[Reprinted from Inorganic Chemistry, 14, 213 (1975).]

## 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 negative.[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.

$$Fe(H_2O)_6^{2+} + Fe(bipy)_3^{3+} \rightarrow Fe(H_2O)_6^{3+} + Fe(bipy)_3^{2+} \quad (1)$$

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

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 $10^{11}$ $M^{-1}$ 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 model[4-8]

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

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

$$\Delta G_{12}^* = \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{\Delta G_{12}^\circ}{2} + \frac{(\Delta G_{12}^\circ)^2}{8(\Delta G_{11}^* + \Delta G_{22}^*)}$$

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

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

where $k_{12}$, $K_{12}$, $\Delta G_{12}^*$, and $\Delta G_{12}^\circ$ refer to the cross reaction and $k_{11}$, $k_{22}$, $\Delta G_{11}^*$, and $\Delta G_{22}^*$ refer to the exchange reactions.[5-10] Usually $\alpha$ is small; it is negative in reactions of negative $\Delta G_{12}^\circ$ and becomes increasingly so with decreasing $\Delta G_{12}^\circ$.

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

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

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

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

It is readily apparent from eq 9 that $\Delta H_{12}^*$ will decrease with decreasing $\Delta H_{12}^\circ$ and that $\Delta H_{12}^*$ will be small or even negative if $\Delta H_{12}^\circ$ is sufficiently negative.

The relationship between $\Delta G^*$, $\Delta H^*$, and $\Delta S^*$ and the usual experimentally derived quantities $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ is

$$\Delta G^\ddagger = \Delta G^* - RT \ln (hZ/kT)$$
$$\Delta S^\ddagger = \Delta S^* + R \ln (hZ/kT) - {}^1\!/_2R \quad (10)$$
$$\Delta H^\ddagger = \Delta H^* - {}^1\!/_2RT$$

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 products[11]) have been neglected. Noncancelation of these stabilities can lead to difficulties[12] 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

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

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

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 form[13]

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

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

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 elsewhere[14] 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 shown[16] 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

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

equilibrium constant for the preequilibrium change. A rapid preequilibrium change will have important consequences. For example, if $\Delta G°$ becomes very negative, then the rate constant will not level off at $k_{\mathrm{diff}}$ as described above, but at $P_1{}^*k_{\mathrm{diff}}$, where $k_{\mathrm{diff}}$ is the diffusion-limited rate.[17,18]

Table I. Thermodynamic and Kinetic Parameters for the Reduction of $Fe(bipy)_3{}^{3+}$ and $Ru(bipy)_3{}^{3+}$ by $Fe(H_2O)_6{}^{2+}$ at 25°[a]

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

[a] The units of $\Delta G$ and $\Delta H$ are kcal $mol^{-1}$, and the $\Delta S$ units are cal $deg^{-1}$ $mol^{-1}$. [b] From eq 6 and 10. [c] From eq 9 and 10. [d] From eq 8 and 10.

**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 $\Delta G_{11}{}^{\ddagger}$, $\Delta H_{11}{}^{\ddagger}$, and $\Delta S_{11}{}^{\ddagger}$ for the $Fe(H_2O)_6{}^{2+}$–$Fe(H_2O)_6{}^{3+}$ 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 cal deg $mol^{-1}$, respectively.[21] The activation parameters for the $Fe(bipy)_3{}^{2+}$–$Fe(bipy)_3{}^{3+}$ and $Ru(bipy)_3{}^{2+}$–$Ru(bipy)_3{}^{3+}$ 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 $\Delta G_{22}{}^{\ddagger}$, $\Delta H_{22}{}^{\ddagger}$, and $\Delta S_{22}{}^{\ddagger}$ values of 6 and 3 kcal $mol^{-1}$ and −10 cal $deg^{-1}$ $mol^{-1}$, 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 $\Delta H_{12}{}^{\ddagger}$ 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 $Co(bipy)_3{}^{3+}$ and $Co(phen)_3{}^{3+}$ by $V^{2+}$ and the rates of oxidation of $Co(phen)_3{}^{2+}$ by $Fe^{3+}$ are consistent with eq 6 and 10.[13,27,28] Finally, because of the highly negative $\Delta H_{12}°$, 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 publications[16] 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 $Fe(H_2O)_6{}^{2+}$ by the

