



THE ROLE OF BOND ORDER AND ENTROPY OF TRANSITION STATES IN ELECTRON TRANSFER REACTIONS

Part 1. — Outer-sphere electron exchange processes.

The current approach of Marcus theory to estimate energy barriers of electron transfer reactions in terms of a least nuclear motion path is questioned. Another approach, based on an expansion of configuration in the transition states is presented. An intersecting-state model is employed to estimate metal-ligand bond distentions at the transition state in terms of bond lengths and force constants, and the transition state bond order. This model can successfully treat electron exchanges, including the case of systems such as $\text{Co}^{2+/3+}_{(aq)}$ and $\text{Fe}(\text{phen})^{2+/3+}_3$ where the Marcus theory estimates rates 10^7 times slower and 10^5 times faster, respectively, than experiment.

INTRODUCTION

The history of science reveals that many times the structure of sciences does not possess a powerful logic. Henri Poincaré in his book «La Science et l'Hypothèse» [1] gives an interesting example from the field of classical mechanics. In the absence of any force the velocity of a body does not change; but of equal logic are other conceptions such as that the acceleration or the position of the body do not change. The choice between these different assumptions is not a matter of logic, but of agreement with experimental observations.

In any particular scientific field it is virtually impossible to fit a new theory to all the relevant experimental facts. The facts which are not accounted for by the theory are «enigmas». These can many times be later explained through refinements of the theory, but if they survive as enigmas for a long time and if the disagreement with the theory is of a large magnitude, they become «anomalies». It is the existence of anomalies that reveals the presence of a «crisis» in any scientific field [2], and a crisis requires new theoretical approaches, which should be able to solve the anomalous facts of the old theory.

The theory of Marcus has been the «paradigm» of the field of electron transfer reactions but, in our view, symptoms of a crisis are becoming apparent. For electron exchange reactions there are examples «of an old system, $\text{Co}^{2+/3+}$ or $\text{Fe}^{2+/3+}$ where, despite the current extensive understanding of electrons transfers, there remains something to be understood» [3]. The aquo $\text{Co}^{2+/3+}$ and $\text{Fe}^{2+/3+}$ pairs have an anomalous behaviour, because the measured self-exchange rates are about 10^7 and 10^3 , respectively, faster than those calculated through the theory of Marcus.

Marcus [4] has predicted nearly three decades ago that an inverted effect on the reaction rates should occur for very exothermic electron transfer reactions. In spite of several

experimental searches, with a few exceptions, the experiments do not conform to this model and other alternative models have been proposed [5-7] to interpret the variety of the energy-gap laws of these reactions. The disagreement between theory and experiment can amount also to several orders of magnitude.

The theory of Marcus predicts also that the rate constants of electron transfer reactions can be obtained from the individual self-exchange reaction rates and the equilibrium constant of the reaction, through the so called «cross-reaction relationship». This simple relation has been perhaps the most widely used and tested in electron transfer theory, but in spite of its success there are cases where disagreements of five orders of magnitude do exist [8].

Hupp and Weaver (9) have recently reported the existence of strong anodic-cathodic asymmetries on the Tafel plots for metal-aquo redox couples which cannot be interpreted within the framework of the theory of Marcus. Such effects amount typically to two orders of magnitude in the relative rates for the cathodic and anodic reactions under the extreme experimental conditions employed.

Finally the theory of Marcus gives a special importance to the outer-shell reorganization energy barriers for electron transfer reactions. Recent results for the ferrocenium — ferrocene self-exchange [10] reveal that the rates of electron transfer in a variety of solvents, from methanol to dimethylsulfoxide, vary by a factor of 2 whereas the theory of Marcus predicts a ca. 20-fold variation.

In view of these anomalous features, it seems worth exploring alternative theoretical procedures to estimate rates of electron transfer reactions. In this paper we will apply a recently developed intersecting-state model [11] to the study of electron exchange processes and in the following papers of this series the other types of «anomalies» will be considered.

THE EXPANSION OF CONFIGURATIONS IN THE TRANSITION STATE

Transition state bond lengths in electron transfer reactions of coordinated or solvated ions are considered to be intermediate between the metal-ligand bond lengths of the oxidized and reduced species [3, 12, 13], i.e., one ion has contracted and the other has expanded in order to reach the configuration of the transition state. This follows a suggestion of Libby [14] that the more similar the inner coordination shells of donor and acceptor ions, the less difficult would be the electron transfer. Support for such an idea was suggested from, for example, the slowness of the $\text{Co}(\text{NH}_3)_6^{2+/3+}$ exchange reaction, because there is a large difference in the Co-N bond lengths ($l_{\text{red}} - l_{\text{ox}} = 0.21 \text{ \AA}$). Although rates $\leq 2 \times 10^{-10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ were initially estimated [15], a recent redetermination of this self-exchange rate ($4.8 \times 10^{-6} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) is at least four orders of magnitude greater [16].

