation is a rapidly established preequilibrium with the subsequent electron transfer within this complex being rate determining ($k_{-1} \gg k_{\text{et}}$). Under these conditions the observed second-order rate constant is equal to $K_0 k_{\text{et}}$ where $K_0 = k_1/k_{-1}$. We will also assume that the electron transfer is adiabatic, that is, that the interaction between the reactants is

large enough for the electron transfer to occur with unit probability in the activated complex. In other words, we assume for the time being that the probability factor $\langle \kappa \rangle$ in the expression

$$k_{\text{et}} = \langle \kappa \rangle \frac{k_{\text{B}}T}{h} \exp[-\Delta G_\lambda^\ddagger/RT]$$

is equal to unity. Under these circumstances the Franck-Condon barrier to electron transfer should account for $\Delta G_\lambda^\ddagger$. For a M(II)/M(III) exchange reaction, the Franck-Condon barrier arises because the metal-ligand bond lengths must rearrange to some common value intermediate between that characteristic for the metal ion in oxidation states II and III before electron transfer can occur. Likewise, the solvent polarization around the reactants, which is sensitive to the charge of the reactant, must rearrange prior to electron transfer. These rearrangements are required to satisfy conservation of energy.^{1,3–10} Therefore if the equilibrium constants for precursor complex formation (k_1/k_{-1}) and the Franck-Condon rearrangement barriers are known, the rate constants for electron-exchange reactions can be calculated.

In this paper the exchange rate constants of the Ru(III)/Ru(II) redox couple in a series of ruthenium ammine complexes are compared with the predictions of various models. The exchange rate constants for the ruthenium complexes were

determined by using subtle modifications of ligands which allowed the true exchange rate constant to be approximated by a net electron transfer reaction rate constant. The rate constants to be compared with theory were either measured in this work or taken from the literature. The use of the Ru(III)/Ru(II) couple allows an evaluation of the inner-sphere rearrangement energy. The differences in the metal-ligand bond distances of the ruthenium(II) and ruthenium(III) complexes used in this work are known to be small either from X-ray crystallographic determinations of the structures of the complexes or from extrapolations from similar complexes. Ruthenium complexes also have the advantage of being inert to substitution in both the II and III oxidation states. As a consequence the reactions discussed in this work are known to be outer sphere. Furthermore, the ruthenium complexes used are not susceptible to hydrolysis in aqueous solution and can be employed at low acidity and hence at low ionic strength.

We have also studied the temperature dependence of one of these exchange reactions as a function of ionic strength. From a comparison of the observed and calculated activation parameters we show under what conditions this simple semi-classical model is applicable and present some possible reasons for deviations from the predicted behavior.

Experimental Section¹¹

Chemicals and Solutions. The preparation of salts of tetraammine-2,2'-bipyridineruthenium(II), Ru(NH₃)₄(bpy)²⁺, and of tetraammine-1,10-phenanthrolineruthenium(II), Ru(NH₃)₄(phen)²⁺, have been previously reported.¹² The procedure reported here represents a significant improvement since the starting material is the readily prepared and air-stable salt [Ru(NH₃)₅(H₂O)](CF₃SO₃)₃.¹³ [Ru(NH₃)₄(bpy)](ClO₄)₂ was prepared by reduction of [Ru(NH₃)₅(H₂O)](CF₃SO₃)₃ with Zn(Hg) amalgam in C₂H₅OH containing a tenfold molar excess of 2,2'-bipyridine under an argon atmosphere for 1 h. The product was precipitated from solution by addition to (C₂H₅)₂O, and the solid was collected by filtration, dissolved in a minimum volume of H₂O, and extracted with CHCl₃ to remove any residual free bipyridine. The perchlorate salt of the desired complex was obtained by adding several milliliters of saturated aqueous NaClO₄ to the solution. The reddish-purple salt was collected by filtration, washed with 1:1 (v/v) C₂H₅OH-(C₂H₅)₂O and then (C₂H₅)₂O, and air dried. The complex was characterized by UV-vis spectra (λ_{max}, nm (ε, M⁻¹ cm⁻¹) H₂O: 522 (3.31 × 10³), 366 (5.51 × 10³), 295 (3.2 × 10⁴) and ruthenium analysis. Anal. Calcd: Ru, 19.2. Found: Ru, 18.6. [Ru(NH₃)₄(phen)](CF₃SO₃)₂·3H₂O was prepared in an analogous manner. [Ru(NH₃)₅(H₂O)](CF₃SO₃)₃ was reduced over Zn(Hg) amalgam in CH₃OH in the presence of a tenfold excess of phenanthroline monohydrate under argon. After 1 h the reaction mixture was filtered to remove the Zn and diluted fivefold with CH₂Cl₂, and the flask was sealed and placed in a refrigerator for 2 days to allow the product to crystallize. The red-black crystals were collected by filtration, washed with CH₂Cl₂, and air dried in the filter funnel. The spectrum in H₂O and analysis of the solid for ruthenium show that the salt is best characterized as a trihydrate. λ_{max}, nm (ε, M⁻¹ cm⁻¹): 471 (6.68 × 10³), 265 (3.5 × 10⁴). Anal. Calcd: Ru, 14.4. Found: Ru, 14.3. [Ru(NH₃)₄(bpy)](ClO₄)₃ was prepared by dissolving the Ru(II) salt in a minimum volume of CH₃CN (MCB spectrograde) and oxidizing with a 10% excess of Br₂ in CH₃CN.¹⁴ There was some precipitate present at this point and the complex was completely precipitated from solution by the addition of several drops of concentrated HCl. The solid was collected by filtration and immediately dissolved in a minimum volume of 0.1 M HCl. The perchlorate salt of the desired complex was obtained by dropwise addition of concentrated HClO₄ until a purple solid appeared. After the flask was cooled in an ice bath the solid was collected by filtration. The crystals were washed with several milliliters of ice-cold 2 M HClO₄, air dried, and then dried in a vacuum desiccator overnight. The solid lost its crystalline appearance and became powdery as it dried. The complex was analyzed by reducing it to ruthenium(II) over Zn(Hg) amalgam in 0.1 M HCl and comparing the spectrum of the reduced product with that of the pure ruthenium(II) complex. The salt was found to be anhydrous. Ru(bpy)₂Cl₂·2H₂O and Ru(phen)₂Cl₂·3H₂O were prepared by a procedure devised by Weaver and reported by Sprintschnik et al.¹⁵ *cis*-Diamminebis(2,2'-bipyridine)ruthenium(II)

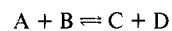
perchlorate trihydrate, [Ru(bpy)₂(NH₃)₂](ClO₄)₂·3H₂O, and *cis*-diamminebis(1,10-phenanthroline)ruthenium(II) perchlorate, [Ru(phen)₂(NH₃)₂](ClO₄)₂, were prepared from Ru(bpy)₂Cl₂·2H₂O and Ru(phen)₂Cl₂·3H₂O, respectively, by the literature procedure.¹⁶ Tris(ethylenediamine)ruthenium(III) bromide, Ru(en)₃Br₃, was also prepared by the literature procedure.¹⁷ Hexaammineruthenium(III) chloride [Ru(NH₃)₆]Cl₃ (Matthey-Bishop), was purified by recrystallization.¹⁸

CF₃SO₃H (3 M) was purified by reduced-pressure distillation. Dilute aqueous solutions of CF₃CO₃H and HClO₄ were standardized by titration with base.

Ru(NH₃)₄(phen)³⁺ was generated in HClO₄ or CF₃SO₃H solution by oxidation of the ruthenium(II) complex with a stoichiometric amount of cerium(IV) in 1 N H₂SO₄, followed by dilution until the concentration of H₂SO₄ was insignificant (<1 × 10⁻³ M). Solutions of Ru(NH₃)₄(bpy)³⁺ were prepared from the solid or by in situ oxidation with cerium(IV) as described above. Ru(phen)₂(NH₃)₂³⁺ was also generated in solution by stoichiometric cerium(IV) oxidation. Solutions of Ru(bpy)₂(NH₃)₂³⁺ were generated by oxidation of an acidic solution of the ruthenium(II) complex with excess PbO₂ followed by filtration through a bed of glass wool to remove the excess oxidant. PbO₂ was unsatisfactory as an oxidant for Ru(phen)₂(NH₃)₂²⁺. Reduction of ruthenium(III) solutions of this complex by excess iron(II) failed to reproduce quantitatively the expected spectrum of Ru(phen)₂(NH₃)₂²⁺. Ru(NH₃)₆²⁺ was generated under an argon atmosphere by Zn(Hg) amalgam reduction of a solution of the ruthenium(III) complex which was kept in an ice-water bath. These solutions were stored at an acidity of 10⁻³-10⁻² M to prevent hydrolysis of NH₃ and were used within 1 h of generation. Solutions of Ru(en)₃³⁺ were kept in 10⁻¹ M acid to suppress autoxidation of the coordinated ethylenediamine and were used within 1 day of preparation.

