

Figure 1. Relative energies of the molecular orbitals in metallocene complexes.⁹

but it is closer in structure to the d^7 than to d^9 case.⁵ These data when considered with the apparent differences in stability between the $C_2B_{10}H_{12}$, $C_2B_{10}H_{12}^-$, and $C_2B_{10}H_{12}^{2-}$ systems may indicate that opening of the icosahedral system occurs simply upon addition of the second electron and may not require a proton.

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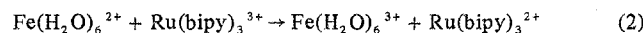
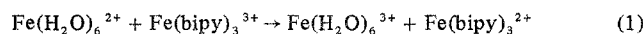
Electron-Transfer Reactions with Unusual Activation Parameters. A Treatment of Reactions Accompanied by Large Entropy Decreases

AIC40369B

Sir:

The activation enthalpies for the oxidation of $Fe(H_2O)_6^{2+}$ by poly(pyridine)iron(III) and -ruthenium(III) complexes

(reactions 1 and 2, for example) are small or slightly nega-



tive.¹⁻³ This has led to the suggestion^{2,3} that these reactions occur by a "non-Marcus" path which includes at least one distinctive feature not considered in a current outer-sphere electron-transfer model.⁴⁻⁸ We wish to point out that small or even negative activation enthalpies are in themselves not necessarily inconsistent with this model and indeed are predicted by it for the systems under consideration.

In terms of the model referred to above, the rate constant for an outer-sphere electron-transfer reaction is given by

$$k = pZe^{-\Delta G^*/RT} \quad (3)$$

where p is the probability of electron transfer in the activated complex and Z , the collision frequency between two uncharged particles in solution, is taken to be $10^{11} M^{-1} \text{ sec}^{-1}$. The following relations between the kinetic parameters for a cross reaction and the component self-exchange reactions can also be derived from this model⁴⁻⁸

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

$$\log f_{12} = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (5)$$

$$\begin{aligned} \Delta G_{12}^* &= \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{\Delta G_{12}^\circ}{2} + \frac{(\Delta G_{12}^\circ)^2}{8(\Delta G_{11}^* + \Delta G_{22}^*)} \\ &= \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{\Delta G_{12}^\circ}{2}(1 + \alpha) \end{aligned} \quad (6)$$

$$\alpha = \frac{\Delta G_{12}^\circ}{4(\Delta G_{11}^* + \Delta G_{22}^*)} \quad (7)$$

where k_{12} , K_{12} , ΔG_{12}^* , and ΔG_{12}° refer to the cross reaction and k_{11} , k_{22} , ΔG_{11}^* , and ΔG_{22}^* refer to the exchange reactions.⁵⁻¹⁰ Usually α is small; it is negative in reactions of negative ΔG_{12}° and becomes increasingly so with decreasing ΔG_{12}° .

The value of ΔS_{12}^* can be obtained by differentiating eq 6 with respect to temperature [$\Delta S = -\partial(\Delta G)/\partial T$]

$$\begin{aligned} \Delta S_{12}^* &= \left[\frac{\Delta S_{11}^*}{2} + \frac{\Delta S_{22}^*}{2} \right] (1 - 4\alpha^2) + \\ &\quad \frac{\Delta S_{12}^\circ}{2} (1 + 2\alpha) \end{aligned} \quad (8)$$

The value of ΔH_{12}^* can similarly be obtained from eq 6 by using a Gibbs-Helmholtz equation [$\Delta H = \partial(\Delta G/T)/\partial(1/T)$] for ΔH_{12}^* , ΔH_{11}^* , ΔH_{22}^* , and ΔH_{12}°

$$\begin{aligned} \Delta H_{12}^* &= \left[\frac{\Delta H_{11}^*}{2} + \frac{\Delta H_{22}^*}{2} \right] (1 - 4\alpha^2) + \\ &\quad \frac{\Delta H_{12}^\circ}{2} (1 + 2\alpha) \end{aligned} \quad (9)$$

It is readily apparent from eq 9 that ΔH_{12}^* will decrease with decreasing ΔH_{12}° and that ΔH_{12}^* will be small or even negative if ΔH_{12}° is sufficiently negative.

The relationship between ΔG^* , ΔH^* , and ΔS^* and the usual experimentally derived quantities ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger is

$$\begin{aligned} \Delta G^\ddagger &= \Delta G^* - RT \ln (hZ/kT) \\ \Delta S^\ddagger &= \Delta S^* + R \ln (hZ/kT) - 1/2R \\ \Delta H^\ddagger &= \Delta H^* - 1/2RT \end{aligned} \quad (10)$$

noting that Z is proportional to \sqrt{T} .

