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Electron transfer reactions in coordination metal complexes. Structure-reactivity relationships

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Abstract - The current approach of Marcus theory to interpret electron transfer is questioned. Another approach based on an expansion of configuration of the transition states is presented, and the rates are estimated in terms of the following parameters: reaction energy, force constants, equilibrium bond lengths, transition state bond order and capacity to store energy. The model can interpret several anomalous features of these reactions, namely electron-exchanges where the Marcus theory estimates rates several orders of magnitude slower and faster than experiment, "cross-relations", solvent effects, the inverted region and the asymmetry of the Tafel plots of metal-aquo ions, and can assess the nonadiabatic character of some outer-sphere processes.

Electron transfer reactions play an essential role in many physical, chemical and biological processes. The investigation of the mechanisms of these reactions rests essentially on the systematic investigation of structure-reactivity relationships that results from the geometric rearrangements which accompany the change in oxidation states of the coordination compounds. Although many theories have been proposed, it is no surprise that the more simpler ones such as Marcus theory are the most popular.[1] In spite of the great success of the theory of Marcus in interpreting several of these structure-reactivity relations namely in terms of the reaction energy (ΔG), changes in equilibrium bond lengths ($l_{red}-l_{ox}$) and metal-ligand force constants (f_{ox} and f_{red}), several problems remain.

ANOMALOUS FEATURES OF ELECTRON TRANSFERS

Marcus theory and related approaches emphasize the importance of the reaction energy barrier of the solvent reorganization around the coordination compounds upon the gain or loss of an electron.[1] This outer-shell contribution is considered often to be larger than the inner-shell contribution due to the changes in geometry within the coordination shell (first-shell for a solvated metal ion). The recent findings of Nelson *et al.*[2] on the electron transfer reactions of several alkylhydrazines$^{0/+}$ which have the same energy barrier in the vapour phase and in solution therefore comes as a surprise. Although these results reveal the importance of the changes in geometry of the different oxidation states of the alkylhydrazines, they reveal also that the outer-shell reorganization is negligible. For example, the estimation of the solvent reorganization according to the theory of Marcus (eq(1)) where γ is the solvent polarity parameter ($\gamma=(n_r^{-2}-\varepsilon^{-1})$ with n_r the refractive index, ε the dielectric constant), and r the distance between the centers of the two solvated reactant species, leads to $\Delta G^{\neq}_{out} \simeq 9$kJ mol^{-1} in acetonitrile[3], which implies electron transfer rates ca. 2×10^{-2} times slower in solution, contrary to the experimental findings.[2]

The outer-shell contribution of eq (1) had been previously criticized by several authors: the self-exchange processes for ferrocenium-ferrocene in a variety of solvents, from methanol to dimethylsulfoxide, vary only by a factor of 2 whereas eq (1) predicts a ca. 20 - fold variation;[4] self-exchange rates of hydrazine do not follow eq (1) at all, because there is a modest increase in the rates with decreasing ε, an order of magnitude smaller than predicted by the theory of Marcus.[5] In contrast, the metallocene self-exchange reactions[6] are ca. 10^4 times faster in the vapour phase than in solution, a variation too large (ca. 2 orders of magnitude) to be easily interpreted by eq (1). The theory of Marcus considers $Co^{2+/3+}_{(aq)}$ and $Fe^{2+/3+}_{(aq)}$ as anomalous ion pairs[1], because the measured self-exchange rates are about 10^7 and 10^3 times faster than those calculated. In contrast, according to Marcus theory calculated the rates for $Fe(phen)_3^{3+/2+}$ are ca. 10^5 times faster than experiment.[7] Disagreements of the same magnitude have also been found for the intramolecular electron exchanges of 1,3-dicyanobenzene radical anion.[3] Marcus[8] predicted that very exothermic electron transfer reactions should show an inverted effect on the reaction rates. A few cases[9] reveal this effect clearly, but the majority of reactions do not conform with this theory in the inverted region. In consequence several classical

and dynamical models have been proposed to interpret the variety of energy-gap laws observed for these reactions.[10] Hupp and Weaver[11] have 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. The discrepancy amounts typically to calculated rates ca. 10^2 times faster in the anodic region. The "cross-reaction relations" used to calculate electron transfer rates is possibly the most widely used and tested equation in electron transfer theory.[1] In spite of its sucess there are cases where disagreements of many orders of magnitude exist.[12]