Kinetic Apparatus and Methods. Rate constants were determined by the stopped-flow method using a Durrum-Gibson instrument which was modified as previously described.¹⁹ This spectrometer employed Teflon-covered drive syringes and a 2-cm path length cuvette. Temperature determinations were made with a calibrated thermometer by measuring the temperature of the thermostating liquid in the drive syringe trough and are accurate to within 0.2 °C. Exchange reactions which involved the substitution of phenanthroline for bipyridine were monitored at 290-295 or at 265 nm (the rate constants were independent of the monitoring wavelength). The Ru(en)₃³⁺-Ru(NH₃)₆²⁺ reaction was followed at 300 nm.

Kinetic Data Treatment. The rate of the Ru(en)₃³⁺-Ru(NH₃)₆²⁺ reaction was measured under conditions such that the concentration of Ru(en)₃³⁺ was in a tenfold or greater excess over the concentration of Ru(NH₃)₆²⁺ and the reaction obeyed first-order kinetics. The reaction systems Ru(NH₃)₄(bpy)^{3+/2+}-Ru(NH₃)₄(phen)^{3+/2+} and Ru(bpy)₂(NH₃)₂^{3+/2+}-Ru(phen)₂(NH₃)₂^{3+/2+} were studied under conditions such that a rate of approach to equilibrium was measured. For these reactions absorbance-time data were fit to the reaction scheme



$$\frac{-d[A]}{dt} = k_f[A][B] - k_r[C][D]$$

The Ru(NH₃)₄(bpy)^{3+/2+}-Ru(NH₃)₄(phen)^{3+/2+} and Ru(bpy)₂(NH₃)₂^{3+/2+}-Ru(phen)₂(NH₃)₂^{3+/2+} reactions both have equilibrium constants near unity. Under these conditions $k_f = k_r = k$ and the rate law for this reaction scheme reduces to a simple expression. When C and D are absent at time zero, the integrated rate expression is²⁰

$$\ln(x_e - x) - \ln x_e = -k([A]_0 + [B]_0)t$$

where x and x_e are the extent of reaction at time t and at equilibrium, respectively, and $[A]_0$ and $[B]_0$ are the concentrations of A and B at time zero. For spectrophotometric monitoring where OD_e, OD₀, and OD_t are the optical densities at equilibrium, time zero, and at any time t , respectively, the integrated rate expression becomes

$$\ln(OD_t - OD_e) - \ln(OD_0 - OD_e) = -k([A]_0 + [B]_0)t$$

For these reactions the observed first-order rate constant is related to the exchange rate constant by the expression

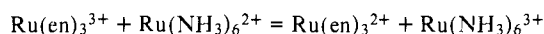
$$k_{\text{obsd}} = k_{\text{ex}}([Ru(II)]_0 + [Ru(III)]_0) \quad (4)$$

Table I. Experimental Data for the $[\text{Ru}(\text{NH}_3)_4(\text{bpy})-\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+/2+}$ Reaction at 25.0 °C in 0.10 M HClO_4

$[\text{Ru}(\text{III})]_0, \text{M}$	$[\text{Ru}(\text{II})]_0, \text{M}$	$k_{\text{obsd}},^a \text{ s}^{-1}$	$k_{\text{ex}},^b \text{ M}^{-1} \text{ s}^{-1}$
$0.50 \times 10^{-5} \text{ c}$	$1.01 \times 10^{-5} \text{ c}$	30.3 ± 0.2	2.01×10^6
$2.01 \times 10^{-5} \text{ c}$	$1.01 \times 10^{-5} \text{ c}$	62 ± 1	2.05×10^6
$1.00 \times 10^{-5} \text{ d}$	$1.01 \times 10^{-5} \text{ d}$	39.7 ± 0.1	1.97×10^6

^a The errors in k_{obsd} are average deviations. ^b The rate constant k_{ex} is calculated from eq 4. ^c Forward direction, $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+} + \text{Ru}(\text{NH}_3)_4(\text{phen})^{2+}$. ^d Reverse direction, $\text{Ru}(\text{NH}_3)_4(\text{phen})^{3+} + \text{Ru}(\text{NH}_3)_4(\text{bpy})^{2+}$.

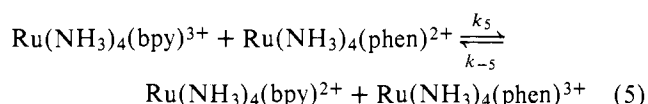
Electrochemical Measurements. A PAR Model 176 and 175 system with a Hewlett-Packard Model 7000A *x-y* recorder was used for potential measurements. The potentials of the $\text{Ru}(\text{en})_3^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couples were measured vs. an internal standard reference reaction, the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ couple. Formal potentials were measured by cyclic voltammetry at a pyrolytic graphite electrode,²¹ taking the midpoint potential of reversible voltammograms to be $E_{1/2}$. Potentials were uncorrected for errors caused by differences in diffusion coefficients between the $\text{Ru}(\text{II})$ and $\text{Ru}(\text{III})$ complexes. It was assumed that this correction would be the same for the two redox couples and that it would cancel in determining ΔE for the reaction



Temperature control was provided by immersing the electrochemical cell in a water bath of the desired temperature. Differences in potentials at 25 °C were measured for the $\text{Ru}(\text{bpy})_2(\text{NH}_3)_2^{3+/2+} - \text{Ru}(\text{phen})_2(\text{NH}_3)_2^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+} - \text{Ru}(\text{NH}_3)_4(\text{phen})^{3+/2+}$ reaction systems by a similar internal reference technique.

Results

$[\text{Ru}(\text{NH}_3)_4(\text{bpy})/\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+/2+}$ Exchange Reaction.²² The rate of the electron transfer reaction



was measured as a function of ionic strength and temperature in ClO_4^- and CF_3SO_3^- media. The equilibrium constant from potential measurements at 25 °C for reaction 5 is essentially unity ($\Delta E \leq 0.005 \text{ V}$ in 0.1 M CF_3SO_3^-) which requires that $k_5 = k_{-5} = k_{\text{ex}}$. Sample data for the rate of approach to equilibrium in 0.1 M HClO_4 at 25 °C are given in Table I. Integrated first-order plots for these runs were generally linear to greater than 90% of the reaction. The rate of approach to equilibrium is well described by eq 4. A more important observation is that the exchange rate constant is independent of the direction from which the equilibrium is approached. A complete listing of the experimental data for this reaction and the other reactions studied in this work are given in supplemental tables. Values of ΔH^\ddagger , ΔS^\ddagger , and least-squares best fit rate constants at 25 °C are given in Table II for the $[\text{Ru}(\text{NH}_3)_4(\text{bpy})/\text{Ru}(\text{NH}_3)_4(\text{phen})]^{3+/2+}$ exchange reaction in both ClO_4^- and CF_3SO_3^- media.

The electron transfer reaction given in eq 5 is expected to be an excellent approximation to the true tetraamminebipyridineruthenium(II)/-(III) exchange reaction. Within error there is no free-energy difference between the reactants and products in reaction 5 and the two complexes are virtually the same size. Moreover, the kinetic data for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction are well fit by the rate expression (eq 4) at all the ionic strengths and temperatures used in this work. This implies that not only is $\Delta G^\circ = 0$ for reaction 5 but also that $\Delta H^\circ = 0$ and $\Delta S^\circ = 0$. From electrode potentials at 25 and 0 °C, ΔH° and ΔS° for reaction 5 are estimated to be $-0.1 \text{ kcal mol}^{-1}$ and $-0.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively.

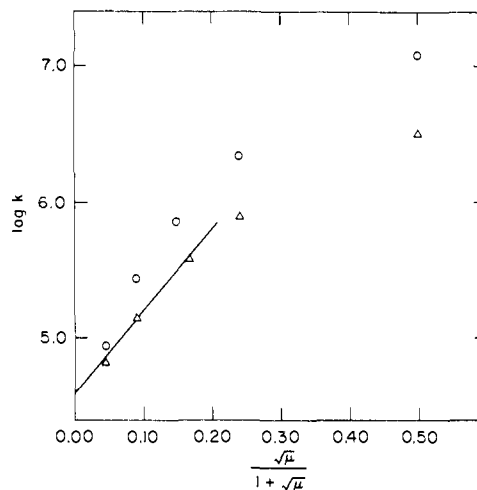


Figure 1. Plot suggested by the Guggenheim equation showing the ionic strength dependence of the rate constants for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction at 25 °C: circles, HClO_4 medium; triangles, $\text{CF}_3\text{SO}_3\text{H}$ medium. The line has the Debye-Hückel limiting slope of 6.12.

