



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

Part 2. — Reaction Energy Effects on Outer-sphere and Inner-sphere Reactions.

A classical intersecting-state model, previously developed for gas phase reactions, has been applied to the study of electron transfer reactions. Activation energies depend on the lengths and force constants of metal-ligand bonds and on the bond orders and entropies of the transition states. Two kinds of transition states have been found, one with a bond order or $n^\ddagger = 1$ for outer-sphere reactions, and another with $n^\ddagger \cong 1.5$ for inner-sphere and fast outer-sphere reactions. The distensions of the metal-ligand bonds in the transition state increase with an increase in the absolute value of the free energy of the reaction. Such a variation depends on the configuration entropy parameter λ , and is strong when λ is low. For solvated or coordinated metal-ions λ is low when ΔS^\ddagger is low, with λ ranging typically between 350 to 100 kJ mol⁻¹. Such variation can interpret the occurrence of the different reaction energy laws which can be found in electron transfer reactions. The inverted region is found when λ is low, but when λ is high only a diffusional plateau is found at low ΔG° . Marcus-equation for the variation of ΔG^\ddagger with ΔG° is a particular case of the present model when $\lambda \gg |\Delta G^\circ|$.

The effect of the reaction free energy, ΔG° , on the rates of electron transfers has been a field of great controversy. Normally, a decrease in ΔG° increases the rate of electron transfer. However, Marcus [1] has predicted that for very exothermic reactions an inverted region occurs, where the rates of reaction decrease with a further decrease in ΔG° . Although there is recent evidence that the predicted inverted effect can be observed [2-4] there are many well documented cases where the inverted region is not observed, and the rates of reaction attain a plateau for very low ΔG° values. For the latter situation, the Marcus-equation is no longer valid in the inverted region and other equations, such as that of Rehm and Weller [5], have to be employed. This has lead us to suggest [6] that such a discrepancy could be solved if one considers that the distance between the potential energy curves of reactants and products would increase with a decrease in ΔG° , following a similar suggestion of Koeppel and Kresge [7] for hydrogen atom transfer reactions. The physical basis for such a variable distance situation was later found through the development of an intersecting-state model (ISM) [8] to estimate energy barriers of chemical reactions, and a preliminar account on its application to the inverted region problem has been given [9]. Rau and coworkers [10] have also developed a model under similar lines to interpret the energy gap laws in electron transfer reactions, while Kakitani and Mataga [11] have also developed a model based on the motion of the molecules in the solvent shell, to interpret the variety of such laws.

In Part 1 of this series [12] we have suggested that electron transfer reactions can be treated as any other ordinary chemical reaction, and have shown that such a hypothesis leads to calculated self-exchange reaction rates in good agreement with experiment, even for cases where a strong disagreement exists between experiment and values given by the theory of Marcus. Here we intend to further

explore this hypothesis to investigate the effect of ΔG° on the rates of outer- and inner-sphere electron transfer reactions.

ENERGY-GAP LAWS

In the previous paper [12] we have shown that Marcus-equation can be considered as a particular case of the general intersecting-state model [8] which was employed for the estimation of the reaction energy barriers. Marcus-equation is valid when the effective force constants in reactants and products are identical and when the sum of the distensions, d , and the reduced bond distension, η , are independent of ΔG° . The former condition is justified for the systems which will be studied, but the latter one needs investigation. The general expression [8] for η is

$$\eta = \frac{a' \ln 2}{n^\ddagger} + \frac{a'}{2 \lambda^2} (\Delta G^\circ)^2 \quad (1)$$

where n^\ddagger is the bond order of the transition state and λ is the configuration entropy parameter established by Agmon and Levine [13], which has dimensions of an energy. For a thermoneutral reaction η is independent of λ . However, for exothermic or endothermic reactions, the reaction energy ΔG° has to be accommodated as internal energy of the activated complexes, through distension of the bonds involved in the reaction and/or in many other degrees of freedom not involved in the reaction coordinate. The parameter λ can be viewed as the activated complex capacity (in terms of free energy) to accommodate the reaction free energy. If λ is high, the activated complexes have many ways to distribute energy and, consequently, only a small fraction of ΔG° is stored as distension of the reactive bonds. However, when λ is low a considerable amount of the reaction energy has to be stored in the reactive bonds, through further bond distension. Consequently, η and d increase with an increase

in $|\Delta G^\circ|$ and the effect of exothermicity in the reaction rates is less pronounced than when λ is high. Marcus-equation corresponds to the cases where $\lambda \gg |\Delta G^\circ|$ for which the inverted region occurs at $\Delta G^\circ < -fd^2/2$.