In view of these "anomalous" features it seems worth exploring alternative theoretical procedures to interpret these reactions. Since the electrical forces decrease with increasing distance from the metal ion, we will admit that the geometric rearrangements which acompany the loss or gain of an electron are large in the coordination shell, but can be neglected for the outer-shell. The inner-shell reorganization barrier from Marcus theory (eq.(2)) does not follow this hypothesis. For example, if $l_{ox}=l_{red}$ and $f_{ox}\neq f_{red}$ eq (2) leads to $\Delta G^{\ddagger}_{in}=0$ even though higher $\Delta G^{\ddagger}_{out}$ contributions can be calculated and a change in the force constants require a reorganization of the coordination shell. Eq (2) implies a transition state bond length intermediate between those of the oxidized and reduced species, $l_{ox}<l^{\ddagger}<l_{red}$, that is the transition state cannot be characterized by a turning point of vibration. If one assumes that there is an explosion in the configuration at the transition state, then $l^{\ddagger}>l_{ox},l_{red}$. This geometric arrangement agrees with the requirements of potential energy surfaces (LEPS surfaces), but does not follow the principle of least nuclear motion implicitly assumed by Marcus theory.[3]

$$\Delta G^{\ddagger}_{out}/kJ\ mol^{-1} = 347\ \gamma/2r(A^{o}) \qquad (1)$$

$$\Delta G^{\ddagger}_{in} = (1/2)[mf_{ox}f_{red}/(f_{ox}+f_{red})](l_{ox}-l_{red})^2 \qquad (2)$$

THE INTERSECTING-STATE MODEL

To estimate the bond extensions of the transition state in an electron transfer reaction when $l^{\ddagger}>l_{ox},l_{red}$, we will employ an intersecting-state model (ISM).[13] The sum of the bond extensions at the transition state, $d=(l^{\ddagger}-l_r)+(l^{\ddagger}-l_p)$, is given by eq (3), where a' is a constant (a'=0.156), l_r and l_p the equilibrium bond lengths of reactant and product, $n^{\ddagger}$ the transition state bond order, ΔG the reaction energy and λ an energy term measuring the transition state capacity to accommodate energy. The transition state configuration can be found at the intersection of the reactant and product potential energy curves (eq. (4)) where f_r and f_p are the force constants of reactant and product and x is the bond extension of the reactant. The energy barrier is then given by (eq. (5)). When $f=f_r=f_p$ and $\lambda>>|\Delta G|$, eqs (3) to (5) lead to the Marcus equation $\Delta G^{\ddagger}=\Delta G^{\ddagger}_{o}\ (1+\Delta G/4\Delta G^{\ddagger}_{o})$ where the intrinsic energy barrier is $\Delta G^{\ddagger}_{o}=(1/8)\ f\ [(a'ln2/n^{\ddagger})(l_r+l_p)]^2$.

For an electron transfer one must average the bond lengths and force constants between the oxidized and reduced species, e.g. $l_r=(l_{ox}+l_{red})/2$. Furthermore, the intersecting-state model is unidimensional and when several bonds suffer a change in geometry, an effective force constant must be defined. Here we treat the metal-ligand vibration as a local mode, and use eq (6). In the following calculations we will employ the procedure of Khan and Bockris[14] to estimate force constants from the metal-ligand symmetric stretching frequencies.