Table II. Rate Constants and Activation Parameters of the $\text{Ru}(\text{bpy})(\text{NH}_3)_4^{3+/2+}$ Electron Exchange Reaction

medium, M	$k_{25^\circ\text{C}},^a \text{ M}^{-1} \text{ s}^{-1}$	$\Delta H^\ddagger,^b \text{ kcal mol}^{-1}$	$\Delta S^\ddagger,^c \text{ cal deg}^{-1} \text{ mol}^{-1}$
0.002 ^d	6.62×10^4	4.1	-23
0.01 ^d	1.40×10^5	4.0	-22
0.04 ^d	3.77×10^5		
0.10 ^d	7.72×10^5	3.1	-21
1.00 ^d	3.25×10^6	2.8	-19
0.002 ^e	8.73×10^4	4.3	-22
0.01 ^e	2.76×10^5	2.9	-24
0.03 ^e	7.3×10^5	2.1	-25
0.10 ^e	2.2×10^6	1.9	-23
1.00 ^e	1.2×10^7	1.2	-22

^a Least-squares best fit value at 25 °C. ^b The error in ΔH^\ddagger is $\pm 0.5 \text{ kcal mol}^{-1}$. ^c The error in ΔS^\ddagger is $\pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$. ^d Medium is HTFMS . ^e Medium is HClO_4 .

Therefore the activation parameters measured for reaction 5 should be an excellent approximation to those for the desired exchange reaction. A similar ligand substitution technique has previously been used by Wilkins and Yelin²³ and by Young et al.²⁴ to estimate the rate constants for the $\text{FeEDTA}^{2-/-}$ and the $\text{Ru}(\text{bpy})_3^{3+/2+}$ exchange reactions, respectively.

The rate constants at 25 °C were fit to the Debye-Hückel equation

$$\log k = \log k_0 + \frac{2z_1z_2\alpha\sqrt{\mu}}{1 + \beta\bar{r}\sqrt{\mu}} \quad (6)$$

and to Guggenheim's modification of the Debye-Hückel equation which sets $\beta\bar{r} = 1$. In eq 6, z_1 and z_2 are the charges of the reactants, α and β are the Debye-Hückel constants, equal to 0.51 and 0.329, respectively, at 25 °C, μ is the ionic strength, and \bar{r} is the distance of approach of the centers of the reactants, which will be discussed in a later section.

A plot of $\log k$ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$ (Guggenheim equation) is shown in Figure 1. Significant deviation from linearity is seen at high ionic strength. This is not surprising in view of the failure of Debye-Hückel theory to fit activity coefficients at high ionic strength.²⁵ The data in CF_3SO_3^- media, however, do have the correct Debye-Hückel limiting slope of 6.12. This is shown by the solid line in Figure 1. These results suggest that the Guggenheim equation adequately accounts for the ionic strength dependence of the rate constants as the CF_3SO_3^- medium approaches infinite dilution. The data in ClO_4^- me-

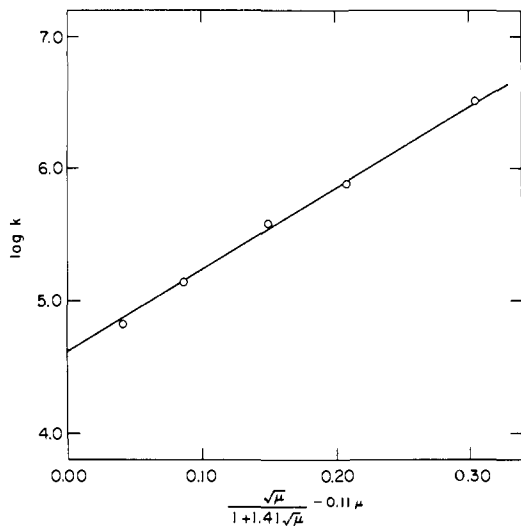


Figure 2. Nonlinear least-squares best fit of the rate constants at 25 °C for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction in $\text{CF}_3\text{SO}_3\text{H}$ media to eq 7.

dium, by contrast, are less well behaved. In this case the limiting slope has a value of 9–10 rather than the theoretical value of 6.12. A plot of the difference in rate constants in ClO_4^- and CF_3SO_3^- media vs. the concentration of ClO_4^- is linear in the range $[\text{ClO}_4^-] = 0.002\text{--}0.10\text{ M}$. This indicates that the data in HClO_4 can be fit by a two-term rate law of the form

$$\text{rate} = k_{\text{ex}}[\text{Ru}(\text{II})][\text{Ru}(\text{III})] + k'[\text{Ru}(\text{II})][\text{Ru}(\text{III})][\text{ClO}_4^-]$$

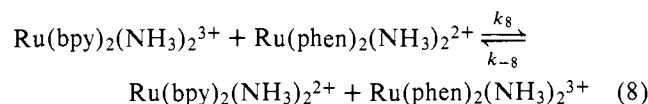
The k' term represents catalysis of the exchange reaction, probably by ion-pair formation of ClO_4^- with the highly charged ruthenium(III) complex. No spectroscopic evidence for ion-pair formation between $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+}$ and ClO_4^- was found.

The correlation of the data with the exact Debye–Hückel equation (eq 6) is less satisfactory. The deviations from the calculated line in CF_3CO_3^- media are in the same direction as the deviations in ClO_4^- media for which an argument for ion-pair formation has been presented. By contrast, the extended equation

$$\log k = \log k_0 + \frac{2z_1z_2\alpha\sqrt{\mu}}{1 + b\sqrt{\mu}} + c\mu \quad (7)$$

with $k_0 = 4.14 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $b = 1.41 \text{ M}^{-1/2}$, and $c = -0.65 \text{ M}^{-1}$, does fit the CF_3SO_3^- data well over the entire ionic strength range studied.²⁶ This is shown in Figure 2. The fitted value of $\beta\bar{r} = b = 1.41$ corresponds to a value of \bar{r} which is roughly a factor of 2 smaller than the value calculated from the mean “hard sphere” radii (see below) of the reactants. Newton²⁷ has found similar effects in treating the influence of ionic strength on the rates of oxidation–reduction reactions of actinide ions.

$[\text{Ru}(\text{bpy})_2(\text{NH}_3)_2/\text{Ru}(\text{phen})_2(\text{NH}_3)_2]^{3+/2+}$ Exchange Reaction. The rate of approach to equilibrium of the electron transfer reaction

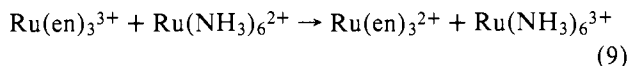


was measured at 25.0 °C in 0.10 M HClO_4 . Potential measurements show that within experimental error the equilibrium constant for reaction 8 is unity ($\Delta E \leq 0.004 \text{ V}$). The data are well fit by the rate expression given in eq 4 and the calculated second-order rate constant is independent of the direction from

which the equilibrium is approached. The exchange rate constant is $(8.4 \pm 1.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C in 0.1 M HClO_4 . The standard deviation of the rate constant is large because the range and absolute values of the concentrations of reactants for which the rate could be measured were small ($1\text{--}2.5 \times 10^{-6} \text{ M}$), and the observed first-order rate constants were near the limit of the stopped-flow method ($260\text{--}410 \text{ s}^{-1}$).

$\text{Ru}(\text{en})_3^{3+} + \text{Ru}(\text{NH}_3)_6^{2+}$ Reaction. The rate of the title reaction was measured in order to confirm the exchange rate constant reported for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couple at $\mu = 0.1 \text{ M}$.²⁸ The $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ exchange rate constant was first reported by Meyer and Taube in an elegant experiment involving the substitution of ND_3 for NH_3 . The most precise value for the exchange rate constant in their study was obtained at $\mu = 0.013 \text{ M}$. The exchange rate constants for the $\text{Ru}(\text{en})_3^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ couples are expected to be similar since the complexes are virtually the same size and the ethylene-diamine ligand is not expected to cause steric restraints as the reactants approach one another.