To illustrate how the effect of ΔG° on the electron transfer rates, k_{et} , depends on the value of λ , Figure 1 presents the calculated

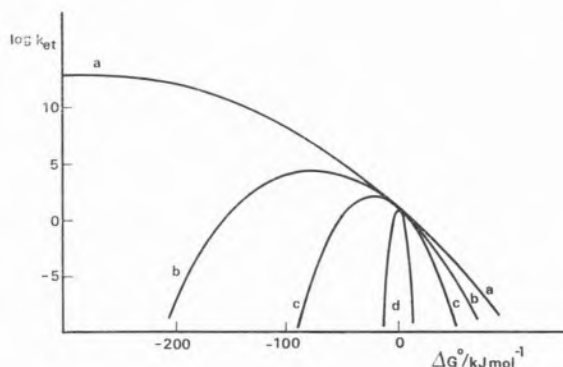


Fig. 1 — Calculated electron transfer rate constants (eq (2)) as a function of ΔG° , for several configuration entropy parameter, λ , values: a) $\lambda \rightarrow \infty$ corresponds to the Marcus-equation; b) $\lambda = 200$ kJ mol⁻¹; c) $\lambda = 100$ kJ mol⁻¹; d) $\lambda = 10$ kJ mol⁻¹. Data employed in the calculation: $l_{ox} + l_{red} = 4$ Å, $f = 2.9 \times 10^3$ kJ mol⁻¹ Å⁻² and $n^\ddagger = 1$.

rates for a prototype situation with $k_{et}/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} = 10^{13} \exp(-\Delta G^\ddagger/RT)$ and

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

The parameter d is proportional to the sum of equilibrium bond lengths of the oxidized and reduced species,

$$d = \eta (l_{ox} + l_{red}) \quad (3)$$

The calculations were undertaken with $l_{ox} + l_{red} = 4$ Å, $f = 2.9 \times 10^3$ kJ mol⁻¹ Å⁻² and $n^\ddagger = 1$. Several curves of $\log k_{et}$ versus ΔG° are presented for different values of λ and for the Marcus case ($\lambda = \infty$). All the curves share a common point at $\Delta G^\circ = 0$, but in the other regions when λ decreases, the

electron transfer rates decrease, both in the normal and in the inverted region. The electron transfer rate is extremely sensitive to λ when $|\Delta G^\circ| > \lambda/2$, is moderately sensitive when $\lambda/4 \leq |\Delta G^\circ| \leq \lambda/2$ and is virtually independent of λ when $|\Delta G^\circ| < \lambda/4$ (Figure 2).

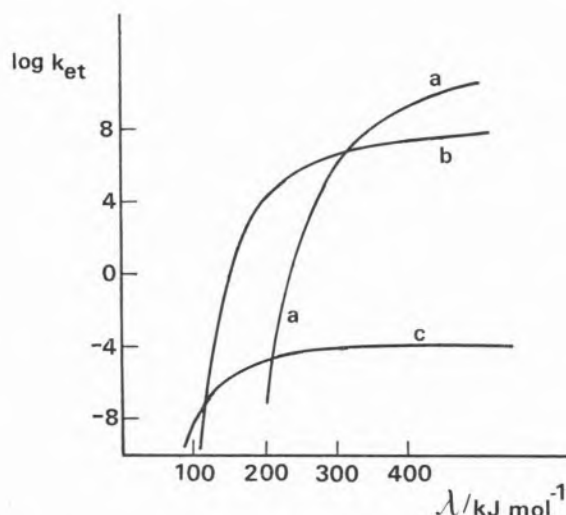


Fig. 2 — Calculated electron transfer rates as a function of λ , for several ΔG° values: a) -200 kJ mol^{-1} ; b) -100 kJ mol^{-1} ; c) 50 kJ mol^{-1} .

Far from the $\lambda \gg |\Delta G^\circ|$ limit, the maximum rate does not correspond to the crossing of the potential energy curves at the minimum of the reactant curve where $\Delta G^\ddagger = 0$. As Figure 1 shows the position of the inverted region varies with λ (with f , l and n^\ddagger constant) ranging between $\Delta G^\circ = -(1/2)fd^2$ ($\lambda \rightarrow \infty$) and $\Delta G^\circ = 0$ ($\lambda \rightarrow 0$); the maximum rate constant decreases with a decrease in λ .