Currently the transition state configuration is determined by finding the lowest potential energy for a system of two bond length coordinates: $\text{Me}^{n+} - \text{L}$ and $\text{Me}^{(n+1)+} - \text{L}$. The bond lengths are $l_{\text{ox}} < l^\ddagger < l_{\text{red}}$ and the contribution of the inner-shell reorganization for the reaction energy barrier is estimated to be

$$\Delta G_{\text{in}}^\ddagger = \frac{m f_{\text{ox}} f_{\text{red}}}{2 (f_{\text{ox}} + f_{\text{red}})} (l_{\text{ox}} - l_{\text{red}})^2 \quad (1)$$

where m is the number of bonds involved in the reorganization process and f_{ox} and f_{red} are the stretching force constants of the metal-ligand bonds. The bulk solvent reorganization energy barrier [1, 3] is given by

$$\Delta G_{\text{out}}^\ddagger = \frac{(\Delta e)^2}{4} \left(\frac{1}{2a_{\text{ox}}} + \frac{1}{2a_{\text{red}}} - \frac{1}{r} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{r}}} \right) \quad (2)$$

where a_{ox} and a_{red} are the radii of the solvated spherical ions: the ionic radius plus

the van der Waals diameter (2.76 Å) of a water molecule [12]; r is the mean distance between the centers of the reactants in the activated complexes, Δe is the charge transferred in the reaction, D_{op} and D_s are the optical and static dielectric constants of the medium respectively. For one electron transfer in water

$$\Delta G_{out}^{\ddagger}/\text{kJ mol}^{-1} = 188 \left(\frac{1}{a} - \frac{1}{r} \right) \quad (3)$$

with $a = 2a_{ox} a_{red}/(a_{ox} + a_{red})$.

Let us consider a spherical metal ion of charge n surrounded, for example, by water molecules in the first and the second coordination shell. When due to the transfer of an electron the charge of the ion changes rapidly to $n + 1$, there is a strong perturbation of the water molecules. Since the energy between an electronic charge and a dipole decreases in absolute value with the increase of the ion-dipole distance, this «instantaneous» perturbation will be stronger for the first-shell and weaker in the second-shell. However, when $l_{ox} = l_{red}$, the theory of Marcus (eq (1)) implies that electron transfer does not cause any energy change in the first-shell, but causes significant energy changes in the second-shell. This is not reasonable, not only in view of the previous argument, but also because the symmetric stretching force constants for the metal-ligand bonds are different in the oxidized and reduced species (vide e.g. the system $\text{Fe}(\text{phen})_3^{2+/3+}$ [17, 18]). Any change in the force constants of the first coordination shell has to proceed via changes in the metal-ligand bonds and consequently has an internal energy barrier. The change in frequencies can be thought to be included in the preexponential term of the rate constants, but for an electron transfer reaction between an oxidized and a reduced species such a term is an average of the frequencies of both partners.

Such facts suggest a different kind of model for the transition state configuration. If one

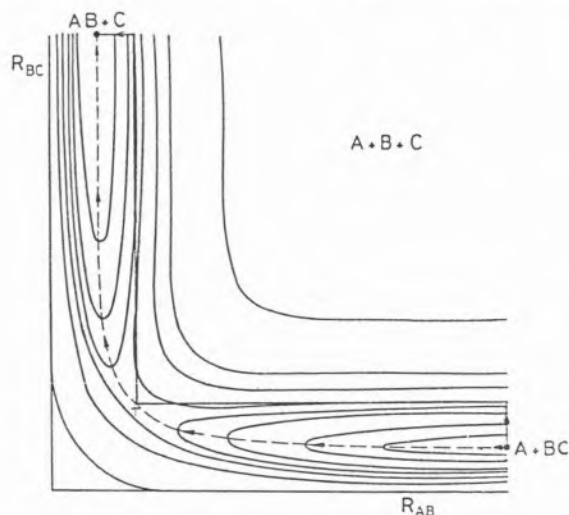
assumes that there is an «expansion» in the transition state, i.e., $l_{ox} \ll l_{red} < l^{\ddagger}$, even when $l_{ox} = l_{red}$, there will be an inner-shell reorganizational energy due to the expansion in configuration. A similar suggestion, with some experimental support, is provided by the study of the volumes of activation. Stranks [19] has discussed in detail the inner- and outer-shell contributions to ΔV^{\ddagger} in oxidation-reduction reactions. The outer-shell contribution results from the changes in coulombic forces in bringing charged reactants to the transition state, the solvent rearrangement on the formation of the transition state and the change in activity due to interionic interactions. For $\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$, Stranks has estimated $\Delta V_{out}^{\ddagger} = -16.5 \text{ cm}^3 \text{ mol}^{-1}$. Assuming that the ions are spherical with radii of a (3.45 Å) ($a = r/2$) and that the transition state compressibility is identical to that of reactants, because the bond lengths are intermediate between the ones of the two reagents, then the change in the inner-shell volume, ΔV_{in}^{\ddagger} , ranges between 0 and $-58 \text{ cm}^3 \text{ mol}^{-1}$. Consequently, ΔV^{\ddagger} ranges between $-16.5 \text{ cm}^3 \text{ mol}^{-1}$ and $-75 \text{ cm}^3 \text{ mol}^{-1}$.

