Application of the Marcus Theory for Outer Sphere Electron Transfer to Reactions Involving Mixed Ammine–Pyridine and Polypyridine Complexes of Ruthenium

Sir:

In two recent papers, kinetic parameters for the oxidation of $Fe(H_2O)_6^{2+}$ by a series of polypyridine complexes of ruthenium(III)[1] and iron(III)[2] (eq 1) were reported.

$$Fe(H_2O)_6^{2+} + M(III) \longrightarrow Fe(H_2O)_6^{3+} + M(II) \qquad (1)$$

(M(III) is $Ru(terpy)_2^{3+}$, $Ru(bipy)_3^{3+}$, $Ru(phen)_3^{3+}$, $Ru(bipy)_2^{3+}$, $Fe(terpy)_2^{3+}$, or $Fe(bipy)_3^{3+}$).[3] The activation parameters for the reactions are unusual since $\Delta H^\ddagger$ values are small or even negative (−2.8 ± 0.5 to 0.3 ± 0.05 kcal/mol) and $\Delta S^\ddagger$ values are large and negative (−31 ± 3 to −41 ± 4 cal/(mol deg)).

In the earlier work it was suggested that the reactions occur by a path which includes at least one distinctive feature not included in the model used by Marcus in deriving his quantitative theory of outer-sphere electron transfer.[4] The suggestion was made on the basis of the unusual values of the activation parameters for the reactions. Also, the earlier work of Sutin and coworkers[5] on the oxidation of $Fe(H_2O)_6^{2+}$ had shown that Fe(III)–Fe(II) polypyridine self-exchange rates, estimated using the Marcus "cross reaction" equation (eq 2), were low by ca. 10^5.

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

$$\alpha = \frac{\Delta G_{12}^\circ}{4(\Delta G_{11}^\ddagger + \Delta G_{22}^\ddagger - 2RT \ln k_BT/hZ} \qquad (3)^{6,8}$$

In 1961, Sutin and Gordon suggested that a relation similar to eq 2 might exist between $\Delta H^\ddagger$ and ΔH°.[5b] In agreement with their suggestion we noted, in an earlier paper, that the pattern of activation parameters for reaction 1 is paralleled by the thermodynamic parameters for the overall reactions.[2] The parallelism between the pattern of activation parameters and the pattern of thermodynamic parameters reinforces the idea that equations for enthalpies and entropies of activation similar in form to eq 2 may exist. Recently Marcus and Sutin[7] have shown that eq 2 can be differentiated giving related equations for enthalpies and entropies of activation (eq 4 and 5).[8] Using the rate data of Chan and Wahl[9] for the M(III)–M(II) polypyridine self-exchange reactions, Marcus and Sutin showed that the activation parameters for reaction 1 can be estimated satisfactorily using eq 4 and 5. Perhaps more importantly, a microscopic picture was developed to explain the negative $\Delta H^\ddagger$ values. In this model the more energetic states of the activated complex have a lower reactivity than the less energetic states as a result of the wider spacing of the products' quantum states relative to the spacing of the reactants' quantum states.

$$\partial(\Delta G/T)/\partial(1/T) = \Delta H_{12}^\ddagger = (\Delta H_{11}^\ddagger/2 + \Delta H_{22}^\ddagger/2) \times (1 - 4\alpha^2) + (\Delta H_{12}^\circ/2)(1 + 2\alpha) + 4\alpha^2RT \qquad (4)$$

and

$$-\partial(\Delta G)/\partial T = \Delta S_{12}^\ddagger = (\Delta S_{11}^\ddagger/2 + \Delta S_{22}^\ddagger/2)\times (1 - 4\alpha^2) + (\Delta S^\circ_{12}/2)(1 + 2\alpha) + 4\alpha^2(R + R \ln k_BT/hZ) \qquad (5)$$

We have measured rates for a series of mixed ammine–pyridine complexes of ruthenium in their reactions with the $Fe(H_2O)_6^{3+/2+}$ couple (Scheme I). The reactions were investigated at several temperatures using syringe mixing or stopped-flow techniques. The cell potentials for the Ru(III)/Ru(II) couples were also measured at several temperatures essentially as described previously.[10] All measurements were made in 1.0 *M* aqueous perchloric acid.