$$d=[(a'ln2/n^{\ddagger})+(a'/2)(\Delta G/\lambda)^2](l_r+l_p) \qquad (3)$$

$$(1/2)\ f_r x^2 = (1/2)\ f_p\ (d-x)^2 + \Delta G \qquad (4)$$

$$\Delta G^{\ddagger} = (1/2)\ f_r x^2 \qquad (5)$$

$$f = \sqrt{m}\ (f_{ox}+f_{red})/2 \qquad (6)$$

ELECTRON EXCHANGE REACTIONS IN SOLUTION

To test our hypothesis we have estimated the rate constants for several electron exchange reactions in water ($\Delta G=0$) using eqs (3) to (6) and the Transition State Theory expression

$$k = \kappa\ (k_B T/h)\ exp\ (-\Delta G^{\ddagger}/RT) \qquad (7)$$

where κ is an electronic factor of adiabaticity. Except where stated we take $\kappa=1$. Since the metal-ligand bonds do not break during the electron transfer reaction, we take $n^{\pm}$ as the metal-ligand bond order in reactants and products, i.e., in general $n^{\pm}=1$. Table 1 presents the results of such calculations and makes a comparison with Marcus theory.[15] All the rates estimated from ISM agree with experiment within an order of magnitude. In contrast, for the reactions of Table 1 the theory of Marcus gives estimates which are too low or too high by several orders of magnitude. When one compares the two approaches one verifies that the theory of Marcus underestimates drastically the bond extensions and overestimates the effect of the force constants; this implies a normal mode behaviour with $f=mf_i$. For many situations these two factors only partially compensate and $\Delta G^{\ddagger}_{in}$ is underestimated. With the added outer-shell reorganization reasonable agreement with experiment is obtained in many cases. However, in cases where $l_{ox}\approx l_{red}$ ($Fe(phen_3)^{2+/3+}$ and $Fe(CN)_6^{4-/3-}$), $\Delta G^{\ddagger}_{in}\approx 0$ and the calculated rates are too high. For $Co(aq)^{2+/3+}$ the internal energy barrier given by the theory of Marcus[15] $\Delta G^{\ddagger}_{in}=62$ kJ mol^{-1}, is very close to that given by ISM ($\Delta G^{\ddagger}=71$ kJ mol^{-1}). Nevertheless, since the theory of Marcus has another important outer-shell contribution, 28.5 kJ mol^{-1}, the overall barrier is too high and the rate constant too low.

Estimation of solvent reorganization at the transition states in terms of solvent dipoles interactions with the metal ion[16] appears to be too small (ca 1-2 kJ mol^{-1})[3,7] to be an important contribution for the overall energy barrier. Although some solvent effects can be due to this, they are more probably due to small changes in the vibrational frequencies with the solvents. Although, solvent effects on rates amount to less than a factor of 10, whereas other structural factors can cause changes of more than 10^{10}, they are worthy of further consideration.

The change in a vibrational dipole and consequently of a stretching force constant, is proportional to $g(n_r)=(2/a^3)[(n_r^2-1)/(2n_r^2+1)]$, with n_r the refractive index of the medium and a the radius of the spherical cavity of the solvent continuum surrounding the dipole.[17] According to eqns (5) and (7), ln k should be proportional to $g(n_r)/a^3$ (since $g(n_r)<<1$, correlations with $g(n_r)$ or $g(n_r)^2$ are both acceptable). Figure 1 presents such an analysis for the rate constants for electrochemical electron exchange of $Cp_2Co^{+/o}$. Weaver and coworkers[18] have analyzed these data in terms of eq (1) and concluded that the alcohols have an anomalous behaviour, with rates ca. 50 times higher than expected. According to Figure 1 the behaviour of alcohols is similar to other solvents, apparently with a slightly smaller solvent cavity ($\sim$1.4 times with respect to acetonitrile).