The experimental change in the volume of activation, $\Delta V^{\ddagger} = -12 \text{ cm}^3 \text{ mol}^{-1}$ [19], is higher than $\Delta V_{out}^{\ddagger}$. This cannot be attributed to the finite compressibility of the solvated-ions, because such a contribution is very small ($\leq 0.5 \text{ cm}^3 \text{ mol}^{-1}$ [19]). Consequently, such findings may suggest that in the activated complexes there is some expansion of the metal-ligand bonds ($r > 2a$) rather than a small interpenetration of the shells ($r < 2a$). The difference between ΔV^{\ddagger} and $\Delta V_{out}^{\ddagger}$ may imply an increase in the metal-ligand bonds at the transition state. The overlap of the electronic wave functions for electron transfer reactions is very small, but can be increased by any spatial increase of those functions due to nuclear motions in the collision complexes. So the electronic coupling, H_{ab} , is expected to be higher for an «explosion» of configuration in the transition states than for the activated complexes configuration of the theory of Marcus.

INTERSECTING-STATE MODEL

To investigate the logic consequences of an expanded transition state for electron transfer reactions, we will employ a recently developed intersecting-state model (ISM) [11] which estimates energy barriers of chemical reactions in terms of thermodynamic, geometric and electronic factors. The model estimates energy changes caused by an expansion in the bond length from a reactant to the transition state and, consequently, is adequate to estimate energy changes due to the expansion in the transition states of electron transfer processes. Nevertheless this point may be further clarified by the following discussion.

ISM has been developed for the study of bond-breaking bond-forming reactions such as $A + BC \rightarrow AB + C$. Figure 1 shows the

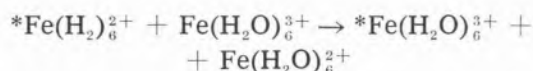


potential energy surface for such a reaction together with the reaction path. This can be simulated by the following nonmonotonous path:

- i) BC stretch to R_{BC}^\ddagger at a constant R_{AB} (large distance (∞));
- ii) a virtually isoenergetic path through the saddle point; R_{AB} decreases from almost infinity to the value R_{AB}^\ddagger at a constant R_{BC}^\ddagger , etc.;
- iii) R_{AB}^\ddagger decreases to the equilibrium value R_{AB}^e at a constant R_{BC}^\ddagger (∞).

This path justifies the estimation of the reaction energy barrier through the intersection of BC and AB potential energy curves, when $R_{AB}^\ddagger > R_{AB}^e$ and $R_{BC}^\ddagger > R_{BC}^e$ (a contraction of the bonds was also possible). However if, for example $R_{BC}^\ddagger < R_{BC}^e$ and $R_{AB}^\ddagger > R_{AB}^e$ the energy barrier cannot be estimated through the intersection of two potential energy curves, because the intermediate path through the transition state configuration is no longer an isoenergetic path.

If one considers now an electron transfer reaction such as



one can represent the expansion in the transition state for each one of the reactants on the potential energy surface of Figure 1. For example one should consider:

- i) an expansion of $^*Fe(II) - O$ equilibrium length up to $R_{Fe(II)-O}^\ddagger$;
- ii) a jump from this configuration to $R_{Fe(II)-O}^\ddagger$, due to the transfer of the electron;
- iii) a contraction of the $R_{Fe(II)-O}^\ddagger$ to the equilibrium length.

At an infinite distance, e.g., $F_{Fe(II)-O}$ is a virtual distance, because the species $Fe_{(aq)}^{(II)}$ only exists after electron transfer.

Although electron transfer and atom transfer are different kinds of processes, for an expanded transition state configuration, electron transfer can be considered a limiting case of the atom transfer situation when the isoenergetic nuclear path tends to zero. But since this path is not involved in the calculation of ΔE^\ddagger , atom and electron transfer reactions or other kinds of no bond-breaking bond-forming processes such as spin exchange [20] can be analyzed through the same intersecting-state model.