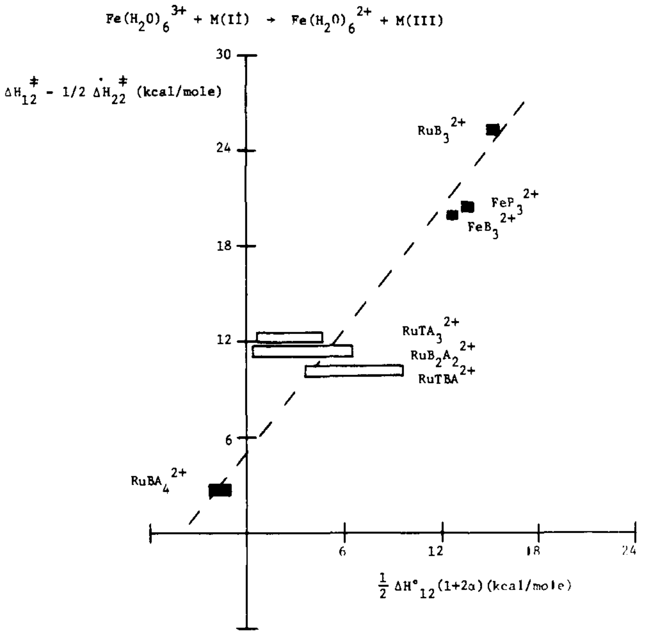


Figure 1. The test of eq 6 using the data for reactions a–g in Scheme I. Abbreviations used in the figure are A for NH_3, B for 2,2′-bipyridine, P for 1,10-phenanthroline, and T for 2,2′,2″-terpyridine. For the cases shown as open rectangles, the data given are for $\Delta H_{12}^\ddagger$, uncorrected for $\frac{1}{2}\Delta H_{22}^\ddagger$.

Scheme I

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

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

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

d $Ru(terpy)(bipy)(NH_3)^{3+} + Fe(H_2O)_6^{2+} \longrightarrow Ru(terpy)(bipy)(NH_3)^{2+} + Fe(H_2O)_6^{3+}$

e $Ru(bipy)_2(NH_3)_2^{3+} + Fe(H_2O)_6^{2+} \longrightarrow Ru(bipy)_2(NH_3)_2^{2+} + Fe(H_2O)_6^{3+}$

f $Ru(terpy)(NH_3)_3^{3+} + Fe(H_2O)_6^{2+} \rightleftharpoons Ru(terpy)(NH_3)_3^{2+} + Fe(H_2O)_6^{3+}$

g $Ru(bipy)(NH_3)_4^{2+} + Fe(H_2O)_6^{3+} \longrightarrow Ru(bipy)(NH_3)_4^{3+} + Fe(H_2O)_6^{2+}$

h $Ru(py)(NH_3)_5^{2+} + Fe(H_2O)_6^{3+} \longrightarrow Ru(py)(NH_3)_5^{3+} + Fe(H_2O)_6^{2+}$

i $Ru(NH_3)_6^{2+} + Fe(H_2O)_6^{3+} \longrightarrow Ru(NH_3)_6^{3+} + Fe(H_2O)_6^{2+}$

With the available data, it is possible to test the Marcus theory with regard to the relationships given in eq 4 and 5. Equation 4 can be rearranged to give eq 6. In eq 6 the α^2 terms have been neglected since they are numerically insignificant for these reactions.

$$\Delta H_{12}^\ddagger - \frac{1}{2}\Delta H_{22}^\ddagger = \frac{1}{2}\Delta H^\circ_{12}(1 + 2\alpha) + \frac{1}{2}\Delta H_{11}^\ddagger \qquad (6)$$