In CF_3SO_3^- media, the rate constant for the net reaction



is $2.70 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $\mu = 0.10 \text{ M}$. In order to calculate an exchange rate constant, the rate constant for the cross reaction was corrected for the free-energy change by means of the Marcus equation

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \\ \log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (10)$$

where k_{12} is the rate constant for the cross reaction, k_{11} and k_{22} are the exchange rate constants of the reactants, K_{12} is the equilibrium constant for the cross reaction, and $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. In the case in question, k_{11} and k_{22} are expected to be virtually the same and consequently $k_{\text{ex}} = k_{12}/(K_{12}f_{12})^{1/2}$. From measurements of the difference in formal potentials of the $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ complexes, K_{12} is 73 and therefore k_{ex} is calculated to be $3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 0.10 \text{ M}$). This is in excellent agreement with the value of $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ reported by Meyer and Taube.

The enthalpy and entropy of activation for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ exchange reaction are also of interest. The values reported by Meyer and Taube²⁸ for ΔH^\ddagger and ΔS^\ddagger at $\mu = 0.013 \text{ M}$ are 10 kcal mol^{-1} and $-11 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively. As will be noted in the Discussion section, the value of ΔS^\ddagger appears to be too positive by a factor of more than 2. For this reason, the activation parameters for reaction 8 were measured ($\Delta H^\ddagger = 2.4 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -30 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$, $\mu = 0.10 \text{ M CF}_3\text{SO}_3^-$). The activation parameters for the desired exchange reaction can be estimated using the equations derived by Marcus and Sutin.²⁹

$$\Delta H_{12}^\ddagger = \left(\frac{\Delta H_{11}^\ddagger + \Delta H_{22}^\ddagger}{2} \right) (1 - 4\alpha^2) + \frac{\Delta H_{12}^\circ}{2} (1 - 2\alpha) \\ \Delta S_{12}^\ddagger = \left(\frac{\Delta S_{11}^\ddagger + \Delta S_{22}^\ddagger}{2} \right) (1 - 4\alpha^2) + \frac{\Delta S_{12}^\circ}{2} (1 - 2\alpha) \\ \alpha = \frac{\Delta G_{12}^\circ}{4(\Delta G_{11}^\circ + \Delta G_{22}^\circ)}$$

where $\Delta G^* = -RT \ln(k/Z)$, $\Delta G^\ddagger = -RT \ln(kh/k_B T)$, $\Delta G^\circ = \Delta G^* - RT \ln(hZ/k_B T)$, $\Delta H^\ddagger = \Delta H^* - RT/2$, and $\Delta S^\ddagger = \Delta S^* - R/2$. As in eq 10, the subscript 12 refers to the cross reaction and 11 (and 22) refers to the exchange reaction. ΔH_{12}° and ΔS_{12}° for reaction 9 were measured from electrode potential data. The measured values of $\Delta E'$ are 0.102 and 0.109 V at 25 and 0 °C, respectively, in 0.10 M CF_3SO_3^- . Thus ΔH° and ΔS° are $-4.3 \text{ kcal mol}^{-1}$ and $-6.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$, respectively. These values are in reasonable agreement

Table III. Electron Exchange Rate Constants of Ruthenium Ammine Complexes at 25 °C

reaction	medium	k_{ex} , $M^{-1} s^{-1}$	\bar{a} , ^a \AA	ref
Ru(NH ₃) ₆ ^{3+/2+}	0.1 M HClO ₄	4.3×10^3	3.3	<i>b</i>
	0.1 M CF ₃ SO ₃ H	3.2×10^3		this work
Ru(NH ₃) ₅ py ^{3+/2+}	0.1 M CF ₃ SO ₃ H	1.1×10^5	3.8	32 ^c
Ru(NH ₃) ₄ (bpy) ^{3+/2+}	0.1 M CF ₃ SO ₃ H	7.7×10^5	4.4	this work
	0.1 M HClO ₄	2.2×10^6		this work
Ru(NH ₃) ₂ (bpy) ₂ ^{3+/2+}	0.1 M HClO ₄	8.4×10^7	5.6	this work
Ru(bpy) ₃ ^{3+/2+}	0.1 M HClO ₄	4.2×10^8	6.8	24

^a Mean radius, $\bar{a} = 1/2(d_1 d_2 d_3)^{1/3}$. ^b T. J. Meyer and H. Taube, quoted in H. Taube, *Adv. Chem. Ser.*, No. 162, 127 (1977). ^c The exchange rate constant at 25 °C and 1.0 M CF₃SO₃H is $4.75 \times 10^5 M^{-1} s^{-1}$; it was empirically corrected to $\mu = 0.1 M$ by multiplying the rate constant at $\mu = 1.0 M$ by 0.23.

with $\Delta H^\circ = -1.1 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = +3.9 \text{ cal deg}^{-1} \text{ mol}^{-1}$ calculated from the data of Lavalley et al.^{30,31} at $\mu = 1.0 M$ CF₃SO₃⁻. The values of $\Delta H^\ddagger = 4.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -27 \text{ cal deg}^{-1} \text{ mol}^{-1}$ are then estimated for the Ru(NH₃)₆^{3+/2+} exchange reaction, using the values of ΔH° and ΔS° measured in this work.

Dependence of Exchange Rates on the Size of the Reactants.

The rate constants at 25 °C and 0.1 M ionic strength for the Ru(NH₃)₆^{3+/2+},²⁸ Ru(NH₃)₅py^{3+/2+},³² Ru(NH₃)₄(bpy)^{3+/2+}, Ru(NH₃)₂(bpy)₂^{3+/2+}, and Ru(bpy)₃^{3+/2+}²⁴ exchange reactions are summarized in Table III. The general trend in the electron exchange reactions of these complexes is an increase in rate with an increase in the size of the complex. Although the complexes Ru(NH₃)₆ⁿ⁺ and Ru(bpy)₃ⁿ⁺ are spherically symmetrical, the other reactants considered here are not. For purposes of comparison of the rates and also for theoretical purposes (the theory which has been developed for outer-sphere electron exchange reactions is for spherical reactants) we have calculated the radii equivalent to the sphere of equal volume using the relation

$$\bar{a} = 1/2(d_1 d_2 d_3)^{1/3}$$

where the d_i are the "diameters" along the three L-Ru-L axes. These radii are included in Table III. Values of d_i were estimated from CPK molecular models and corrected to agree with known crystallographic results. For NH₃-Ru-NH₃, NH₃-Ru-pyridine, and pyridine-Ru-pyridine diameters, the values used are 6.6, 10.2, and 13.6 Å, respectively.

A plot of $\log k$ vs. $1/\bar{r}$, where k is the rate constant for electron exchange and \bar{r} is the mean distance of separation of the ruthenium centers, taken to be $2\bar{a}$, is presented in Figure 3. The plot shows good linearity. Figure 3 can be used to predict the exchange rate constants of other ruthenium ammine-pyridine complexes. Accordingly we estimate exchange rate constants of 8×10^6 and $2 \times 10^8 M^{-1} s^{-1}$ for the couples Ru(terpy)(NH₃)₃^{3+/2+} ($\bar{r} = 9.7 \text{ \AA}$) and Ru(terpy)(bpy)(NH₃)₃^{3+/2+} ($\bar{r} = 12.3 \text{ \AA}$), respectively, at 25 °C and $\mu = 0.1 M$.

Discussion

The results will be compared with the predictions of two adiabatic electron transfer models. The two models that will be discussed are the Marcus reactive-collision description and the ion-pair preequilibrium scheme outlined in the Introduction. We start first with the equations of the Marcus theory (eq 11-13).³⁻⁶

$$k = Z \exp[-(w_r + \Delta G_{in}^* + \Delta G_{out}^*)/RT] \quad (11)$$

$$\Delta G_{in}^* = \frac{6f_1 f_2 (\Delta a^\circ)^2}{2(f_1 + f_2)} \quad (12)$$

$$\Delta G_{out}^* = \frac{e^2}{4} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{n^2} - \frac{1}{D_s} \right) \quad (13)$$

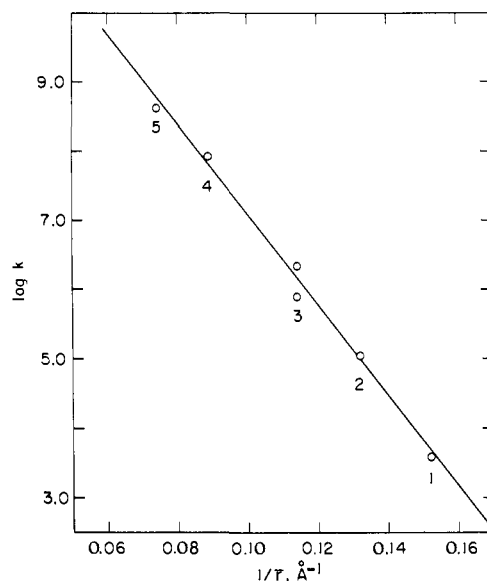


Figure 3. Plot of the logarithm of the observed exchange rate constant vs. the reciprocal of the mean distance of closest approach of the ruthenium centers: 1, Ru(NH₃)₆^{3+/2+}; 2, Ru(NH₃)₅py^{3+/2+}; 3, Ru(NH₃)₄(bpy)^{3+/2+}; 4, Ru(bpy)₂(NH₃)₂^{3+/2+}; 5, Ru(bpy)₃^{3+/2+}.