A similar procedure will be applicable to the $Fe_{(aq)}^{(III)}$ species. In general one would average the potential energies for the two reactant and the two product species, after taking as

the origin of coordinates the equilibrium bond length of each one of the species involved, and only one reaction coordinate will be employed in the calculations. It might be argued that one should use two reaction coordinates. This is essential in the theory of Marcus, because one of the coordinates is expanded whereas the other is contracted. However, for the present model both coordinates are in expansion and one can use a reaction coordinate where the bond distensions of the two reactants is the same. So a single coordinate will do. In consequence, if f_{ox} and f_{red} are the stretching force constants of the metal-ligand bonds, this assumption leads to an average force constant for the single coordinate $f_{\text{av}} = (f_{\text{ox}} + f_{\text{red}})/2$. ISM has been presented in detail elsewhere [11] but will be briefly reviewed here. Let us assume, for simplicity, that the potential free energy curve for a reactant and product can be represented by harmonic oscillators of force constants f_r and f_p and equilibrium bond lengths l_r and l_p . The configuration of the transition state can be found at the intersection of the potential energy curves of the reactant and product. Then one can write

$$\frac{1}{2} f_r x^2 = \frac{1}{2} f_p (d - x)^2 + \Delta G^\circ \quad (4)$$

where ΔG° is the reaction free energy, x is the bond distension from the reactant to the transition state, $x = l^\ddagger - l_r$, and d ($d > 0$) is the sum of the bond distensions from the reactant and the product species to the transition state,

$$d = (l^\ddagger - l_r) + (l^\ddagger - l_p) \quad (5)$$

and represents also the horizontal displacement of the potential energy curves. The activation free energy of the reaction is given by

$$\Delta G^\ddagger = \frac{1}{2} f_r x^2 \quad (6)$$

where x is estimated through eq (4), once d is known.

The sum of bond distensions up to the transition state [11] was shown to be related to the sum of the equilibrium bond lengths of reactants and products

$$d = \eta (l_r + l_p) \quad (7)$$

where η measures the relative increase in the bond lengths. This equation has a simple physical meaning: when an equilibrium bond length is small its bond distension is expected to be small, but when it is large the bond distension is also expected to be large.

The reduced bond distension η is related [11] to the chemical bond order of the transition state, n^\ddagger , and a parameter λ which is associated with the so called «configuration entropy»,

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2\lambda^2} (\Delta G^\circ)^2 \quad (8)$$

λ has dimensions of an energy and can be viewed as an energy capacity of the activated complexes; a' is a constant ($a' = 0.156$). Eq (8) shows that the reduced bond distension depends on n^\ddagger and ΔG° . It is small when the bond order of the transition state is high, and *vice versa*. For a thermoneutral reaction η and d are independent of λ .

When $f_r = f_p = f$ then eqs (4) and (6) lead to

$$\Delta G^\ddagger = \frac{(\Delta G^\circ + (1/2) f d^2)^2}{2 f d^2} \quad (9)$$

Furthermore when d is independent of ΔG° , i.e. $\lambda \gg |\Delta G^\circ|$, eq (9) reduces to the Marcus-equation

$$\Delta G^\ddagger = \Delta G(0)^\ddagger \left(1 + \frac{\Delta G^\circ}{4 \Delta G(0)^\ddagger}\right)^2 \quad (10)$$

where $\Delta G(0)^\ddagger$ is the kinetic energy barrier for the thermoneutral situation, which is

$$\Delta G(0)^\ddagger = \frac{1}{8} f \left[\frac{a' \ln 2}{n^\ddagger} (l_r + l_p) \right]^2 \quad (11)$$

On neglecting the work terms of bringing the reactants together, the Marcus-equation is found to be a particular case of ISM. Eq (11)

reveals also that the intrinsic energy barrier for electron exchange reactions is controlled by the metal-ligand force constants and bond lengths, and by the transition state bond order.

ELECTRON EXCHANGE REACTIONS

Coordinated or solvated metal ions have several metal-ligand bonds which are involved in the inner-shell reorganization. In order to keep the model unidimensional, one has to define an effective force constant f for the coordination shell. Let us consider, to start with, two bonds of force constants f_1 and f_2 . In general terms the effective force constant is given by

$$f_{\text{eff}}^2 = f_1^2 + f_2^2 + 2f_1 f_2 \cos\theta$$

If the vibrations of the two bonds are in-phase, $\theta = 0^\circ$ and $f_{\text{eff}} = f_1 + f_2$. When the motions have a destructive interference $\theta = 180^\circ$ and $f_{\text{eff}} = |f_1 - f_2|$. For a random motion of the two bonds $\theta = 90^\circ$ and $f_{\text{eff}} = \sqrt{f_1^2 + f_2^2}$. These considerations can be generalized to any number of oscillators.

For a metal-ion with a coordination number of m , then the possible effective force constants are

$$f = m(f_{\text{ox}} + f_{\text{red}})/2 \quad (12)$$

as considered in the theory of Marcus, and

$$f = \sqrt{m(f_{\text{ox}} + f_{\text{red}})/2} \quad (13)$$

which we have found appropriate to deal with several chemical reactions [21]. In the calculations we have employed the force constants estimated by Khan and Bockris [22] from metal-ligand symmetric stretching frequencies ν_i ; $f_i = 4\pi^2 c^2 \mu \nu_i^2$ where c is the velocity of the light and μ the reduced mass of the vibrating ligand.