OUTER-SPHERE REACTIONS

Having examined the energy gap law in a more formal way, it is now useful to investigate the effect of ΔG° in some real systems. To undergo this task it is more convenient to estimate the distensions (d and η) which reproduce the experimental ΔG^\ddagger , rather than to compare activation free energies. For many reactions the ΔG^\ddagger values are not known and

have to be estimated from the rate constants of electron transfer ⁽¹⁾

$$k_{\text{et}} = \kappa \nu c_0^{1-m'} \exp(-\Delta G^\ddagger/RT) \quad (4)$$

where κ is an electronic factor which takes into account any nonadiabaticity of the reaction, c_0 is the standard concentration 1 mol dm^{-3} , m' is the molecularity of the reaction, and ν is the frequency of vibration which destroys the activated complexes. We assume, following other authors [14, 15] that the interaction, H_{ab} , between the orbitals of the reactive species is small enough so that it may be neglected in calculating the free energy of activation, but large enough ($H_{ab} \geq 1 \text{ kJ mol}^{-1}$) so that the reactions are adiabatic, i.e., $\kappa \approx 1$. We take $\nu = 10^{13} \text{ s}^{-1}$.

The stretching force constants are based on the set values presented by Khan and Bockris [16] calculated from experimental symmetric stretching frequencies, or were taken from ions of similar structure. The overall force constant is $f = \sqrt{6} (f_{\text{ox}} + f_{\text{red}})/2$ [12]. The length of the metal-ligand bonds [17] when not known, were estimated as the sum of the radius of the central ion and a covalent radius for the atom of the ligand which is linked to the metal ion [18]. Ionic radii were obtained from crystal data [19] and for the ligands we have used 1.38 \AA for H_2O [18] and 1.4 \AA for NH_3 . Force constants were obtained from low frequency vibrational data [20, 21]. Table 1 presents the calculated reduced distension η for several exchange outer-sphere reactions. In spite of the uncertainties on the

(1) The observed rate constant is usually expressed as $k_{\text{obs}} = K_p k_{\text{et}}$, where K_p is the equilibrium constant for forming the precursor complex. Therefore $k_{\text{obs}} = \kappa \nu c_0^{1-m'} \exp(-\Delta G_p/RT) \exp(-\Delta G'^\ddagger/RT)$ where $\Delta G'^\ddagger$ is the activation free energy for electron transfer in the precursor complex. As long as the formation of the precursor complex does not alter the energy of the transition state, the activation free energy with respect to the reactants, ΔG^\ddagger , is simply $\Delta G^\ddagger = \Delta G_p + \Delta G'^\ddagger$ and consequently eq (4) is valid. force constants and the bond length data, the η values are close to the theoretical value of 0.108 for $n^\ddagger = 1$, obtained from eq (1)

Table 1

Bond distensions for Electron Transfer Reactions of Aquo-Metal Ions

Reactants	$f/\text{kJ mol}^{-1} \text{ \AA}^{-2}$	$(l_r + l_p)/\text{\AA}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$d/\text{\AA}$	η
$\text{Fe}^{2+}/\text{Fe}^{3+}$	3.0×10^3	4.12	72.5 (a)	0.44	0.107
$\text{Cr}^{2+}/\text{Cr}^{3+}$	3.0×10^3	4.28	82.0 (b)	0.464	0.108
$\text{V}^{2+}/\text{V}^{3+}$	3.0×10^3	4.38	84.2 (c)	0.474	0.108
$\text{Mn}^{2+}/\text{Mn}^{3+}$	3.1×10^3	4.22	93.0 (c)	0.49	0.116
$\text{Ce}^{3+}/\text{Ce}^{4+}$	2.95×10^3	4.72	82.0 (c)	0.47	0.100

(a) Ref. 17.

(b) W.L. Reynold and R.W. Lumry, «Mechanisms of Electron Transfer Reactions», Ronald Press, New York, 1966, chap. 3 and p. 34.

(c) F. Basolo and R.G. Pearson, «Mechanisms of Inorganic Reactions», Wiley, 2nd ed., 1968, p. 466.

when $\Delta G^\circ = 0$. As discussed in the previous paper [12], this means that the free energy barrier for electron transfer is due largely to the inner-shell reorganization.