In the above expressions, f_1 and f_2 are the breathing force constants of the two reactants, Δa° is the difference between the equilibrium metal-ligand bond distances of the two reactants, a_1 and a_2 are the radii of the two reactants, r is the separation of the metal centers in the activated complex (assumed equal to $a_1 + a_2$), and n and D_s are the refractive index and static dielectric constant of the solvent, respectively. Z is the collision frequency of neutral molecules in solution and w_r is the work required to bring the two reactants together. Z is usually taken to be $10^{11} M^{-1} s^{-1}$ and is calculated from the equation

$$Z = \frac{N[8\pi k_B T(m_1 + m_2)/m_1 m_2]^{1/2} r^2}{1000} \quad (14)$$

which has been derived for gas-phase collisions (m_1 and m_2 are the masses of the two reactants and N is Avogadro's number). In terms of the transition state theory expression

$$k = \frac{k_B T}{h} \exp[-\Delta G^\ddagger/RT]$$

the free energy of activation for an exchange reaction according to the Marcus model is

$$\Delta G^\ddagger = -RT \ln \frac{hZ}{k_B T} + w_r + \Delta G_{in}^* + \Delta G_{out}^* \quad (15)$$

The term $RT \ln (hZ/k_B T)$ in this formulation arises from the loss in rotational and translational degrees of freedom in

forming the activated complex from the separated reactants and is given the symbol ΔG_{trans} .

We next consider the formulation of the electron exchange process in terms of an ion-pair preequilibrium (eq 1-3). In this description the exchange rate constant is given by eq 16-19.²

$$k = K_0 k_{\text{et}} \quad (16)$$

$$k_{\text{et}} = \frac{k_{\text{B}}T}{h} \exp[-\Delta G_{\lambda}^{\ddagger}/RT] \quad (17)$$

$$\Delta G_{\lambda}^{\ddagger} = \Delta G_{\text{in}}^* + \Delta G_{\text{out}}^* \quad (18)$$

$$K_0 = \frac{4\pi N r^3}{3000} \exp[-w_r/RT] \quad (19)$$

The above expression for K_0 , the ion-pair equilibrium constant, has been derived from both diffusional^{33a} and free volume^{33b} considerations and has been applied with some success to the rates of substitution reactions which are believed to go by an interchange mechanism.³⁴ In terms of transition state theory the activation free energy according to the ion-pair preequilibrium model is

$$\Delta G^{\ddagger} = -RT \ln \frac{4\pi N r^3}{3000} + w_r + \Delta G_{\text{in}}^* + \Delta G_{\text{out}}^* \quad (20)$$

The Marcus and ion-pair formulations of the rate constant can be put on a common basis by writing eq 11 in the form

$$k = \frac{Z h}{k_{\text{B}}T} \exp[-w_r/RT] \frac{k_{\text{B}}T}{h} \exp[-\Delta G_{\lambda}^{\ddagger}/RT] \quad (21)$$

Comparison of eq 21 with eq 16 and 17 shows that the rate constant for electron transfer in the Marcus formulation can also be formally expressed as the product of an equilibrium constant for precursor complex formation, given by eq 22, and a rate constant for electron transfer within the precursor complex, given by eq 17.

$$K_0 = \frac{Z h}{k_{\text{B}}T} \exp[-w_r/RT] \quad (22)$$

The preequilibrium assumption for precursor complex formation and the use of eq 19 and 22 for K_0 merit additional comment. The preequilibrium assumption requires that the dissociation of the precursor complex be rapid compared to the rate of electron transfer within the precursor complex, that is, that the electron transfer not be diffusion controlled. If the electron transfer is diffusion controlled then it is necessary to make a steady-state assumption for the concentration of the precursor complex. So far as the expressions for K_0 are concerned, eq 19 has been derived for ion-pair formation between oppositely charged reactants. For such systems the potential energy of interaction is a minimum when the two reactants are in contact. The same is not true for similarly charged reactants. For the latter systems eq 19 (and other analogous equations) can still be used with $r = (a_1 + a_2)$. However, although the equilibrium constant in this case still gives the statistical distribution of reactants that are in contact, $r = (a_1 + a_2)$ no longer corresponds to a minimum in the interaction free energy.³⁵ With this reservation in mind, we will continue to use eq 19 for similarly charged reactants. Equation 22, which has been derived from the kinetic theory of gases, glosses over the details of the diffusional process in liquids. Nevertheless, the use of Z is justified by the fact that it provides a reasonable estimate of the total number of collisions per unit time between a pair of molecules in solution.

The ratio of the equilibrium constants for precursor complex formation given by eq 19 and 22 is

$$\frac{K_0(\text{eq 19})}{K_0(\text{eq 22})} = \frac{(\pi M R T)^{1/2} r}{3 N h} = 0.24 M^{1/2} r \quad (23)$$

where $m_1 = m_2 = m$, $M = Nm$, and r is in ångströms. The difference between the two methods of calculating the rate constants is small for small reactants but, as will be pointed out in the next section, is significant for the reactions discussed here.

An important term in the expressions for the free energy of activation is the work required to bring the two reactants together. Since the Debye-Hückel theory fits the ionic strength dependence reasonably well to $\mu = 0.1$ M (for the Ru(NH₃)₄(bpy)^{3+/2+} exchange reaction the error in the rate constant at $\mu = 0.10$ M from Debye-Hückel theory is only a factor of 2 based on the rate constant extrapolated to $\mu = 0$) we will use the expression for the work term appropriate to the Debye-Hückel theory.

$$w_r = \frac{z_1 z_2 e^2}{D_s \bar{r} (1 + \kappa \bar{r})} \quad (24)$$

$$\kappa = \left(\frac{8\pi N^2 e^2 \mu}{1000 D_s R T} \right)^{1/2} = \beta \sqrt{\mu} \quad (25)$$

where the symbols have been previously defined. In the limit of infinite dilution the above expressions are simply a statement of Coulomb's law which gives the energy required to bring two charged spheres from infinity to a separation distance \bar{r} in a medium of dielectric constant D_s .

Comparison of Observed and Calculated Rate Constants. As noted in the Introduction, the contribution to the electron exchange activation energy from the reorganization of the inner-coordination spheres in ruthenium ammine complexes is small. For the Ru(NH₃)₆^{3+/2+} exchange reaction, Δa° is known from X-ray crystallographic determination to be 0.04 Å.³⁶ The symmetrical Ru-N stretching frequency of Ru(NH₃)₆³⁺ is reported to be 500 cm⁻¹³⁷ and assuming that the force constants of Ru(II) and Ru(III) are not appreciably different $f_1 = f_2 = 2.5 \times 10^5$ dyn cm⁻¹ can be calculated. Thus using eq 12, ΔG_{in}^* for the Ru(NH₃)₆^{3+/2+} exchange reaction is 0.9 kcal mol⁻¹. Crystal structures have also been determined for pentaamminepyrazineruthenium(II) and -(III)³⁸ and for *cis*-tetraamminebis(isonicotinamide)ruthenium(II) and -(III),³⁹ which are good analogues for estimating ΔG_{in}^* for the Ru(NH₃)₅py^{3+/2+} and Ru(NH₃)₄(bpy)^{3+/2+} exchange reactions, respectively. For both of these exchange reactions ΔG_{in}^* is estimated to be 1.0 kcal mol⁻¹. Within the error of the measurements there is no difference in metal-nitrogen bond lengths between tris(phenanthroline)iron(II) and -(III).⁴⁰ This result suggests that ΔG_{in}^* for the Ru(bpy)₃^{3+/2+} exchange reaction is negligible. Although there are no structural results available for the Ru(bpy)₂(NH₃)₂^{3+/2+} system, ΔG_{in}^* for this exchange reaction is also expected to be very small.⁴¹

The observed rate constants for the electron exchange reactions of the ruthenium complexes can now be compared with the theoretical predictions using the equation

$$k_{\text{calcd}} = Q \exp[-(w_r + \Delta G_{\text{out}}^* + \Delta G_{\text{in}}^*)/RT] \quad (26)$$