The following are among the more important assumptions made in deriving eq 4–6.¹¹

(1) Differences in the stabilities of the precursor and successor complexes for the various reactions (including work terms for bringing the reactants together and separating the products¹¹) have been neglected. Noncancellation of these stabilities can lead to difficulties¹² since the derived relations are really between Franck–Condon reorganization energies rather than between free energies of activation. If the stability constants of the precursor and successor complexes are included, then eq 4 becomes

$$k_{12} = \left[\frac{P_{12}P_{21}k_{11}k_{22}K_{12}f}{P_{11}P_{22}} \right]^{1/2} \quad (11)$$

$$\log f = \frac{[\log(K_{12}P_{21}/P_{12})]^2}{4 \log(k_{11}k_{22}/P_{11}P_{22}Z^2)}$$

where P_{11} , P_{22} , and P_{12} are the stability constants of the precursor complexes, and P_{21} is the stability constant of the successor complex for the cross reaction (the successor complex for a forward reaction is the precursor complex for the reverse reaction). Evidently eq 11 reduces to eq 4 if $P_{12}P_{21} \approx P_{11}P_{22}$ and $f \approx 1$.

(2) It has been assumed that none of the reactions involved in the rate comparisons are nonadiabatic. If allowance is made for the possibility that one or more of the reactions could be nonadiabatic, then eq 4 takes the form¹³

$$k_{12} = p_{12} \left[\frac{k_{11}k_{22}K_{12}f}{P_{11}P_{22}} \right]^{1/2} \quad (12)$$

$$\log f = \frac{(\log K_{12})^2}{4 \log(k_{11}k_{22}/p_{11}p_{22}Z^2)}$$

Equation 12 reduces to eq 4 if $p_{12} \approx (p_{11}p_{22})^{1/2}$ and $f \approx 1$.¹⁰ Equations 4–6 also assume that, if adiabatic, the interaction energies are not large enough to decrease significantly the free energies of activation.

(3) Nuclear tunneling contributions have been neglected in deriving eq 4. A nuclear tunneling contribution for the usual electron-transfer reactions is discussed elsewhere¹⁴ in terms of Franck–Condon vibrational overlap factors and is presumed to be small. However in the so-called “inverted” region, where the intersection of the *potential energy surfaces* of the reactants and products occurs on the left-hand side of the reactants curve, for example, when $\log K_{12} \geq 2 \log(Z^2/k_{11}k_{22})$, the electron-transfer can only occur via a nonadiabatic mechanism.¹⁵ Indeed, it has been shown¹⁶ that in this “inverted” region, nuclear tunneling effects may become important. Because of nuclear tunneling, rates will remain constant at the diffusion-controlled limit rather than decreasing again as the standard free energy change for the reaction becomes very negative. In other words, the “inverted” behavior predicted by the simple model^{5,9} may not be seen because of nuclear tunneling considerations.¹⁶

(4) In deriving eq 4 it has been assumed that no very rapid preequilibrium changes (for example, a spin change) take place prior to the electron-transfer step. If such a change does occur in one of the reactants, then the system will still be described by eq 4 but with f now given by eq 13 where P_1^* is the

$$\log f = \frac{\log(K_{12}/P_1^*)}{4 \log(k_{11}k_{22}/P_1^*Z^2)} \quad (13)$$

equilibrium constant for the preequilibrium change. A rapid preequilibrium change will have important consequences. For example, if ΔG° becomes very negative, then the rate constant

Table I. Thermodynamic and Kinetic Parameters for the Reduction of $\text{Fe}(\text{bipy})_3^{3+}$ and $\text{Ru}(\text{bipy})_3^{3+}$ by $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ at 25°C ^a

Parameter	$\text{Fe}(\text{bipy})_3^{3+}$	$\text{Ru}(\text{bipy})_3^{3+}$	Ref
ΔG_{12}°	-8.1	-13.9	19, 20
ΔH_{12}^\ddagger	-23.3	-26.8	19, 20
ΔS_{12}^\ddagger	-51	-43	19, 20
ΔG_{12}^\ddagger (obsd)	11.4 ± 0.1	9.52 ± 0.9	3, 2
ΔG_{12}^\ddagger (calcd)	7.8	5.8	b
ΔH_{12}^\ddagger (obsd)	-0.8 ± 0.5	-0.30 ± 0.05	3, 2
ΔH_{12}^\ddagger (calcd)	-3.2	-2.9	c
ΔS_{12}^\ddagger (obsd)	-41 ± 2	-33 ± 3	3, 2
ΔS_{12}^\ddagger (calcd)	-37	-29	d