Table 1. Calculated rates constants for electron exchange reaction[a]

	k/M^{-1}s^{-1}		
	experimental	calculated ISM [e]	Marcus
$Fe(OH_2)_6^{2+/3+}$	4.2	0.9	3x10^{-2} [f]
$Co(OH_2)_6^{2+/3+}$	3.3	3	2x10^{-8} [f]
$Fe(phen)_3^{2+/3+}$	10^5	2x10^4	10^{10} [g]
$Fe(CN)_6^{4-/3-}$ [b]	9x10^2	3x10^2	8x10^5 [g]
$Mo(CN)_8^{4-/3-}$ [c]	3x10^4	2x10^4	-
NC-⟨⟩-CN$^-$ [d]	>10^{10} [i]	4x10^{10}	20 [h]

[a] $n^{\pm}=1$ except where stated otherwise; [b] $n^{\pm}=1.54$; [c] $n^{\pm}=1.7$; [d] $n^{\pm}=2.5$; [e] ref. 7 except the last reaction (ref. 3); [f] ref. 15; [g] ref.7 with a frequency factor of 10^{13}; [h] ref. 3; [i] s^{-1}.

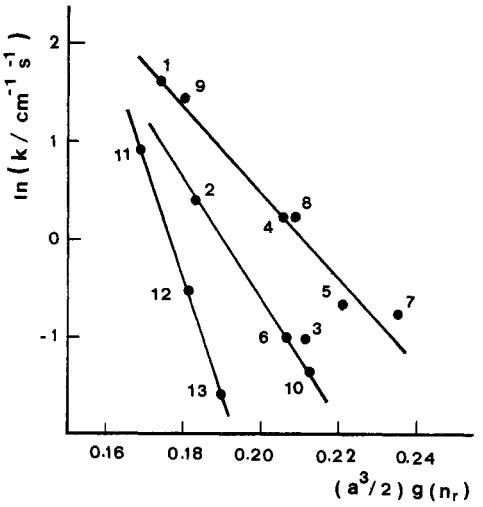

Figure 1. Logarithm of the observed rate constants of electrochemical reaction $Cp_2Co^{+/o}$ in various solvents (ref. 18) as a function of $(a^3/2)\,g(n_r)$: 1 acetonitrile; 2 CH_2Cl_2; 3 formamide; 4 dimethylformamide; 5 $(CH_3)_2SO$; 6 methylformamide; 7 benzonitrile, 8 dimethylacetamide; 9 acetone; 10 methanol; 12 ethanol; 13 propanol-1.

Another interesting problem is the interligand transfer of the electron localized on a single ligand in the complexes $Fe(bpy)_3^{\ddagger}$ and $Ru(bpy)_3^{\ddagger}$; the activation energy for this intramolecular process is ca. 12 kJ mol^{-1}.[19] A rough estimate of this rate can be made with $\sqrt{2}(f_{ox}+f_{red})$ = 1.58x10^3 kJ mol^{-1} A^{o-2} and $l_{ox}+l_{red}$ = 3.94 A^o.[7] The transition state

bond order can be assessed in terms of a molecular orbital diagram for the ligand having the reduction electron, $2\sigma^2\ 3\pi^2\ \pi^{*1}$. This results from the interaction of the metal d orbitals with ligand σ and π^* orbitals, so each metal ligand bond has a bond order n=4.5/2=2.25. For the nonreducted ligand we will take n=1 for the metal-ligand bonds (the force constants and bond lengths are virtually identical to the ammine complexes). Therefore $n^{\ddagger}=(2.25+1)/2=1.63$. With this the estimated energy barrier is 13.5 kJ mol^{-1}, close to the experimental value.

REACTION ENERGY EFFECTS

Electron exchange reactions are a convenient test of our model, because they allow absolute estimates of rate constants, as shown in Table 1. For other systems ISM is employed essentially to help suggest mechanistic interpretations. An important structural effect is that of the reaction energy on k. This can be assessed in terms of eq (3), once d is estimated through eqs (5) and (4) from the experimental $\Delta G^{\ddagger}$ values.