The reactive-collision and ion-pair preequilibrium formulations differ only in the expressions used for the preexponential term Q : in the former case Q is simply equal to Z while in the latter case it is equal to $(k_{\text{B}}T/h)(4\pi N \bar{r}^3/3000)$. The expressions for w_r , ΔG_{out}^* , and ΔG_{in}^* have been previously given (eq 24, 13, and 12, respectively). The formulas for w_r and ΔG_{out}^* with constants at 25 °C and at $\mu = 0.1$ M are

$$w_r = \frac{4.24 z_1 z_2}{\bar{r} (1 + 0.104 \bar{r})} \quad (27)$$

$$\Delta G_{\text{out}}^* = \frac{45.0}{\bar{r}} \quad (28)$$

in kcal mol⁻¹ for $\bar{r} (= 2\bar{a})$ in ångströms. The observed rate constants are compared with the predictions of eq 26 in Figure

Table IV. Comparison of Terms Contributing to Calculated Rate Constants for the Electron Exchange Reactions of Ruthenium(II)/-(III) Couples at 25 °C and $\mu = 0.1$ M

exchange reaction	Ru(NH ₃) ₆ ^{3+/2+}	Ru(NH ₃) ₅ py ^{3+/2+}	Ru(NH ₃) ₄ (bpy) ^{3+/2+}	Ru(bpy) ₂ (NH ₃) ₂ ^{3+/2+}	Ru(bpy) ₃ ^{3+/2+}
\bar{r} , Å	6.6	7.6	8.8	11.2	13.6
Z, M ⁻¹ s ⁻¹ ^a	2.1×10^{11}	2.4×10^{11}	2.9×10^{11}	4.0×10^{11}	5.2×10^{11}
Q, M ⁻¹ s ⁻¹ ^b	4.5×10^{12}	6.9×10^{12}	1.1×10^{13}	2.2×10^{13}	3.9×10^{13}
w_r , kcal mol ⁻¹	2.28	1.87	1.51	1.05	0.77
ΔG_{out}^* , kcal mol ⁻¹	6.82	5.92	5.11	4.02	3.31
ΔG_{in}^* , kcal mol ⁻¹	0.9	1.0	1.0	~0 ^c	~0 ^c
k_{calcd} , M ⁻¹ s ⁻¹ ^d	4.7×10^3	3.7×10^4	2.6×10^5	1.9×10^7	1.0×10^8
k_{calcd} , M ⁻¹ s ⁻¹ ^e	9.6×10^3	8.6×10^4	7.5×10^5	7.7×10^7	5.3×10^8
k_{calcd} , M ⁻¹ s ⁻¹ ^f	2.1×10^5	2.5×10^6	2.8×10^7	4.3×10^9	4.0×10^{10}
k_{obsd} , M ⁻¹ s ⁻¹	4×10^3 ⁱ	1.1×10^5 ^j	7.7×10^5 ^g	8.4×10^7 ^g	4.2×10^8 ^h
	3.2×10^3 ^g				

^a Z calculated from eq 14. ^b Q is equal to $(k_B T/h)(4\pi N\bar{r}^3/3000)$. ^c Assumed to be zero. ^d Equation 11 with $Z = 10^{11}$ M⁻¹ s⁻¹. ^e Equation 11 with Z calculated from eq 14. ^f Equations 16-19. ^g This work. ^h Reference 24. ⁱ Reference 28. ^j Reference 32.

4 and in Table IV for both the reactive collision formulation (eq 11) and the ion-pair preequilibrium formulation (eq 16).

The agreement between the observed and calculated rate constants is much better using eq 11. The agreement using a fixed value of Z is acceptable but the agreement with the observed rate constants improves when Z is calculated from eq 14. The latter equation allows for differences in the sizes and masses of the reactants. Calculations based on eq 16 show the expected slope but the absolute rate constants are about a factor of 40 too high. The agreement between the experimental results and eq 16 can be improved if a value of \bar{r} equal to approximately 70% of $2\bar{a}$ (Table III) is used. That a smaller value of \bar{r} may be appropriate was also suggested by the fit of the ionic strength dependence of the rate constants to eq 7. Note, however, that this would require that the ligands of one reactant penetrate the other reactant's inner-coordination sphere.⁴²

Enthalpy and Entropy of Activation. The entropy of activation for an electron exchange reaction can be calculated by differentiating the equation for the free energy of activation with respect to temperature (Gibbs-Helmholtz equation), $\Delta S^\ddagger = -\partial(\Delta G^\ddagger)/\partial T$

$$\Delta S^\ddagger = \Delta S_{trans} - \frac{\partial w_r}{\partial T} + \Delta S_{out}^* + \Delta S_{in}^* \quad (29)$$

$$\frac{\partial w_r}{\partial T} = \frac{w_r}{2T(1 + \beta\bar{r}\sqrt{\mu})} \left[\frac{2}{\partial \ln T} \frac{\partial \ln D_s}{\partial \ln T} + \beta\bar{r}\sqrt{\mu} \left(\frac{\partial \ln D_s}{\partial \ln T} \right) + \beta\bar{r}\sqrt{\mu} \right] \quad (30)$$

where the Debye-Hückel expression (eq 24) for the electrostatic work has been used. At infinite dilution this equation simplifies to

$$\frac{\partial w_r^\circ}{\partial T} = \frac{w_r^\circ}{T} \frac{\partial \ln D_s}{\partial \ln T} \quad (31)$$

where $\partial \ln D_s/\partial \ln T = -1.368$ for water at 25 °C. The two formalisms for the free energy of activation differ in the equation for ΔG_{trans} and thus will also differ in ΔS_{trans} . The expressions for ΔS_{trans} derived for the reactive collision and the ion pair preequilibrium formulations are given by eq 32 and 33, respectively.

$$\Delta S_{trans} = R \ln \frac{hZ}{k_B T} - \frac{R}{2} \quad (32)$$

$$\Delta S_{trans} = R \ln \left(\frac{4\pi N d^3}{3000} \right) \quad (33)$$

There is good evidence that ΔS_{out}^* and ΔS_{in}^* can be ignored. The energy required to rearrange the inner coordination spheres of the ruthenium complexes is very small and thus

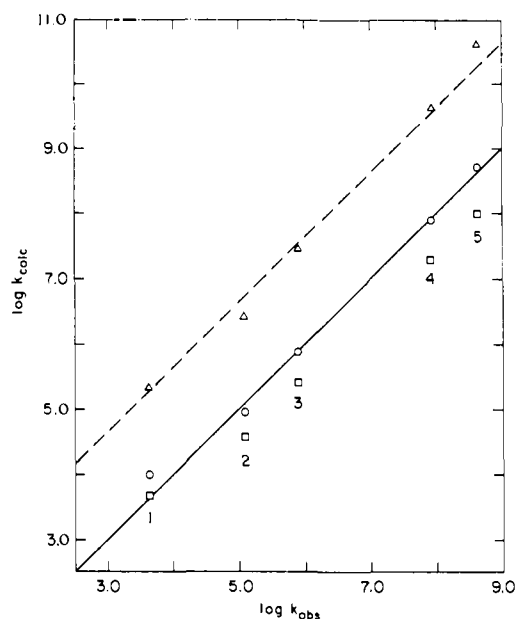


Figure 4. Plot of the logarithm of the calculated rate constant vs. the logarithm of the observed rate constant for the series of ruthenium complexes: triangles, calculated from eq 16-19; circles, calculated from eq 11 with Z calculated from eq 14; squares, calculated from eq 11 with Z fixed at 10^{11} M⁻¹ s⁻¹. 1, Ru(NH₃)₆^{3+/2+}; 2, Ru(NH₃)₅py^{3+/2+}; 3, Ru(NH₃)₄(bpy)^{3+/2+}; 4, Ru(bpy)₂(NH₃)₂^{3+/2+}; 5, Ru(bpy)₃^{3+/2+}.

ΔS_{in}^* will also be very small. ΔS_{out}^* is also expected to be very small from theoretical considerations. In the studies of Fischer et al.⁴³ and of Rieder et al.,⁴⁴ the entropy of activation for intramolecular electron transfer within binuclear Co(III)-Ru(II) complexes was found to be near zero. Based on these considerations, we will neglect any contribution to the entropy of activation from these terms and assume that $\Delta G_{out}^* = \Delta H_{out}^*$ and $\Delta G_{in}^* = \Delta H_{in}^*$.