^a The units of ΔG and ΔH are kcal mol^{-1} , and the ΔS units are $\text{cal deg}^{-1} \text{mol}^{-1}$. ^b From eq 6 and 10. ^c From eq 9 and 10. ^d From eq 8 and 10.

will not level off at k_{diff} as described above, but at $P_1^*k_{\text{diff}}$, where k_{diff} is the diffusion-limited rate.^{17,18}

Application to the Oxidation of Iron(II) by Poly(pyridine)iron(III) and -ruthenium(III) Complexes. The above considerations may be applied to the oxidation of iron(II) by the tris(bipyridine) complexes of iron(III) and ruthenium(III). The relevant thermodynamic^{19,20} and kinetic^{2,3} parameters for the cross reactions are summarized in Table I. The values of ΔG_{11}^\ddagger , ΔH_{11}^\ddagger , and ΔS_{11}^\ddagger for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ – $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ exchange reaction which were used to calculate the activation parameters for the cross reactions are 16.8 and 9.3 kcal mol^{-1} and $-25 \text{ cal deg}^{-1} \text{mol}^{-1}$, respectively.²¹ The activation parameters for the $\text{Fe}(\text{bipy})_3^{2+}$ – $\text{Fe}(\text{bipy})_3^{3+}$ and $\text{Ru}(\text{bipy})_3^{2+}$ – $\text{Ru}(\text{bipy})_3^{3+}$ exchange reactions in 0.3–1.0 *M* perchloric acid have not been measured directly; however, the rates are very close to being diffusion controlled^{22,23} and for purposes of calculation we will assume ΔG_{22}^\ddagger , ΔH_{22}^\ddagger , and ΔS_{22}^\ddagger values of 6 and 3 kcal mol^{-1} and $-10 \text{ cal deg}^{-1} \text{mol}^{-1}$, respectively.²⁴ It is apparent from Table I that the calculated activation enthalpies and entropies are in satisfactory agreement with the observed ones. In particular, it should be noted that negative values of ΔH_{12}^\ddagger are predicted by the simple model. Nevertheless, some difficulties remain. The free energies of activation calculated from eq 6 and 10 are several kilocalories per mole lower than the observed ones (see also ref 25). This discrepancy could be due to the breakdown of the first, second, and/or third assumptions made above. Thus the relatively low observed cross-reaction rates could be due to $P_{12}P_{21} \ll P_{11}P_{22}$, a condition which could arise because of an unfavorable hydrophobic–hydrophilic interaction in the cross reaction or because of the need for the Fe^{2+} to penetrate between the phenanthroline rings in the cross reaction.^{1,26} Alternatively, the slow rate could arise from a nonadiabaticity such that $p_{12} < (p_{11}p_{22})^{1/2}$. Although it is difficult to assess the magnitude of the p factors, it would be surprising if p_{22} were much less than unity. In this connection it is of interest that the rates of reduction of $\text{Co}(\text{bipy})_3^{3+}$ and $\text{Co}(\text{phen})_3^{3+}$ by V^{2+} and the rates of oxidation of $\text{Co}(\text{phen})_3^{2+}$ by Fe^{3+} are consistent with eq 6 and 10.^{13,27,28} Finally, because of the highly negative ΔH_{12}° , the states of the system that do react may be in the inverted region so that nuclear tunneling corrections may be needed.¹⁶ Such corrections would lead to a lowering of the calculated activation energy. To decide whether this last factor is important one would need to know the shapes of the lowest potential energy surfaces for reaction, so as to determine whether they are of the inverted type. If they turn out to be of this type, then one would have to modify the basic equations either along the lines used in recent publications¹⁶ or perhaps by using different methods.

A Molecular Interpretation of the Negative Activation Enthalpies. The above considerations show that the negative activation enthalpies for the oxidation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ by the