Since we are dealing with metal-ligand single bonds and during the electron transfer process there are no chemical bond-breaking

process, we take $n^\dagger = 1$ for all cases except where stated otherwise.

Table 1 presents the necessary spectroscopic data for the calculation of the $\text{Fe}(\text{H}_2\text{O})_6^{2+/3+}$ inner-shell energy barrier [17, 22, 23]. The calculation based on eq (11) and for the random situation (eq (13)) is in good agreement with the experimental value: $\Delta G^\ddagger(\text{exp}) = 72.5 \text{ kJ mol}^{-1}$ and $\Delta G^\ddagger(\text{calc}) = 74 \text{ kJ mol}^{-1}$. For the in-phase situation (eq (12)) the calculated energy barrier is too high, 181 kJ mol^{-1} .

The calculated values are only the inner-shell contribution to the energy barrier. The outer-shell contribution can be estimated from the reorganization in the second-shell due to the expansion of the first-shell, where $E = -nZe\mu'/r^2$ is the energy of a metal ion charge Ze surrounded of n dipoles of dipole moment μ' at a metal distance r . When this distance is estimated for a spherical solvated ion, i.e., under the hypothesis that all the bonds had the same distension y ($(6/2)f y^2 = (\sqrt{6}/2)f_1 x^2$) then the outer-shell reorganization energy ($\geq 2 \text{ kJ mol}^{-1}$) is more than an order of magnitude lower than the inner-shell energy barrier. This finding is also in agreement with the negligible (a factor of 2) variation of the rates of ferrocenium-ferrocene self-exchange from methanol to dimethylsulphoxide [10]; these findings also lead to $\Delta G_{\text{out}}^\ddagger = 1.8 \text{ kJ mol}^{-1}$ in water. In view of these facts we can take the inner-shell reorganization as a good estimation of the reaction energy barrier. Under this assumption ISM estimates the rate constant for $\text{Fe}_{(\text{aq})}^{2+/3+}$ within a factor of 2 times slower than the experimental rate, but not 10^3 times as it is the case with the theory of Marcus [3].

Table 1 presents also the ΔG^\ddagger values for several other electron exchange reactions. The agreement with experiment is quite good. An in-phase motion of all the bonds (eq (12)) is implied by the theory of Marcus [12] and such a force constant leads to an overestimation of the free energy barrier, which is in general balanced by the underestimation of the bond distensions at the transition state,

Table 1
Inner-Shell Reorganization Energy Barrier for Electron Exchange Reactions.

Reaction	$l_{\text{Me-X}}/\text{\AA}$		$f_{\text{Me-X}}/\text{kJ mol}^{-1} \text{\AA}^{-2} \text{ (c)}$		n^\ddagger	$\Delta G^\ddagger/\text{kJ mol}^{-1} \text{ (j)}$			Experimental
	Me(II)	Me(III)	Me(II)	Me(III)		Marcus theory ^(d)	Intersecting state model ^(e)		
							In-phase motion ^(f)	Random motion ^(g)	
$\text{Fe}(\text{OH}_2)_6^{2+ / 3+}$	2.123	1.955 ^(a)	9.6×10^2	1.5×10^3	1	20	181	74	72.5 ^(a)
$\text{Cr}(\text{OH}_2)_6^{2+ / 3+}$	2.30	1.98 ^(a)	9.6×10^2	1.5×10^3	1	73	203	80	82 ^(h)
$\text{V}(\text{OH}_2)_6^{2+ / 3+}$	~2.26	~2.12 ^(b)	9.6×10^2	1.5×10^3	1	—	206	84	84.2 ⁽ⁱ⁾
$\text{Co}(\text{OH}_2)_6^{2+ / 3+} \text{ (k)}$	2.12	1.91 ^(a)	9.6×10^2	1.5×10^3	1	77.5	174	71	68.7 ⁽ⁱ⁾
$\text{Fe}(\text{CN})_6^{4- / 3-}$	1.900	1.926 ^(a)	3.1×10^3	2.4×10^3	1.54	3	147	60	57.0 ^(h)
$\text{Mo}(\text{CN})_8^{4- / 3-} \text{ (l)}$	—	—	—	—	1.70	—	142	50	48.5