The enthalpy of activation can be calculated from an alternative formulation of the Gibbs-Helmholtz equation, $\Delta H^\ddagger = \partial(\Delta G^\ddagger/T)/\partial(1/T)$.

$$\Delta H^\ddagger = \left(w_r - T \frac{\partial w_r}{\partial T} \right) + \Delta H_{trans} + \Delta H_{out}^* + \Delta H_{in}^* \quad (34)$$

For the reactive-collision model the equation is

$$\Delta H_{trans} = -RT/2 \quad (35)$$

while for the ion-pair preequilibrium model ΔH_{trans} is equal to zero. The values of ΔH^\ddagger for the two formulations will therefore differ by only $RT/2$ or 0.3 kcal mol⁻¹. The difference between the entropies of activation calculated from the two

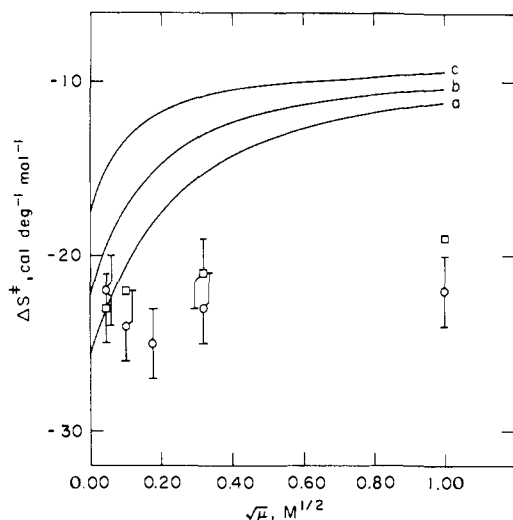


Figure 5. Plot showing the entropy of activation for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction as a function of ionic strength: squares, $\text{CF}_3\text{SO}_3\text{H}$ medium; circles, HClO_4 medium. The lines were calculated from eq 29 and 32 with the following values of \bar{r} : a, 7.0 Å; b, 9.0 Å; c, 14.0 Å.

Table V. Comparison of Observed and Calculated Entropies and Enthalpies of Activation at Zero Ionic Strength for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ Exchange Reaction

ΔS_0^\ddagger (obsd), cal deg ⁻¹ mol ⁻¹	-24 ± 3	
ΔH_0^\ddagger (obsd), kcal mol ⁻¹	4.0 ± 0.5	
\bar{r} , Å	9.0	4.5
ΔS_0^\ddagger (calcd, eq 37), cal deg ⁻¹ mol ⁻¹	-22.1	
ΔS_0^\ddagger (calcd, eq 40), cal deg ⁻¹ mol ⁻¹	-11.7	-22.6
ΔH_0^\ddagger (calcd, eq 38), kcal mol ⁻¹	4.7	
ΔH_0^\ddagger (calcd, eq 39), kcal mol ⁻¹	5.0	8.9

models depends upon the size of the reactants and will typically be some 5–15 cal deg⁻¹ mol⁻¹ for the complexes considered in this study.

The ionic strength dependence of the entropy and enthalpy of activation for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction is shown in Figures 5 and 6, respectively. The solid line in each figure has been calculated from eq 29 and 34 using $Z = 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and $\bar{r} = 9 \text{ Å}$. It will be seen (Figure 5) that the observed entropy of activation does not show the predicted increase with increasing ionic strength; instead the entropy is essentially independent of ionic strength. The increase in rate constant with increasing ionic strength is reflected almost entirely in a decrease in the enthalpy of activation. This is contrary to the expectation from eq 34 in which a slight increase in enthalpy with increasing ionic strength is predicted (Figure 6). This behavior is not unique to this ruthenium system but has also been observed for the electron transfer reactions of some aquo metal ions.⁴⁵

A smaller ionic strength dependence of the entropy of activation is predicted by the Guggenheim modification of the Debye-Hückel equation and by the extended Debye-Hückel equation derived by Waisman et al.⁴⁶ However, the predicted ionic strength dependence is still larger than observed for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction and for the aquo metal ions. The observed trend in ΔH^\ddagger and ΔS^\ddagger with increasing ionic strength in ClO_4^- media vs. CF_3SO_3^- media suggests that ion pairing or other specific anion effects are responsible for the deviations from the predicted behavior. As discussed above, there is good evidence for ion pairing between the $\text{Ru}(\text{III})$ complex and ClO_4^- relative to CF_3SO_3^- media. There is, however, an alternative explanation for the dependence of the activation parameters on the ionic strength of the

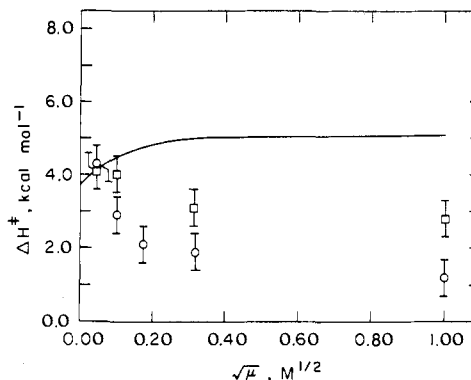


Figure 6. Plot showing the enthalpy of activation for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction as a function of ionic strength: squares, $\text{CF}_3\text{SO}_3\text{H}$ medium; circles, HClO_4 medium. The line was calculated from eq 34 and 35 with $\bar{r} = 9.0 \text{ Å}$ and $\Delta G_{\text{in}}^* = 0$.

medium. The expression in eq 36 is the equivalent of expressing the ionic strength dependence of the rate constant by eq 7.

$$w_r = w_r^\circ - \frac{w_r^\circ b \sqrt{\mu}}{1 + b \sqrt{\mu}} + 2.303 RT c \mu \quad (36)$$

Here $w_r^\circ = z_1 z_2 e^2 / D_s \bar{r}$ and b and c are empirical constants taken from the nonlinear least-squares fit of the data to eq 7. Utilizing this expression an entropy of activation which is independent of ionic strength can be obtained if the dielectric constant or its temperature derivative is assumed to be a function of ionic strength. Although the ionic strength data can be rationalized in this manner, a more fundamental difficulty lies in the use of a dielectric continuum model for highly charged ions such as those employed in this study.

Because of the difficulty in interpreting the ionic strength dependence of the activation entropy and enthalpy, activation parameters for the $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ exchange reaction at infinite dilution were obtained by extrapolating the rate constants to $\mu = 0$ using eq 7. This was done at each temperature. The entropy and enthalpy of activation at infinite dilution within the reactive-collision formulation are given by eq 37 and 38, respectively.

$$\Delta S_0^\ddagger = \left(\frac{w_r^\circ}{T} \frac{\partial \ln D_s}{\partial \ln T} \right) + R \ln \frac{hZ}{k_B T} - \frac{R}{2} \quad (37)$$

$$\Delta H_0^\ddagger = w_r^\circ \left(1 - \frac{\partial \ln D_s}{\partial \ln T} \right) - \frac{RT}{2} + \Delta G_{\text{out}}^* + \Delta G_{\text{in}}^* \quad (38)$$

The value of ΔH_0^\ddagger calculated from the ion-pair preequilibrium formulation

$$\Delta H_0^\ddagger = w_r^\circ \left(1 - \frac{\partial \ln D_s}{\partial \ln T} \right) + \Delta G_{\text{out}}^* + \Delta G_{\text{in}}^* \quad (39)$$

differs only slightly from the reactive-collision formulation. The entropy of activation calculated from the ion-pair preequilibrium formulation is given by

$$\Delta S_0^\ddagger = \frac{w_r^\circ}{T} \left(\frac{\partial \ln D_s}{\partial \ln T} \right) + R \ln \left(\frac{4\pi N \bar{r}^3}{3000} \right) \quad (40)$$

The experimental activation parameters are compared with the calculated values in Table V. The values of ΔS_0^\ddagger and ΔH_0^\ddagger , calculated from eq 37 and 38, respectively, are in excellent agreement with the observed values. By contrast, the entropy of activation calculated from the ion-pair preequilibrium formulation is much too positive. If a smaller value of \bar{r} is used, the agreement between the observed entropy and that calculated from eq 40 is improved. However, using a value of \bar{r} derived from the ionic strength dependence of the rate constant at 25 °C increases the value of ΔH_0^\ddagger calculated from eq

39 to such an extent that it is in poor agreement with the observed value.

One further point with regard to the activation parameters deserves mention. The entropy and enthalpy of activation for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ exchange reaction were calculated from the net reaction between $\text{Ru}(\text{en})_3^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$. If the entropy of activation is not a strong function of ionic strength, then the observed value at $\mu = 0.10 \text{ M}$, $-27 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$, is reasonably close to the expected value for an \bar{r} of 7 Å. The reported entropy of activation for the $\text{Ru}(\text{bpy})_3^{3+/2+}$ exchange reaction at $\mu = 0.1 \text{ M}$, $-6.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$,²⁴ is more positive than expected on the basis of the present treatment.

Conclusions and Implications for Other Exchange Reactions.