Equation 6 is tested in Figure 1 using enthalpy data for the reactions written as oxidations by $Fe(H_2O)_6^{3+}$ (eq 7). The uncertainties shown in the figure reflect the experimental errors as determined by standard methods of error anal-

$$Fe(H_2O)_6^{3+} + M(II) \longrightarrow Fe(H_2O)_6^{2+} + M(III) \qquad (7)$$

ysis.[11] Complete data or reasonable estimates are known only for reactions a, b, c, and g (the filled blocks).[12] For the experiments where the data are shown as open rectangles, the results must be corrected by subtracting $\Delta H_{22}^{\ddagger}/2$, where $\Delta H_{22}^{\ddagger}$ is the enthalpy of activation for the Ru(III)–Ru(II) self-exchange reaction.[13] From available data, $\Delta H_{22}^{\ddagger}$ is expected to be between 3 and 10 kcal/mol for the other reactions[9,10,13] and it is clear that they too will fall close to the dashed line drawn in the figure.

The data in Figure 1 are in agreement with the expected linear relationship predicted by eq 6. Similar agreement is found for eq 7 but the large uncertainties in the $\Delta S°_{12}$ values calculated from cell potential measurements make such plots almost meaningless. Although the data are limited, the slope of the line is clearly close to 1.0 as predicted and the intercept at $\Delta H°_{12} = 0$ is close to $\frac{1}{2}\Delta H_{11}^{\ddagger}$ for the $Fe(H_2O)_6^{3+/2+}$ self-exchange.

The agreement between experiment and theory shown in Figure 1 is important for several reasons. There is no longer a need to invoke a special pathway for the oxidation of $Fe(H_2O)_6^{2+}$ by the M(III) polypyridine complexes. The replacement of purely σ-bonding, small, NH_3 ligands by large, π back-bonding pyridine groups has no apparent effect on the ability of the Marcus theory and the Marcus model to account for the details of the electron transfer act. The successful application of eq 6 and 7 to the reactions reported here mean that these equations can be used to probe reactions where factors not explicitly considered in the model used to derive eq 2, 6, and 7[7] may be important.

Acknowledgments are made to the National Science Foundation through Grants GP17083 and GP42846X and to Professors N. Sutin and R. A. Marcus for providing a preprint of their work.

References and Notes

(1) J. N. Braddock and T. J. Meyer, *J. Am. Chem. Soc.*, **95**, 3158 (1973).

(2) J. L. Cramer and T. J. Meyer, *Inorg. Chem.*, **13**, 1250 (1974).

(3) Abbreviations used here include terpy or T for 2,2′,2″-terpyridine, bipy or B for 2,2′-bipyridine, phen or P for 1,10-phenanthroline, py for pyridine, and A for NH_3.

(4) For pertinent reviews see (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1966); (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, N.Y., 1966.

(5) (a) M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961); (b) N. Sutin and B. M. Gordon, *ibid.*, **83**, 70 (1961).

(6) $\Delta G_{12}^{\ddagger}$ is the free energy of activation of a net reaction like eq 1, and $\Delta G°_{12}$ is the overall free energy change in the medium used: $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the free energies of activation for the self-exchange reaction.

(7) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).

(8) $\Delta H_{12}^{\ddagger}$ is the enthalpy of activation of a net reaction and $\Delta H°_{12}$ is the overall enthalpy change in the medium used; $\Delta H_{11}^{\ddagger}$ is the enthalpy of activation for the self-exchange reaction and similarly for $\Delta H_{22}^{\ddagger}$. R is the gas constant, k_B is the Boltzmann constant, h is Planck's constant, and Z is the collision frequency between two neutral molecules in solution which is assumed to be 10^{11} sec^{-1}.

(9) M. Chan and A. C. Wahl, Abstracts of the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR-97.

(10) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

(11) (a) W. J. Youden, "Statistical Methods for Chemists", Wiley, New York, N.Y., 1951; (b) D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld, "Experiments in Physical Chemistry", 3rd ed, McGraw-Hill, New York, N.Y., 1974.

(12) Thermodynamic data for the polypyridine reactions with the $Fe(H_2O)_6^{3+/2+}$ couple is known at zero ionic strength. All other data were measured in 1.0 M $HClO_4$. Data are available for $Ru(NH_3)_6^{3+/2+}$ but in a different medium. The $Ru(py)(NH_3)_5^{3+/2+}$ couple is not sufficiently stable to make formal half-cell potential measurements.