The present model also allows the evaluation of the effect of the reaction free energy, ΔG° , on the electron transfer process. Table 2 pre-

sents the bond distension parameters which reproduce the experimental ΔG^\ddagger values, calculated through eq (4); ΔG° values were estimated from redox potentials [19]. Now the reduced distensions are considerably higher than 0.108. According to eq (1) η should increase with an increase in $|\Delta G^\circ|$, and a

Table 2

Effect of Reactions Free Energy on the Bond distensions for Electron Transfer Reactions of Aquo-Ions and Ammino-Ions

	$f/10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$	$(l_r + l_p)/\text{\AA}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ (a)	$\Delta S^\ddagger/\text{J mol}^{-1} \text{ K}^{-1}$ (a)	$\Delta G^\circ/\text{kJ mol}^{-1}$	$d/\text{\AA}$	η
1 $\text{Np}^{4+}/\text{NpO}_2^{2+}$	3.1	4.485	80.7		— 38.4	0.506	0.1128
2 $\text{Cu}^{+}/\text{Fe}(\text{OH})_2^{2+}$	2.5	4.285	43.5		— 58.8	0.473	0.110
3 $\text{Ti}^{3+}/\text{Fe}^{3+}$	3.4	4.17	65.3		— 68.3	0.47	0.113
4 $\text{Cr}^{2+}/\text{Fe}^{3+}$	3.0	4.21	56.6	— 117	— 113	0.526	0.125
5 $\text{Fe}^{2+}/\text{Co}^{3+}$	3.1	4.165	57.7		— 103	0.515	0.1236
6 $\text{Eu}^{2+}/\text{Fe}^{3+}$	3.0	4.47	49.0		— 115	0.512	0.115
7 $\text{Cr}^{2+}/\text{Co}^{3+}$	3.0	4.195	49.4	— 32.6	— 214	0.596	0.142
8 $\text{Mn}^{3+}/\text{V}^{4+}$	3.5	4.175	61.3	— 50.2	— 216	0.585	0.140
9 $\text{Ce}^{3+}/\text{V}^{4+}$	3.5	4.422	77.7	+ 25.2	— 235.5	0.634	0.1434
10 $\text{V}^{4+}/\text{Co}^{3+}$	3.5	4.045	76.0		— 246	0.638	0.1577
11 $\text{Fe}^{2+}/\text{Ti}(\text{OH})_2^{2+}$	3.0	4.94	83.0	— 29.3	— 81.4	0.562	0.114
12 $\text{Eu}^{2+}/\text{V}^{3+}$	3.0	4.59	85.0	— 125.4	— 16.8	0.499	0.1087
13 $\text{Eu}^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$	3.2	4.46	89.0	— 175.6	— 51.0	0.533	0.120
14 $\text{Cr}^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$	3.1	4.21	98.8	— 217	— 50.0	0.559	0.133

(a) Ref. 22, Chapter 13.

quadratic dependence of η on ΔG° is expected. Figure 3 presents the variation of η with

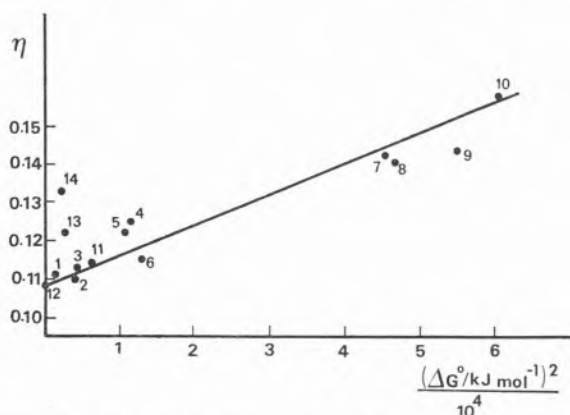


Fig. 3 — Variation of the reduced bond distension, η , with the reaction free energy, ΔG° , for electron transfer reactions of aquo- and hydroxoions. Legend for reactions in Table 2.

$(\Delta G^\circ)^2$. A linear dependence is suggested, although there is considerable scatter. However, such a dependence depends on the parameter λ . In order to test this prediction of the model we have estimated the λ values according to eq (1) and have searched for any possible relationship of λ with the entropic contribution to the activation energy ($-T\Delta S^\ddagger$) for electron transfer reactions where the activation entropies are known [22]. Figure 4 reveals a linear relationship between λ and $T\Delta S^\ddagger$; for 298 K and a standard state of 1 mol dm⁻³, the observed relation is

$$\lambda/\text{kJ mol}^{-1} = 360 + 4 T \Delta S^\ddagger \quad (5)$$

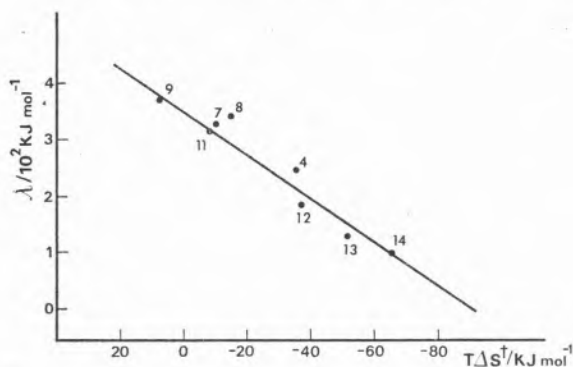


Fig. 4 — Variation of the configuration entropy parameter λ with the activation entropy (standard state 1 mol dm⁻³; $T = 298$ K). Legend for reactions in Table 2.