An interesting case is electron-transfer between several coordination complexes of Co^{2+}/Co^{3+}, as for these systems the "cross-reaction" estimates of Marcus theory are ca. 10^5 times higher than experiment.[20] Our studies[12] shown in Figure 2 reveal a dependence of the reduced bond extension $\eta=d/(l_{ox}+l_{red})$ on ΔG^2. The intercepts lead to $\eta(o)=0.108$, which corresponds to $n^{\ddagger}=1$, typical of outer-sphere reactions of metal-complexes where metalligand bonds have a single-bond character. Figure 2 presents two slopes which correspond to two different values of λ. Since λ is comparable to $|\Delta G|$, the theory of Marcus is not valid for the ΔG-effect, thus explaining the failure of the crossrelationship. Many other outer-sphere reactions follow eq(3) and λ has been found for several electron transfer reactions to be linearly dependent on $\Delta S^{\ddagger}$, as illustrated in Figure 3.[21]

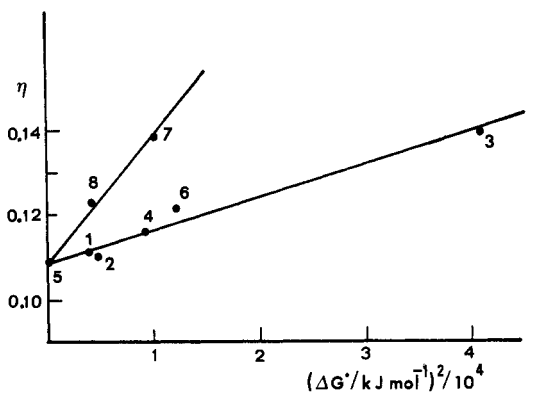

Figure 2. Plot of η versus ΔG^2 for the transfer of $Co(terp)_2^{2+}$ with: 1 $Co(biper)_3^{3+}$; 2 $Co(phen)_3^{3+}$; 3 $Co^{3+}_{(aq)}$; 4 $Co(phen)_2^{3+}$. 5 $Co^{2+}_{(aq)}/Co^{3+}_{(aq)}$; 6 $Co(terp)^{2+}/Co(phen)^{3+}$; 7 $Fe^{2+}_{(aq)}/Co^{3+}_{(aq)}$; 8 $Fe(phen)_3^{2+}/Co^{3+}_{(aq)}$ (adapted from ref. 12).

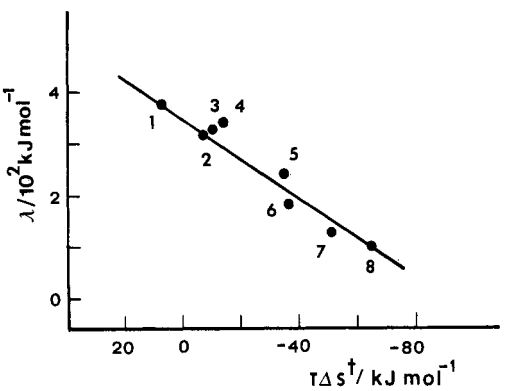

Figure 3. Linear dependence of λ versus $\Delta S^{\ddagger}$ for outer-sphere reactions in water: 1 Ce^{3+}/V^{4+}; 2 $Fe^{2+}/Tl(OH)^{2+}$; 3 Cr^{2+}/Co^{3+}; 4 Mn^{3+}/V^{4+}: 5 Cr^{2+}/Fe^{3+}; 6 Eu^{2+}/V^{3+}; 7 $Eu^{2+}/Co(NH_3)_6^{3+}$; 8 $Cr^{2+}/Co(NH_3)_6^{3+}$ (adapted from ref. 21).

Figure 4 illustrates some electron transfer rates calculated with different λ values.[21] The interesting conclusion is that ocurrence of an inverted region for experimentally accessible ΔG requires a low λ, i.e., a transition state with a low capacity to accommodate energy (notice that the inversion does not imply $\Delta G^{\ddagger}=0$); for reactions in solution with the same number of molecules in the solvation shell a low λ corresponds to very tight activated complexes. Furthermore strong inverted effects[10b] are also observed in the charge recombination reactions $A^-...D^+ \rightarrow A...D$ because there is a strong decrease in the capacity to store energy of the transition state due to the poor solvation of the products. In contrast, the photoinduced charge separation in the quenching of excited states $A^*...D \rightarrow A^-...D^+$ which should have a high λ, has no inverted region.