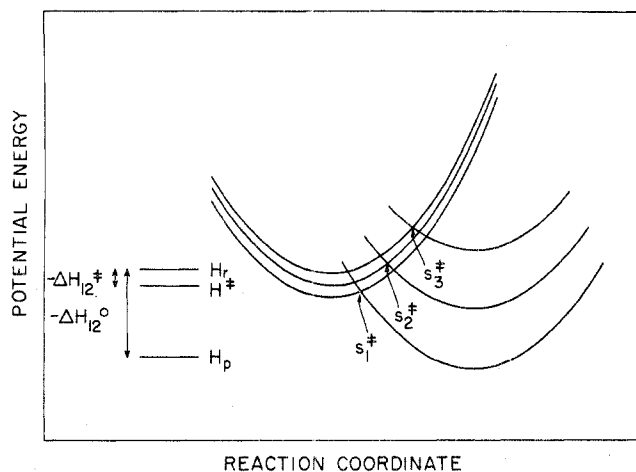


Figure 1. Positions s_i^\ddagger of activated complexes for a reaction of very negative ΔS_{12}^\ddagger . Potential energy curves for a few of the many quantum states of the system are given. For brevity, the usual adiabatic splittings at the intersections of corresponding curves for a given pair of reactants and products, to yield three adiabatic curves, have been omitted.

poly(pyridine) complexes of iron(III) and ruthenium(III) are not necessarily inconsistent with eq 4–6. We next explore the reasons for the negative ΔH_{12}^\ddagger in molecular terms. The standard entropy changes for the reactions ΔS_{12}^\ddagger are very negative (Table I) indicating that the quantum states of the products are more widely spaced than those of the reactants, as discussed in footnote 29. Figure 1 gives a schematic description of this behavior using the usual^{5–9,14} pair of intersecting potential energy curves for the reactants and products.²⁹ Here, however, we have sketched the curves for several of the quantum states of the reactants and for several of the corresponding quantum states of the products.²⁹ (The case where curves for two low-lying quantum states of the system “intersect” in an “inverted” configuration, while the high ones intersect in a normal one, is shown in Figure 2.) For a few quantum states labelled 1, 2, 3, ..., the intersection of corresponding curves occurs at values of the reaction coordinate given by $s_1^\ddagger, s_2^\ddagger, s_3^\ddagger, \dots$. The mean energy of the reactants is obtained from the energy of each quantum state of the system for a given pair of reactants, multiplied by the probability of finding the system (reactant pair plus surrounding solution) in that state and summed over all states. (The probability involves the usual Boltzmann weighting factor.) In solution, the average energy E of a specified system (reactant pair plus solution) is essentially equal to the thermodynamic heat content H of that system, since PV is negligible. This average for reactants is indicated by a horizontal line H_r in Figure 1, while the corresponding quantity for the products is indicated by the line H_p .

The positions of the activated complexes, indicated by the s_i^\ddagger 's in the figures, are seen to be quantum state dependent. The internal energy of any quantum state i of the activated complex is the value of this energy at s_i^\ddagger . The mean energy for the activated complexes is a Boltzmann-weighted average and is indicated by the horizontal line labeled H^\ddagger in Figure 1. It is defined more precisely for quantum state dependent activated complexes in a recent article.³⁰ The method described there shows how a free energy maximum criterion can be used to define an effective activated complex at some mean s_i^\ddagger for a reaction whose activated complexes each occur at positions which are quantum state dependent.

In Figure 1, where ΔH_{12}^\ddagger is very negative, ΔH_{12}^\ddagger can be negative also: the principal reason, in the case of the system under consideration, is that the more energetic states of the activated complex are less reactive than the less energetic ones,

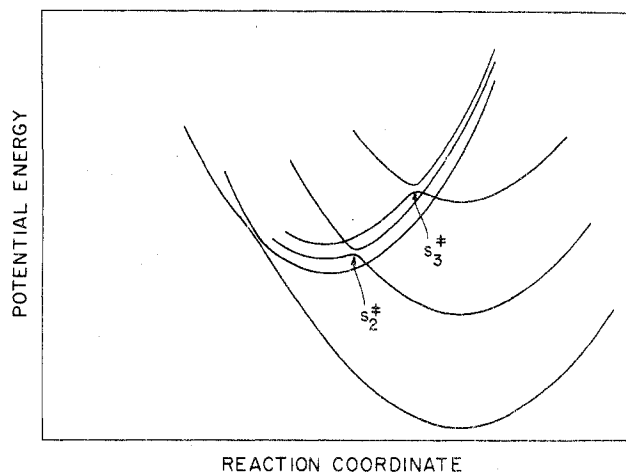


Figure 2. This figure is the same as Figure 1, except that two low potential energy curves “intersect” in an “inverted” configuration and the high ones intersect in a normal one.²⁹ Only one example of the first and two of the second are shown. In the first case, a dynamical calculation involves corrections for nonadiabaticity (e.g., as in ref 16) and so s_1^\ddagger is not shown.

a result directly due to the wider spacing of the product quantum states (compared to reactant states spacing) and to the lack of appreciable activation energy for the lowest state (for this diagram). Thus, only the lower energy states of the reactants react readily, and the mean energy of the species which do react is less, therefore, than the mean thermal energy of the reactants. By Tolman's theorem³¹ the activation energy is therefore negative.