For a positive entropy of activation ($\Delta S^\ddagger \gg 0$) there is a small dependence of η on $(\Delta G^\circ)^2$, which approaches the situation considered in the theory of Marcus [15], where the distance between the minima of the potential energy curves is independent of ΔG° . However, for large negative activation entropies there is a large increase of η with an increase in $|\Delta G^\circ|$. In this situation the distance between the minimum of the potential energy curves of reactants and products increases with an increase in $|\Delta G^\circ|$, and Marcus-equation is no longer obeyed.

INNER-SPHERE REACTIONS

The essential feature of this kind of electron transfer reactions is that one ligand molecule is shared between the two reacting species forming a bridge between the two metal ions. This requires that the ligand should have at least one pair of electrons available for interaction with the metal orbitals [22]. In general such electron transfer reactions have lower activation free energies than those of outer-sphere reactions. Although Marcus theory is not strictly applicable to inner-sphere reactions, the present model can deal with such a problem.

Let us illustrate the application of ISM to the $\text{Fe}(\text{CN})_6^{4-}/\text{IrCl}_6^-$ system, where both ions share one chloride atom in the reacting complex. Whereas the effective force constant and bond length of IrCl_6^- can be taken as that of an outer-sphere reaction, for the other reacting partner ($f = (5f_{\text{Fe-C}}^2 + f_{\text{Fe-Cl}}^2)^{1/2}$). However since this introduces only a small correction, we have neglected these effects in f and l . Therefore calculations are undertaken with $f = \sqrt{6} (f_{\text{Fe}(\text{CN})_6}^2/4 + f_{\text{Fe}(\text{CN})_6}^2/3 - f_{\text{IrCl}_6}^2 + f_{\text{IrCl}_6}^2)/4$ and $l_{\text{ox}} + l_{\text{red}} = (l_{\text{Fe(II)-C}} + l_{\text{Fe(III)-C}} + l_{\text{Ir(V)-Cl}} + l_{\text{Ir(IV)-Cl}})/2$. Since we are dealing with inner-sphere reactions which are controlled by the electron transfer step, we have assumed a fast formation of the reacting complexes. Therefore activation free energies with respect to reactants can be estimated through eq (4).

Table 3

Bond distensions for Inner-Sphere and Fast Outer-Sphere Electron Transfer Reactions

Reactants	$f/10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$	$(l_r + l_p)/\text{\AA}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\Delta G^\circ/\text{kJ mol}^{-1}$	$d/\text{\AA}$	η
1 $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ (a)	6.7	3.83 (e)	57 (f)	0	0.261	0.068
2 $\text{Fe}(\text{CN})_6^{4-}/\text{IrCl}_6^-$	4.4	4.54	38.5 (b)	-63.5	0.344	0.076
3 $\text{Fe}(\text{CN})_6^{4-}/\text{OsCl}_6^-$	4.9	4.74	77.3 (b)	-6.7	0.359	0.0757
4 $\text{Os}(\text{dipy})_3^{2+}/\text{Ru}(\text{dipy})_3^{3+}$	3.0	4.74	27.2 (b)	-42.0	0.349	0.0736
5 $\text{Os}(\text{dipy})_3^{2+}/\text{IrCl}_6^-$	2.6	4.87	27.2 (b)	-22.2	0.34	0.070
6 $\text{Co}(\text{NH}_3)_5(\text{OH})^{2+}/\text{Cr}^{2+}$	3.2	4.20	38.4 (c)	-49.0	0.389	0.093
7 $\text{Fe}^{2+}/\text{duroquinone}$	2.3/3.7 (d)	4.14	95.9 (b)	84.8	0.362	0.087
8 $\text{Fe}^{2+}/\text{dichlorosemiquinone}$	2.3/3.7 (d)	4.14	72.5 (b)	37.4	0.384	0.093

(a) Outer-sphere.

(b) Ref. c. of Table 1, 508, 509.

(c) Ref. 22, p. 430.

(d) Different force constants for reactants and products; in the reactants the force constant for the organic molecules was neglected.

(e) Ref. 17.