The rate constants of heterogeneous electron transfer are given by

$$k_{het}=\kappa Z \exp(-\Delta G^{\ddagger}_{het}/RT) \qquad (8)$$

where Z is the preexponential factor taken as $Z=10^4$ cm s^{-1} and κ an electronic transmission factor.[22] Work-corrected electron transfer rates can be studied in the same manner as the rates of homogeneous processes with $2\Delta G^{\neq}_{het}=\Delta G^{\neq}_{hom}$ and $\Delta G \simeq F(E-E_f)$ where F is the Faraday, E the electrode potential and E_f the standard potential.[22]

Hupp and Weaver[11] have reported a strong asymmetry on the Tafel plots of metal-aquo ions on the cathodic and anodic region. This effect is not interpretable in terms of the differences in the force constants of the oxidized and reduced species. Figure 5 illustrates the $Cr^{2+/3+}$ system and shows that ISM can reproduce the experimental data with different values of λ.[23] The standard entropy values ($S^o(Cr^{3+}_{(aq)})=-292$ and $S^o(Cr^{2+}_{(aq)})=-84$ J mol^{-1} K^{-1}) allow one the estimate a high entropy of activation for the cathodic reduction $\Delta S^{\neq}_{cat} \geq 0$ J mol^{-1} K^{-1} which corresponds to a high λ ($\lambda >> |\Delta G|$); in contrast for the anodic oxidation $\Delta S^{\neq}_{an} \leq -210$ J mol^{-1} K^{-1} is low and λ is much lower (λ=110 kJ mol^{-1}). The curvature of the anodic plot suggests that at higher potentials an inverted region might be observed. The different values of λ for the forward and backwards reactions are interpreted in terms of a nonequilibrium situation at the transition states.[23]

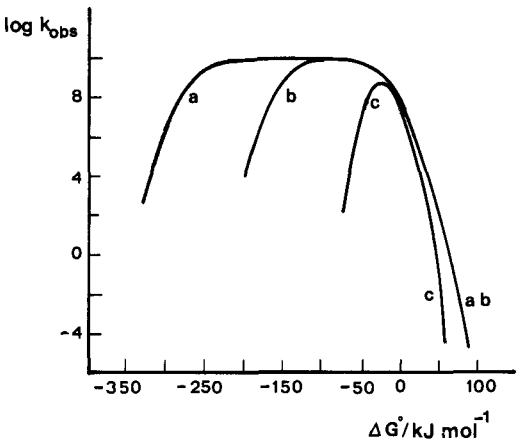

Figure 4. Calculated rates of electron transfer in solution with λ/kJ mol^{-1} a) 290 and b) 145 c) 90. Other parameters: $n^{\neq}=1.54$, $f=2.9\times10^3$ kJ mol^{-1} A^{o-2}, $l_r+l_p=4A^o$, diffusion rate 10^{10} $M^{-1}s^{-1}$ (adapted from ref. 21).

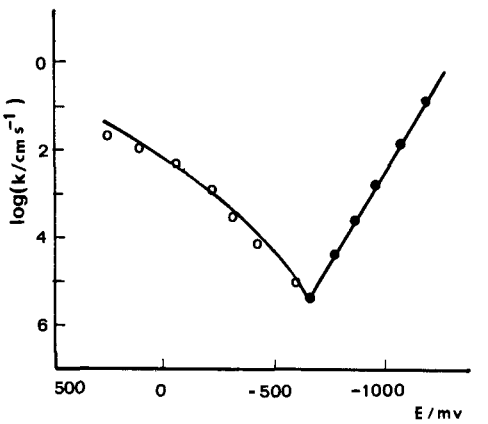

Figure 5. Tafel plots for $Cr(OH_2)_6^{2+/3+}$: ——— experimental plots (ref. 11). Calculated data with $f/10^3$ kJ $mol^{-1}A^{o-2}$; • cathodic reduction $f_r=3.67$, $f_p=2.36$ and a constant $d=0.545$ A^o; o anodic oxidation: $f_r=2.36$, $f_p=3.67$, $d(o)=0.545A^o$ and λ=110 kJ mol^{-1} (adapted from ref. 23 with a correction of the λ value).