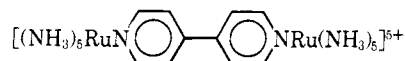
The ionic strength dependence of the rate constants and activation parameters determined in this work cannot readily be interpreted in terms of the models used. Consequently activation parameters were computed at zero ionic strength and compared with the experimental values. At zero ionic strength the semiclassical model derived on the basis of the reactive collision formulation of an activated complex (Marcus theory) gives excellent agreement with the rates and activation parameters for the exchange reactions of the ruthenium ammine complexes. This model also accounts satisfactorily for the linear dependence of $\log k$ on $1/\bar{r}$.

As shown above, the Marcus equations can be recast in terms of the preequilibrium formation of a precursor complex followed by rate-limiting electron transfer within the complex. The expression for the equilibrium constant for the formation of the precursor derived in this manner differs from the conventional expression for ion pair formation. From the better agreement of the rate constants calculated from the reactive collision model with the experimental data it might be concluded that the preexponential term given by the reactive collision model is the appropriate one. However, this conclusion is not necessarily correct. The data in Table IV show that ΔG_{in}^* is small and that the largest contribution to ΔG^\ddagger for each exchange is from ΔG_{out}^* . Thus it could still be that the conventional ion-pair expression is the appropriate one to use, but that the expression for ΔG_{out}^* is in error. For this explanation to be correct the "real" value of ΔG_{out}^* would have to be larger than the value given by eq 13.

Additional information on this point can be obtained from a consideration of the barrier to electron transfer within binuclear complexes. In such systems the question of the stability constant of the precursor complex (and ionic strength effects) is circumvented. Theoretical considerations show that provided that the distortions are harmonic and the electronic interaction between the two metal centers is not too large, the barrier for light-induced electron transfer within the binuclear complex should be equal to four times the thermal activation barrier, in other words,⁴⁷

$$E_{\text{op}} = 4E_{\text{th}} = 4(\Delta G_{\text{in}}^* + \Delta G_{\text{out}}^*)$$

Thus $(\Delta G_{\text{in}}^* + \Delta G_{\text{out}}^*)$ for the thermal electron transfer in a binuclear complex can be estimated from the position of the intervalence absorption band in the complex. For



λ_{max} is 1050 nm in D_2O corresponding to $E_{\text{op}} = 27.2 \text{ kcal mol}^{-1}$ and $(\Delta G_{\text{in}}^* + \Delta G_{\text{out}}^*) = 6.8 \text{ kcal mol}^{-1}$.⁴⁸ If we now assume that the thermal electron transfer within the binuclear complex provides a good model for the electron transfer within the precursor complex for the $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ exchange,^{32,49} then the barrier $(\Delta G_{\text{in}}^* + \Delta G_{\text{out}}^*)$ for the latter exchange is calculated to be $\sim 6.8 \text{ kcal mol}^{-1}$. This value is in excellent agreement with the reorganization barrier calculated for the $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ exchange reaction using eq 13 for

ΔG_{out}^* (Table IV). The above comparisons thus provide no evidence that the expression for ΔG_{out}^* is in error.

Other factors which have been neglected in the above discussion are steric effects, nonadiabaticity, and alternative forms of the frequency factor. The absolute rate theory preexponential term kT/h has been used in this discussion. Other expressions for the frequency factor have been proposed.² Including these effects may improve the agreement between the kinetic parameters calculated for the ion-pair model and the observed values.⁵¹ A calculation of the electronic interaction energy of the Ru(II)-Ru(III) system will evidently be of considerable interest. In the absence of this information we may conclude that the Marcus equations provide a better rationalization of the kinetic data.

Finally, if the ionic strength dependence of the entropy of activation for the Ru(II)/Ru(III) exchange reaction can be generalized to other reactions, then the measured entropy of activations for aquo metal ions of ca. $-25 \text{ cal deg}^{-1} \text{ mol}^{-1}$ at 0.1–1.0 M ionic strength cannot be taken as evidence for nonadiabaticity when observed and calculated values are compared (as has been done, for example, in ref 46). Thus, when extrapolations are made to infinite dilution, the calculated entropy of activation for the $\text{Fe}(\text{H}_2\text{O})_6^{3+/2+}$ exchange is in good agreement with the experimental value.¹⁰ The calculated activation enthalpy is, however, several kilocalories per mole too high. It has been proposed^{1,10} that nuclear tunneling is occurring in this exchange reaction and recent calculations indeed show that such effects are appreciable in this system.⁵⁰ However, nuclear tunneling effects are not important for systems where the inner-shell reorganization energies are small. This is the case for the ruthenium ammine systems discussed here.

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Supplementary Material Available: Tables containing the raw kinetic data (3 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of Decamethylmanganocene and Decamethylferrocene. Static Jahn-Teller Distortion in a Metallocene

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Abstract: The crystal and molecular structures of bis(pentamethylcyclopentadienyl)manganese(II) and -iron(II) have been determined by single-crystal X-ray diffraction. The crystal packing of the two compounds is closely related and highly ordered, allowing a detailed comparison of structural parameters. Both metallocenes contain planar, staggered Me_5Cp rings. The ferrocene corresponds to a molecular symmetry of D_{5d} with average Fe-C and C-C distances of 2.050 (2) and 1.419 (2) Å, respectively. The low-spin manganocene has an orbitally degenerate ${}^2E_{2g}$ ground state in D_{5d} symmetry. This degeneracy is relieved in the solid state by (1) a distortion of the Cp rings in which C-C ring distances range from 1.409 (2) to 1.434 (2) Å and (2) a small slippage of the top and bottom halves of the metallocene "sandwich" to give Mn-C bond lengths which range from 2.105 (2) to 2.118 (2) Å. In both structures the methyl groups bend away from the metal atom 0.06 Å from the Cp rings. Orange crystals of $(\text{C}_5(\text{CH}_3)_5)_2\text{Mn}$ conform to the space group $C2/c$ with $a = 15.143$ (4) Å, $b = 12.248$ (3) Å, $c = 9.910$ (3) Å, and $\beta = 93.56$ (3)°. For 2581 independent reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 3.6\%$, $R_w = 5.0\%$. Orange crystals of $(\text{C}_5(\text{CH}_3)_5)_2\text{Fe}$ conform to the space group $Cmca$ with $a = 15.210$ (3), $b = 11.887$ (2), and $c = 9.968$ (2) Å. For 1217 independent reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 3.9\%$ and $R_w = 5.5\%$. Both structures have four molecules per unit cell with C_i (Mn) and C_{2h} (Fe) crystallographic site symmetry, respectively.

Introduction

Previous structural investigations of metallocenes have demonstrated the dependence of the metal-to-(ring carbon) distance [$R(\text{M}-\text{C})$] on the spin state of the molecule. Manganocene [$(\eta\text{-C}_5\text{H}_5)_2\text{Mn}$ or Cp_2Mn] possesses a high-spin ${}^6A_{1g}$ ($[e_{2g}^2 a_{1g}^1 e_{1g}^2]$) electronic configuration in benzene solution¹ and in the vapor phase.² Bünder and Weiss³ have determined the structure of solid Cp_2Mn , which is polymeric, while a gas-phase electron diffraction⁴ study yielded an $R(\text{Mn}-\text{C})$ of 2.383 (3) Å. This is an exceptionally long metal to ring bond when compared to other metallocenes of the first transition series, where $R(\text{M}-\text{C})$ ranges from 2.064 (3) Å for Cp_2Fe to 2.280 (5) Å for Cp_2V .⁵ Magnetic susceptibility, EPR,⁶ and UV photoelectron² studies of 1,1'-dimethylmanganocene

$[(\text{MeCp})_2\text{Mn}]$ have demonstrated a thermal equilibrium between high-spin (${}^6A_{1g}$) and low-spin (${}^2E_{2g}$, $[e_{2g}^3 a_{1g}^2]$) electronic configurations, with the high-spin form predominating at elevated temperatures. A gas-phase electron diffraction investigation similarly revealed the presence of two isostructural species in the vapor at 100 °C, with average $R(\text{M}-\text{C})$ s of 2.433 (8) and 2.144 (12) Å.⁵ Comparison of these bond lengths with the bond length observed in the high-spin Cp_2Mn led to the conclusion that the former distance represents high-spin and the latter low-spin $(\text{MeCp})_2\text{Mn}$. An unusually large Mn-C vibrational amplitude (0.160 Å) was noted for low-spin $(\text{MeCp})_2\text{Mn}$, and it was concluded that this was a manifestation of a dynamic Jahn-Teller distortion involving ring-tilting modes. The ${}^2E_{2g}$ configuration is orbitally degenerate; thus in theory the low-spin manganocene is subject to