(f) Ref. b of Table 1.

Table 3 presents the calculated bond distensions which reproduce the ΔG^\ddagger values for several inner-sphere reactions, and Figure 5 presents the dependence of η on $(\Delta G^\circ)^2$. A linear dependence is found for two series of reactions. Just as in the case of outer-sphere reactions, we attribute the differences in slopes to the differences in λ , although we have no experimental data to verify the relationship between λ and $T\Delta S^\ddagger$ for this kind of reactions. The most significant difference between the inner-sphere and outer-sphere reactions is the reduced bond distension at $\Delta G^\circ = 0$. The intercepts in Figure 5 lead to values of $\eta(0) = 0.067$ which corresponds to a transition state bond order of $n^\ddagger \cong 1.6$ (eq (1)), which is higher than the value of $n^\ddagger = 1$ found for the majority of outer-sphere reactions [12].

For electron transfer reactions n^\ddagger values higher than 1 can be expected when there is an increase in the total bond order at the transition state, e.g. when nonbonding or antibonding electrons in reactants (or products) acquire a bonding character in the

activated complexes [8, 9]. For example, for the reaction $\text{Cr}(\text{H}_2\text{O})_6^{2+}/(\text{Co}(\text{NH}_3)_5\text{X}^{2+})$ the bond order of the metal-ligand bonds is 1 in

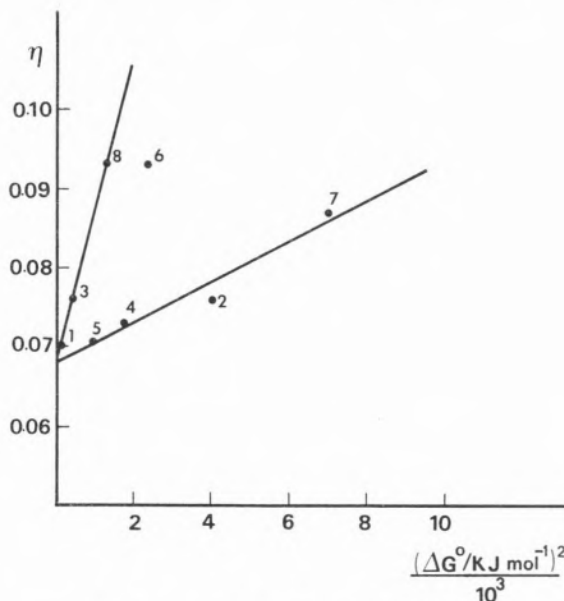
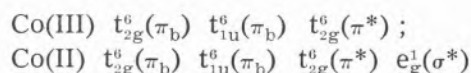
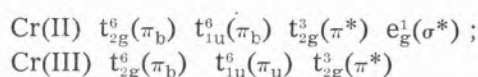


Fig. 5—Variation of the reduced bond distension, η , with the reaction energy, ΔG° , for inner-sphere electron transfer reactions. Legend for reactions in Table 3.

reactants and products. However, at the transition state some distortion can occur which allows some interaction of the metal d orbitals and the nonbonding p orbitals of the ligands. A better description of the electronic configuration of the transition state is now in terms of molecular orbitals. To estimate the bond order of the metal-ligand bond at the transition state, we can average the bond order for the appropriate electronic configurations. Considering only the highest orbitals the relevant configurations are:



The bond order contribution for one bond from all these configurations is $[(12-4) + (12-3) + (12-6) + (12-7)]/(4 \times 2 \times 6) = 0.583$. This contribution together with the $n = 1$ contribution of the σ bond leads to $n^\ddagger = 1.583$. With this value eq (1) gives $\eta(0) = 0.068$, a value in good agreement with the intercept in Figure 5.

Obviously the metal-ligand bonds can already have a bond order higher than 1 in reactants and products, as found in the $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$ and $\text{Mo(CN)}_8^{4-}/\text{Mo(CN)}_8^{3-}$ systems. Consequently, such reactions, although mechanistically outer-sphere, as we have discussed in Part 1 of this series [12], are similar to the inner-sphere processes in terms of rate constants.

THE INVERTED REGION

The study of the effect of ΔG° on outer-sphere and inner-sphere reactions within a ISM formalism reveals that for the majority of these systems Marcus theory is not exactly obeyed. The variety of λ values found experimentally (ca. 350 to 100 kJ mol^{-1}) shows that electron transfer reactions can display virtually a continuum of energy gap laws.