A CRITERION OF NONADIABATICITY FOR OUTER-SPHERE REACTIONS

Whereas reliable absolute values for the rates of electrochemical processes are difficult to estimate due to electrode double-layer and adsorption effects, this does not happen with homogeneous reactions, where it is possible to assess the factor κ of eq (7). Although the majority of outer-sphere reactions are adiabatic processes, the question of the adiabaticity of electron transfer has been a matter of considerable discussion, particularly for ions involving f-orbitals.[24,25] Europium ions have even been suggested to be involved in strong nonadiabatic reactions ($\kappa<10^{-5}$).[24b]

The rate of electron exchange $Eu^{2+/3+}_{(aq)}$ is 3×10^{-5} M^{-1} s^{-1}.[24] An estimation of $\Delta G^{\neq}$ can be made with force constants ($f=f_{ox}+f_{red}$) $=2.7\times10^3$ kJ mol^{-1} A^{o-2}) estimated from the vibrational frequencies[26] $\nu(Eu^{3+}_{(aq)})=433$ cm^{-1} and $\nu(Eu^{2+}_{(aq)})=340$ cm^{-1}. The bond lengths were estimated from the ionic radius 1.4A^o; $l=4.8A^o$[27]. Since for this reaction $n^{\neq}=1$, ISM allows the estimation of $k=7\times10^{-4}$ M^{-1} s^{-1} and consequently $\kappa=0.04$. Therefore the reaction has a small nonadiabatic character.

REACTIONS IN THE VAPOUR PHASE

According to the view presented here that outer-shell reorganization does not play a dominating role in electron transfers, these reactions will have virtually the same barrier in the gas phase and in solution, as found with the alkylhydrazines.[2] However, a different situation occurs with the metallocenes[6] which have rates ca. 4 orders of magnitude higher in the gas phase. The question we address now is if such behaviour can be interpreted

in terms of a change in the inner-shell barrier? Such variations cannot be interpreted in terms of a change in force constants which require a decrease by ca. an order of magnitude from solution to vapour. As will be shown such variations are interpretable in terms of a change in $n^{\ddagger}$.

Let us consider the molecular orbitals for ferrocene,[28] resulting from the interaction of the ligands and the 3d, 4s and 4p iron orbitals, with the following electronic distribution: $a_{1g}^2\, a_{2u}^2\, 2e_{1u}^4\, 2e_{1g}^4\, a_{1g}^1\, 2e_{2g}^2$. Considering that in the transition state, in the most favourable situation, only 5 electrons contribute for the π system of each ligand, a contribution of 4 pairs of electrons remains for the two iron-cyclopentadienyl bonds. So the bond order is n=2. In the reduced species another electron occupied an antibonding orbital, so n'=1.75. The average bond order, taken as the bond order of the transition state is $n^{\ddagger}$=1.875. The relevant data to estimate the rate constant is l=4.17 A° and $\sqrt{2}f$=2.4x10^3 kJ mol^{-1} A°$^{-2}$.[4] At 375K the estimated rate is 2x10^{10} M^{-1} s^{-1}, close to the vapour phase rate for the thermoneutral situation, 1.3x10^{10} M^{-1} s^{-1}.[6]

In liquid solutions the π electrons of the ligands can interact with the solvent molecules[29] and an electronic shift from the metal center to the ligand can occur. So $n^{\ddagger}$<1.875. For example, for $Cp_2Fe^{+/o}$ Nielsen et al.[30] measured a rate of 1.6x10^6 M^{-1} s^{-1} in DMSO. With the same f and l data such rate corresponds to $n^{\ddagger}$=1.3. For electrochemical reactions $n^{\ddagger}$ is even smaller, k=0.85 cm^{-1} s^{-1} in DMSO,[4] which corresponds to $n^{\ddagger}$=1.18.

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