(a) Ref. 17; (b) Atomic radii + 1.38 Å; (c) Data for $\text{Fe}^{2+/3+}$ from ref. 22 and 23; other data assumed to be equal to the one of $\text{Fe}_{(\text{aq})}^{2+/3+}$; (d) Eq. (1) (e) Eqs (11) and (7) and (8) with $\Delta G^0 = 0$; (f) Eq. (12), $m = 6$; (g) Eq. (13), $m = 6$; (h) Ref. 24; (i) Ref. 25; (j) room temperature; (k) We have neglected the change from a high spin to a low spin state because it has a very low activation energy; (l) Average force constant $f = 6.8 \times 10^3 \text{ kJ mol}^{-1} \text{\AA}^{-2}$ estimated from the comparison of $\nu = 473 \text{ cm}^{-1}$ for $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$ with $m = 8$, ref. 23 (b) p. 171, 172; $l_r + l_p = 3.83 \text{ \AA}$ as for $\text{Fe}(\text{CN})_6^{4-/3-}$; ΔG^\ddagger ref. 24 p. 137 with a preexponential factor 10^{13} s^{-1} .

owing to the $l_{\text{ox}} < l^\ddagger < l_{\text{red}}$ situation. This cancellation of errors explains the good estimations that the theory of Marcus provides for several electron exchange reactions [12, 13]. However, for $\text{Co}(\text{H}_2\text{O})_6^{2+/3+}$ where the change in equilibrium bond lengths is large, Sutin [12] overestimates $\Delta G_{\text{in}}^\ddagger$ (vide Table 1) and further considers a significant $\Delta G_{\text{out}}^\ddagger$ contribution. It is not surprising, then, that the rate calculated through such a procedure is eight orders of magnitude slower than experiment. ISM provides an estimation in very good agreement with experiment (2.5 times slower).

Like the other examples presented here, the electron transfer reaction between $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ is an outer-sphere process, because the inner coordination spheres are inert to substitution [24-26]. However ΔG^\ddagger is smaller than the free energy barrier of the other exchange reactions in Table 1, in spite of the fact that the force constants are higher. This behaviour can be attributed to differences in bond orders at the transition state as

a result of interactions between π orbitals of the CN^- ligands and the metal orbitals, leading to a new set of π molecular orbitals. With electronic configurations (only for π bonds) such as $t_{2g}^6(\pi_b)$ $t_{1u}^6(\pi_b)$ $t_{2g}^6(\pi^*)$ for $\text{Fe}(\text{CN})_6^{4-}$ and $t_{2g}^6(\pi_b)$ $t_{1u}^6(\pi_b)$ $t_{2g}^5(\pi^*)$ for $\text{Fe}(\text{CN})_6^{3-}$, the average bond order can be estimated as 1.54. For example, with $\text{Fe}(\text{CN})_6^{3-}$ which has 6 bonds in the reagent, the bond order contribution of the π electrons is $(12-5)/2 \times 6$; this contribution should be added to the contribution $n = 1$ from the σ bonds. Considering the bond order of the transition state as $n^\ddagger = 1.54$, eq (8) shows that the reduced bond distension η is much smaller than when $n^\ddagger = 1$. Consequently, ΔG^\ddagger is also smaller. The calculated value for a random vibrational motion of the bonds is also in good agreement with experiment (Table 1). A similar situation is also found with $\text{Mo}(\text{CN})_8^{4-/3-}$ where the estimated bond order is $n^\ddagger = 1.70$ for d^4 and d^3 metal ion configurations.

The present model can reproduce the experimental ΔG^\ddagger values which are not related to any systematic variations in ΔH^\ddagger and $T\Delta S^\ddagger$. For example, typical values [24, 25] for some of the reactions of Table 1 are:

	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$-T\Delta S^\ddagger/\text{kJ mol}^{-1}$ (298K)	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
$\text{V}^{2+/3+}_{(\text{aq})}$	53.0	31.0	84
$\text{Fe}^{2+/3+}_{(\text{aq})}$	46.4	26.1	72.5
$\text{Co}^{2+/3+}_{(\text{aq})}$	52.7	16.0	68.7
$\text{Fe}(\text{CN})_6^{4-/3-}$	17.1	39.9	57

Such an agreement is obtained with a simple model of harmonic oscillators. This is not surprising, because the energy barriers are not very high and the crossing point of the curves is still on the region where the potential energy curves have a harmonic behaviour. Furthermore, the close agreement between theory and experiment shows that outer-shell reorganization does not have a significant contribution to the activation free energy barrier. It may have significant contributions for ΔH^\ddagger and $T\Delta S^\ddagger$, but such contributions appear to cancel out.

An interesting case to study is the system $\text{Fe}(\text{phen})_3^{2+/3+}$; because $l_{\text{ox}} \cong l_{\text{red}}$ and, consequently, for the theory of Marcus $\Delta G^\ddagger_{\text{in}} = 0$. This is not the case within the present model. The major difficulty in analysing such a system is the fact that the stretching force constants cannot be estimated from the stretching frequencies, since the effective mass of the oscillator Fe^{n+} — phenanthroline is not accurately known. Considering, however, that the stretching force constant is similar to the one of the ammine complexes, $f \cong 2.7 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$ [18, 20], with $l_{\text{ox}} + l_{\text{red}} = 3.94 \text{ \AA}$ [17] and $n^\ddagger = 1$, the energy barrier due to internal reorganization $\Delta G(\text{ISM})^\ddagger = 60 \text{ kJ mol}^{-1}$ is higher than the