(13) The $Ru(bipy)(NH_3)_4^{3+/2+}$ self-exchange rate data were estimated from a stopped-flow study of the reaction: $Ru(bipy)(NH_3)_4^{3+} + Ru(phen)(NH_3)_4^{2+} \rightleftharpoons Ru(bipy)(NH_3)_4^{2+} + Ru(phen)(NH_3)_4^{3+}$. For the reaction, $\Delta H° = 0$ and $\Delta S° = 0$ in 1 *M* $HClO_4$.

James N. Braddock, Jeffrey L. Cramer, Thomas J. Meyer*

W. R. Kenan Research Laboratories
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received December 14, 1974

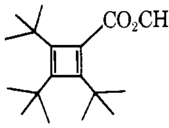
The [4]Annulene System. Direct Proof for Its Rectangular Geometry

Sir:

The central and most crucial issue of the [4]annulene system now concerns its geometry. The (presumably) most recent theoretical treatment[1] (GVB and 4-31G) of this eight-point problem concludes that the system possesses a triplet ground state of D_{4h} symmetry (square), thus conforming to the conclusion derived from the infrared analysis of the parent compound (**1**) detained in an argon matrix at 4°K.[1,2] In view of the limitations imposed upon the various methods of approximation applied to this theoretically complex molecule (**1**), it is not surprising that the above conclusion is in sharp contrast with several earlier predictions[3] that a singlet rectangle corresponds to the true minimum on the multidimensional energy surface calculated for **1**.[4] Further, there has been presented no experimental evidence against the singlet ground state *e.g.*, (i) the repeated failures to observe ESR signals that may be ascribed to the triplet,[5] (ii) the absence of allowed ultraviolet transitions above 300 nm[6] in agreement with Allinger's confident prediction[3a] for the singlet **1**, and (iii) the chemical behavior of **1** and its behavior toward dienes.[7]

An obvious and indisputable solution of this controversial problem would be a crystallographic analysis of **1**. The reactivity of **1**, however, forces us to choose for this purpose a derivative in which (i) the electronic state of **1** is least perturbed,[8] yet its reactivity is suppressed by sterically blocking the approach of another molecule by bulky substituents, thus allowing its isolation in a crystalline form, and (ii) substituents are so chosen as to preserve symmetry in an important way.[9] Our previous work[5] was aimed at the synthesis of a derivative to satisfy exactly these conditions. We have now completed an X-ray analysis of methyl tri-*tert*-butyl[4]annulenecarboxylate (**2**) and wish to record the remarkable, unambiguous outcome—**2** is definitely NOT square but a slightly distorted rectangle.

1



2

Compound **2** crystallizes by sublimation at 50° (0.01 mm) in an argon atmosphere. As these crystals were extremely sensitive to oxygen, all manipulations were carried out in a drybox under N_2. The light orange-brown plates (crystal forms present {100}, {012}, {001}) were mounted with their *b* axes parallel to the length of a Lindemann glass capillary which was sealed with wax. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions a = 16.796 (6) Å, b = 8.960 (3) Å, c = 12.087 (4) Å, and β = 90.76 (2)°. Intensity data were collected from a single-crystal measuring 0.30 × 1.00 × 0.57 mm with respect to the *a*, *b*, and *c* axes, on a Picker FACS-1 diffractometer with Cu Kα radiation to $2\theta = 120°$. A total of 2339 unique and space group allowed reflections were used in the structure solution and refinement. Corrections for Lorentz and polarization factors were made, and an empirical absorption correction[10] was applied.

The structure was solved by the application of the direct method.[11] The initial *E* map clearly showed the atoms of the [4]annulene ring, the non-hydrogen atoms of the methoxycarbonyl group, and two of the *tert*-butyl groups but only the tertiary carbon atom of the third *tert*-butyl group (on C(4)). The present *R* factor of 0.105 was obtained from a model in which all the non-hydrogen atoms were refined