In liquid solution the observed rate constants are limited by diffusion,

$$k_{\text{obs}} = \frac{k_d k_{\text{et}}}{k_{-d} + k_{\text{et}}} \quad (6)$$

where k_d is the diffusion rate constant, k_{-d} the back dissociation rate constant of the collision complex and k_{et} the electron transfer rate. Figure 6 presents the calculated

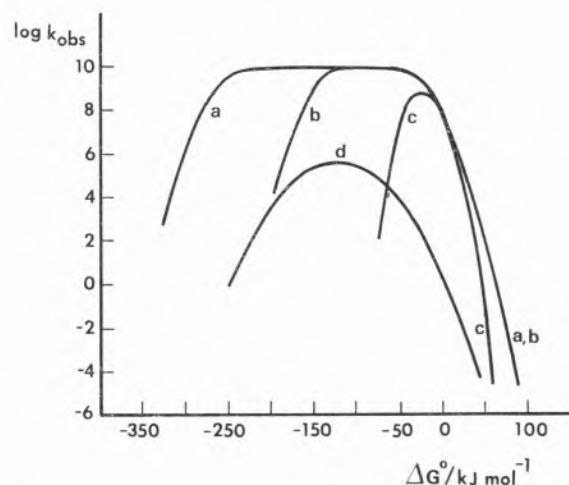


Fig. 6 — Calculated rates of electron transfer reactions in solution with: $n^\ddagger = 1.54$ a) $\lambda = 290 \text{ kJ mol}^{-1}$, b) $\lambda = 145 \text{ kJ mol}^{-1}$ and c) $\lambda = 90 \text{ kJ mol}^{-1}$; d) $n^\ddagger = 1$ and $\lambda = 290 \text{ kJ mol}^{-1}$. Other parameters: $f = 2.9 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$, $l_r + l_p = 4 \text{ \AA}$, $k_d = 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, $k_{-d} = 10^{10} \text{ s}^{-1}$; $T = 298 \text{ K}$.

rates for typical kinetic data. It is immediately obvious that the occurrence of the inverted region depends on the values of λ and on the nature of the activated complexes. For activated complexes with $n^\ddagger = 1$ there is an inverted region at relatively low ΔG° , but for transition states with $n^\ddagger \approx 1.5$ the inverted region can only be observed for reasonable ΔG° values when λ is low. For example, with $\lambda = 290 \text{ kJ mol}^{-1}$ the inverted region is only noticeable when $\Delta G^\circ < -240 \text{ kJ mol}^{-1}$, a value not normally attainable under experimental conditions in solution.

Let us now examine a system where the inverted region has been experimentally

observed. Miller et al. [3] have studied the intramolecular electron transfer in anions of bifunctional steroids (5α -androstane) A-Sp-B⁻ (B = 4-biphenyl; A is an acceptor group). The ions are formed on subjecting solutions of these molecules to short pulses of solvated electrons. Figure 7 presents the calculated rate constants for a thermal activation mechanism for solvent reorganization. Good agreement is found with experimental data in the normal and in the inverted regions, with the following set of parameters: $f = 8 \times 10^2 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$, $\kappa \nu = 10^{13} \text{ s}^{-1}$, $d = 0.642 \text{ \AA}$ ($\eta = 0.108$ and $l_r + l_p = 5.94 \text{ \AA}$; or $\eta = 0.072$ and $l_r + l_p = 8.9 \text{ \AA}$), $k_d/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} = k_d/\text{s}^{-1} = 3.5 \times 10^{10}$; $\lambda = 110 \text{ kJ mol}^{-1}$. In spite of the fact that this reaction is an intramolecular process, we have considered it to be rate determined by rotational and/or translational diffusion of the two reacting moieties linked by a rigid hydrocarbon spacer.

In the intermediate region where ΔG^\ddagger has a minimum, the experimental rates are an order of magnitude lower than the calculated ones (Figure 7). This can be attributed to some