experimental value $\Delta G^\ddagger = 45 \text{ kJ mol}^{-1}$ (1) (ref. 25 p. 475). Such a discrepancy can be attributed to the uncertainty in f and/or to some electronic siphoning from the aromatic rings into the iron-nitrogen bonds at the transition state, as is observed in spin exchange of N-Fe(II) and Fe(III) complexes ($\eta = 0.098$) [20]. Under these assumptions the estimated energy barrier $\Delta G^\ddagger = 50 \text{ kJ mol}^{-1}$ is much closer to the experimental value, and the calculated rate is an order of magnitude slower than experiment ($10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). It is worth comparing such results with those of the theory of Marcus. For this system $\Delta G^\ddagger_{\text{in}} = 0$ and $\Delta G^\ddagger_{\text{out}} = 13 \text{ kJ mol}^{-1}$ with $a = 7.5 \text{ \AA}$ and $r = 15 \text{ \AA}$. Such a value compares well with data for similar systems, e.g., $\text{Co}(\text{bpy})_3^{2+/3+}$ where $\Delta G^\ddagger_{\text{out}} = 13.8 \text{ kJ mol}^{-1}$ with $a = 6.8 \text{ \AA}$ and $r = 13.6 \text{ \AA}$ [12]. With these external and internal energy barriers, the electron exchange rate in $\text{Fe}(\text{phen})_3^{2+/3+}$ is calculated to be diffusion controlled. So the theory of Marcus predicts a rate five orders of magnitude higher than experiment.

CONCLUSIONS

We have shown that the hypothesis of an expansion of configuration in the transition states of electron transfer reactions, provides reasonable estimates of the reaction energy barriers in terms of inner-shell reorganization. This does not necessarily mean that there are no contributions from the second-shell reorganization, but they are certainly smaller than the ones from the first-shell, and both are so intimately connected that they can be dealt with in terms of an overall metal-ligand potential energy curve [27].

Discrepancies on the estimated rates within the Marcus formalism as, for example, $\text{Co}^{2+/3+}_{(\text{aq})}$ which proceeds 10^6 - 10^8 times faster than the calculated rate [3, 12], are absent in

(1) The activation free energy is estimated for an adiabatic process

$$k_{\text{et}}/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} = 10^{13} \exp(-\Delta G^\ddagger/RT)$$

the present model. Previous suggestions [28] for a different pathway for this exchange reaction, are unnecessary to explain the experimental rates. In any case, suggestions of competitive mechanisms for the system $\text{Fe}(\text{phen})_3^{2+/3+}$ where the Marcus rate is now 10^5 times faster than the experimental value are not possible.

The theory of Marcus employs essentially the Principle of Least Motion [29] to estimate the inner-shell reorganization for electron transfer reactions. For current chemical reactions it is known that the least-motion path is seldom the least-energy path [30]. It may well be the same for the electron transfer processes. On comparing with the rigorous theoretical treatment of the Marcus theory, the present approach may appear to be *ad hoc* and arbitrary. So we have a rigorous theory that does not account for all the experimental facts which, at present, are considered to be relevant in the field, and a semi-empirical approach which reproduces well the experimental facts. This is a dilemma. None the less ISM can rationalize experimental results and has some predictive value in the field of electron transfer reactions.

ACKNOWLEDGMENTS

I am grateful to Prof. R. A. Marcus for most stimulating and helpful discussions, where points of disagreement, naturally, arose. I am also grateful to Profs H. D. Burrows, S. M. B. Costa, A. J. C. Varandas, B. J. Herold and A. L. Maçanita for helpful discussions and suggestions and to Prof. H. Rau for making available to us some work prior to publication. This work is supported by the Instituto Nacional de Investigação Científica.