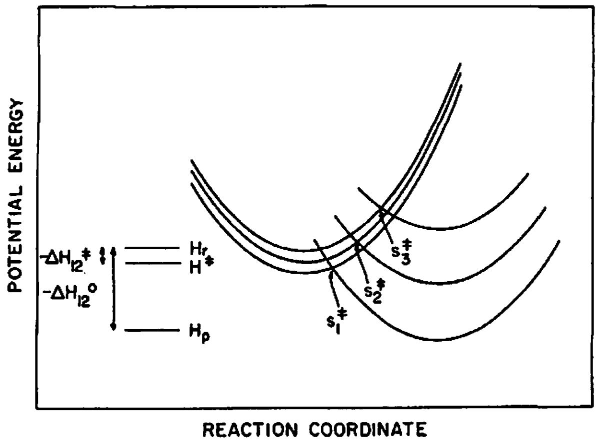

**Figure 1.** Positions $s_i^{\ddagger}$ of activated complexes for a reaction of very negative $\Delta S_{12}^{\circ}$. Potential energy curves for a few of the many quantum states of the system are given. For brevity, the usual adiabatic splittings at the intersections of corresponding curves for a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

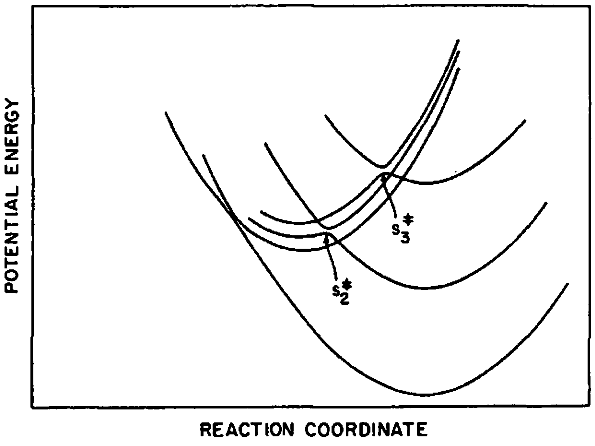

**Figure 2.** This figure is the same as Figure 1, except that two low potential energy curves "intersect" in an "inverted" configuration and the high ones intersect in a normal one.[29] Only one example of the first and two of the second are shown. In the first case, a dynamical calculation involves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

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 $\Delta H_{12}^{\ddagger}$ in molecular terms. The standard entropy changes for the reactions $\Delta S_{12}^{\circ}$ 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 $s_1^{\ddagger}$, $s_2^{\ddagger}$, $s_3^{\ddagger}$, .... 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 $\Delta H_{12}^{\circ}$ is very negative, $\Delta H_{12}^{\ddagger}$ 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, 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 theorem[31] the activation energy is therefore negative.

With the approximation[30] 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.

**Acknowledgment.** This work was performed under the auspices of the U. S. Atomic Energy Commission and was supported in part by a grant from the National Science Foundation.

**Registry No.** $Fe(bipy)_3^{3+}$, 13479-48-6; $Ru(bipy)_3^{3+}$, 18955-01-6; $Fe(H_2O)_6^{2+}$, 15365-81-8.

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(29) The quantum states in Figure 1 can be regarded as quantum states of a pair of reactants (products) plus solvent medium, each quantum state being a vibrational–rotational–translational state of this system. The (many-particle) translational states would be those appropriate to the given volume of the system of reacting pair plus surrounding medium. The quantum states, being so many in number, are very closely spaced on the average, the spacing being much less than $kT$. It is possible for a reacting system in one of these quantum states to proceed to any of the quantum states of the products in Figures 1 and 2, though with varying degrees of probability. The splitting at the intersection of the curves for reactants with those of products occurs, thereby, with all the curves but is shown in Figure 2 only for some of the main intersections, for illustration purposes. Since the entropy of a system can be written as $S = -k\Sigma_i W_i \ln W_i$, where $W_i$ is the probability of finding the system in some quantum state $i$, it is clear that $S°$ is given by a similar expression, using values of $W_i$ appropriate to the standard state of the system. When, as in Figures 1 and 2, the states are much more closely spaced for the reactants than they are for the products, in the standard thermodynamic state for each, the $W_i$'s for the reactants are on the average much less than they are for the products (remembering that $\Sigma_i W_i = 1$), and so $S°$ for the reactants is much larger than that for the products. *I.e.*, $\Delta S_{12}°$ is very negative for the systems under consideration. Conversely, a very negative $\Delta S_{12}°$ implies an average closer spacing of the states of reactants than of those of the products.

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*Received June 11, 1974*