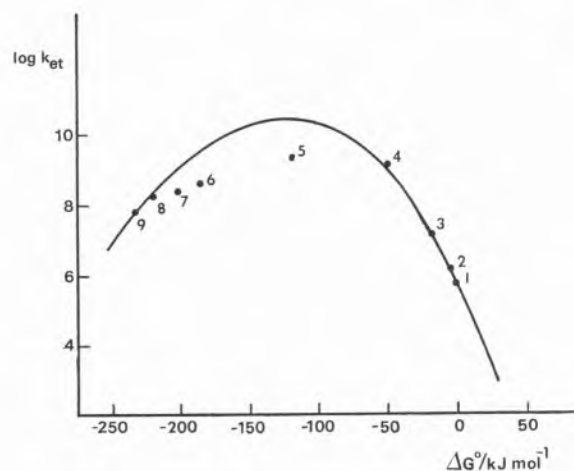


Fig. 7—Calculated intramolecular electron transfer rate constants in anions of bifunctional steroids A-Sp-B⁻ as a function of free energy in MTHF solution at 296 K; B = 4-biphenyl. Experimental data points (ref 3) with the acceptor groups A: 1. 4-biphenyl; 2. 2-naphthyl; 3. 9-phenanthryl; 4. 1-pyrenyl; 5. hexahydronaphthoquinon-2-yl; 6. 2-naphthoquinon-yl; 7. 2-benzoquinon-yl; 8. 5-chlorobenzoquinon-5-yl; 9. 5,6-dichlorobenzoquinon-2-yl.

contribution of an internal rotational energy barrier ($\Delta G^\ddagger = 5.5 \text{ kJ mol}^{-1}$) for the fastest electron transfer processes. Another possible cause of this effect can be a diffusion controlled capture of the electrons by the solute molecules. If nuclear tunnelling was a significant process in the inverted region, we would have expected experimental rates higher than those due to thermal activation, contrary to the present findings.

Different energy gap laws have been reported [11] for three types of electron transfer reactions in polar media: the photoinduced charge separation $A^* \dots D \rightarrow A^- \dots D^+$ shows no inverted region; the charge shift $A \dots D^\pm \rightarrow A^\pm \dots D$ shows a moderate decrease of rates when ΔG° is negative; the charge recombination $A^- \dots D^+ \rightarrow A \dots D$ shows a strong inverted region effect. Such findings can also be accounted for by ISM in terms of the variation of λ .

For the charge recombination process the final state involves neutral species which interact weakly with the solvent molecules. Consequently, the activated complexes of the type $A \dots D$ have a small energy of solvation and then λ is low; when λ is low we have shown that the inverted region can be easily observed at moderately negative ΔG° . In contrast the charge separation process involves charged activated complex species $A^{\delta-} \dots D^{\delta+}$ and the interaction with polar molecules is much stronger than for $A \dots D$. Consequently, the solvated activated complexes have a relatively high capacity to store energy and λ is high. For such a situation no inverted effect is observed at normal ΔG° values.

CONCLUDING REMARKS

The present model provides new insights for the understanding of electron transfer reactions. In contrast to current theories for outer-sphere reactions which consider bulk solvent reorganization as an important part of the activation process, our model suggests that the main activation free energy barrier for outer- and inner-sphere reactions is domi-

nated by inner-shell reorganization. The role of the bond order of the transition state is assessed and provides a unifying feature to deal with outer- and inner-sphere reactions within the same theoretical framework. The configuration entropy parameter λ was also found to play a significant role on the driving force effect of ΔG° for the electron transfer processes. A high λ favours the driving force effect of ΔG° , but a low λ hinders such an effect. As a consequence, different types of reaction energy gap laws can be found for exothermic reactions. In fact there is a continuum of laws from the strong inverted effect to a constant diffusion rate, when ΔG° is negative. The fact that, in general, λ is reasonably high for electron transfer reactions of solvated or coordinated metal ions explains the success of the theory of Marcus in the treatment of these systems, except for the inverted region.

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RESUMO

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

Parte 2 — O efeito da energia da reacção nas transferências de electrões de camada externa e interna.

O modelo de intersecção de estados, desenvolvido inicialmente para o estudo de reacções em fase gasosa, foi aplicado ao estudo de reacções de transferência de electrões em solução. As barreiras de energia são controladas por comprimentos e constantes de força das ligações metal-ligando e pelas ordens de ligação e entropia dos estados de transição. As reacções de camada externa têm, em geral, $n^\ddagger = 1$, mas quer as reacções rápidas de camada externa, quer as de camada interna tem $n^\ddagger \approx 1.6$. As distensões das ligações metal-ligando aumentam com o aumento de $|\Delta G^\circ|$. Esta variação depende do parâmetro da entropia de configuração λ e é pequena quando λ é elevado e acentuada quando λ é baixo. λ está relacionado com a entropia de activação, e os seus valores variam tipicamente entre 350 e 100 kJ mol⁻¹. Esta variação permite interpretar a existência das diferentes leis de variação das constantes de velocidade com ΔG° . A região invertida ocorre quando λ e (ΔS^\ddagger) é baixo, mas se λ é elevado, as constantes cinéticas são controladas pela difusão quando ΔG° é baixo. A equação de Marcus é um caso particular do presente modelo quando $\lambda \gg |\Delta G^\circ|$.