Recebido em 17 de Outubro de 1986

REFERENCES

- [1] H. POINCARÉ, «La Science et l'Hypothèse», Flammarion, Paris, 1909, p. 112-119.
- [2] T.S. KUHN, «The Structure of Scientific Revolutions», University of Chicago Press, Chicago, 2nd ed. 1970; Chaps. 5 to 7.
- [3] R.A. MARCUS in «Understanding Molecular Properties» ed A.E. Hansen et al., Reidel, 1986, to be published.
- [4] R.A. MARCUS, J. Chem. Phys., **24**, 966 (1956); Disc. Faraday Soc., **29**, 21 (1960); J. Chem. Phys., **43**, 679 (1965).
- [5] D. REHM and A. WELLER, Ber. Bunsenges. Phys. Chem., **73**, 834 (1969).
- [6] T. KAKITANI and N. MATAGA, Chem. Phys., **93**, 381 (1985); J. Phys. Chem., **90**, 993 (1986).
- [7] H. RAU, R. FRANCK and G. GREINER, J. Phys. Chem., **90**, 2476 (1986); H. RAU, J. Am. Chem. Soc., submitted for publication.
- [8] See for example C. CREUTZ and N. SUTIN, J. Am. Chem. Soc., **99**, 241 (1977).
- [9] J.T. HUPP and M.J. WEAVER, J. Phys. Chem., **88**, 6128 (1984).
- [10] T. GENNETT, D.F. MILNER and M.J. WEAVER, J. Phys. Chem., **89**, 2787 (1985).
- [11] A.J.C. VARANDAS and S.J. FORMOSINHO, J. Chem. Commun., 163 (1986); J. Chem. Soc. Faraday Trans. 2, **82**, 953 (1986).
- [12] N. SUTIN, Prog. Inorg. Chem., **30**, 441 (1983).
- [13] For a recent review see R.A. MARCUS and N. SUTIN, Biochem. Biophys. Acta **811**, 265 (1985).
- [14] W.F. LIBBY, J. Phys. Chem., **56**, 863 (1952).
- [15] D.R. STRANKS, Discuss. Faraday Soc., **29**, 73 (1960); N.S. BIRADAR, D.R. STRANKS and M.S. VAIDYA, Trans. Faraday Soc., **58**, 2421 (1962).
- [16] A. HAMMERSHØI, D. GASELOWITZ and H. TAUBE, Inorg. Chem., **23**, 979 (1984).
- [17] B.S. BRUNDSCHWIG, C. CREUTZ, D. H. MCCARTNEY, T.K. SHAM and N. SUTIN, Faraday Disc. Chem. Soc., **74**, 113 (1982).
- [18] J.R. FERRARO, «Low Frequency Vibrations of Inorganic and Coordination Compounds», Wiley — Interscience, New York, 1970, chap 7.
- [19] D.R. STRANKS, Pure Appl. Chem., **38**, 303 (1974).
- [20] H.D. BURROWS and S. J. FORMOSINHO, J. Chem. Soc., Faraday Trans 2, **82**, 1563 (1986).
- [21] S.J. FORMOSINHO, Mol. Protochem., **7**, 41 (1976); L.G. ARNAUT, S.J. FORMOSINHO and A.M. SILVA, J. Photochem., **27**, 185 (1984); S.J. FORMOSINHO, Pure Appl. Chem., **58**, 1173 (1986).
- [22] S.U.M. KHAN and J.O'M. BOCKRIS, J. Phys. Chem., **87**, 4012 (1983).
- [23] (a) J. NAKAGAWA and T. SHIMANOCHI, Spectrochim. Acta, **20**, 429 (1964).

- (b) K. NAKAMOTO, «Infrared Spectra of Inorganic Coordination Compounds», Wiley, New York, 1970.
- [24] W.L. REYNOLDS and R. W. LUMRY, «Mechanisms of Electron Transfer Reactions», Ronald Press, New York, 1966, chapter 3 and p. 34.
- [25] F. BASOLO and R. G. PEARSON, «Mechanisms of Inorganic Reactions», Wiley, New York, 2nd ed, 1968, p. 71, p. 466.
- [26] H. TAUBE, «Electron Transfer Reactions of Complex Ions in Solutions», Academic Press, New York, 1970, p. 49-70.
- [27] E. SACHER and K.J. LAIDLER, Trans. Faraday Soc., 59, 396 (1963).
- [28] J.F. ENDICOTT, B. DURHAM and K. KUMAR, Inorg. Chem., 21, 2437 (1982); D.H. MACARTNEY and N. SUTIN, Inorg. Chem., 24, 3403 (1985).
- [29] F.O. RICE and E. TELLER, J. Chem. Phys., 6, 489 (1938); *ibid.*, 7, 199 (1939).
- [30] L. SALEM, «Electrons in Chemical Reactions», John-Wiley, New York, 1982, p. 44-46.

RESUMO

O papel da ordem de ligação e da entropia dos estados de transição nas reacções de transferência de electrões.

Parte 1 — Processos de transferência de electrões de camada externa.

A utilização da teoria de Marcus no cálculo das barreiras de energia das reacções de transferência de electrões é examinada criticamente e, perante as dificuldades desta teoria em explicar algumas destas reacções, propõe-se um modelo teórico alternativo. Este modelo, baseado no Modelo de Intersecção de Estados, admite que no estado de transição as ligações reactivas metal-ligando sofrem uma expansão. As barreiras de energia dependem das constantes de força e comprimentos destas ligações e da ordem de ligação do estado de transição. O novo modelo consegue interpretar as reacções de troca de electrões em solução, nomeadamente $\text{Co}^{2+/3+}_{(aq)}$ e $\text{Fe}(\text{fenantro-lina})^{2+/3+}$, em que a teoria de Marcus calculava constantes de velocidade 10^7 vezes inferior e 10^5 vezes superiores aos valores experimentais.