With the approximation³⁰ embodied in the free energy maximum criterion, one then uses the usual electron-transfer theory^{4–8} to obtain eq 3–10.

Further studies on these and related systems should prove very illuminating.

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Registry No. Fe(bipy)₃³⁺, 13479-48-6; Ru(bipy)₃³⁺, 18955-01-6; Fe(H₂O)₆²⁺, 15365-81-8.

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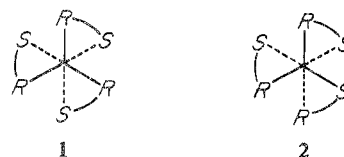
Isomerism in Complexes of Bidentate Meso Chelates

AIC404113

Sir:

The possibility of α , β (or facial, meridional) isomerism in octahedral complexes of unsymmetrical bidentate ligands is well known.¹ However, that a similar type of isomerism is possible in octahedral complexes of meso chelates, whose halves are distinguishable by their chirality (in the simplest case, R and S), has generally gone unrecognized.² Thus, recent papers^{3,4} interpreting pmr spectra of $\text{Ni}(\text{ms-bn})_3^{2+}$ ($\text{bn} = 2,3$ -diaminobutane) have failed to consider the possible presence of two diastereomers—the *fac* isomer (**1**) with dissymmetric sites of only one chirality about each trigonal

face and the *mer* isomer (**2**), obtained from **1** by switching a ligand end for end.



The distinction between the two isomers is not a trivial one nor is their interconversion. Molecular models show a significant difference between the proton environments in *fac*- and *mer*- $\text{Ni}(\text{ms-bn})_3^{2+}$. The *fac* isomer, apparently the only one considered to date in pmr spectral interpretations for these and similar complexes,^{4,5} has C_3 symmetry (ignoring ligand conformation) and contains two magnetically nonequivalent sets of three methyl groups (or methine protons) each. The nonequivalence of the two methyl groups of a chelate in *fac*- $\text{Ni}(\text{ms-bn})_3^{2+}$ is easily explained since the R and S dissymmetric centers must be chemically distinct in the overall Δ or Λ dissymmetry of the complex. In the *mer* isomer (C_1 symmetry), all methyl groups and all methine protons are magnetically nonequivalent.

Though the room-temperature pmr spectrum of $\text{Ni}(\text{ms-bn})_3^{2+}$ solutions can be interpreted assuming only the presence of the *fac* isomer, the extreme broadness reported for the spectral peaks may indicate a mixture of *fac* and *mer*.⁴ Molecular models indicate slightly more favorable nonbonded contacts in *fac*- $\text{Ni}(\text{ms-bn})_3^{2+}$; however, the *mer* isomer has a statistical entropy contribution of $R \ln 3$ to its stability.⁶ Thus the temperature-dependent pmr studies reported⁴ for $\text{Ni}(\text{ms-bn})_3^{2+}$ may, in fact, be affected by the presence of a temperature-dependent diastereomer equilibrium.

In their pioneering paper on ligand conformation,⁷ Corey and Bailar, likewise, failed to notice the unique symmetry properties of meso chelates when they stated that "even though α , β isomerism does not exist, there are 20 possible isomers of the ion $[\text{Co}(\text{stien})_3]^{3+}$ " (*stien* = stilbenediamine). Isomer enumeration by literature methods^{8,9} for a system of RR , SS , and RS tris chelates shows that there are actually 32 isomers possible. Neglecting Δ , Λ isomerism, there are two structures each for the complexes $\text{Co}(\text{ms-stien})_3^{3+}$ and $\text{Co}(d\text{-stien})(l\text{-stien})(\text{ms-stien})_3^{3+}$ and three structures each for the complexes $\text{Co}(d\text{-stien})(\text{ms-stien})_2^{3+}$ and $\text{Co}(l\text{-stien})(\text{ms-stien})_2^{3+}$.

Isomers similar to those discussed above for an octahedral geometry are also possible for square-planar and tetragonal systems, where chelate ends of the same chirality may be either *cis* or *trans*. The presence of such isomers may explain some of the variations observed in $(\text{ms-stien})_2\text{Ni}^{\text{II}}$ and related complexes.^{10,11} Appleton and Hall have recently proposed *cis*-*trans* structures for two isomers of square-planar bis-(*meso*-pentane-2,4-diamine)platinum(II).¹²

References and Notes

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