Estimation of the reorganization and reaction free energies for electron transfer processes from optical and thermal data. An application to the reaction $[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(NH_3)_5]$

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Taking into account the relationship between optical and thermal electron transfer processes, that is, the relation between kinetic and spectroscopic data, the reaction and reorganization free energies for the reaction: $[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(NH_3)_5]$ have been obtained for different reaction media constituted by water + co-solvent mixtures. A comparison of data for this reaction and another closely related process, the oxidation of $[Fe(CN)_6]^{4-}$ with $[Co(NH_3)_5pz]^{3+}$, is made. From this comparison it is concluded that the coupling of the iron(II) and cobalt(III) centers, through the pyrazine ligand, has a strong influence on the rate of the intramolecular electron transfer at the binuclear complex.

Introduction

Electron transfer reactions are processes of paramount importance in physics, chemistry and biology. The study of this kind of reaction is stimulated by the fact that, since the seminal papers of Marcus[1] and Hush,[2] there has been a good theoretical framework for the interpretation of kinetic data in this field. The Marcus–Hush ideas, classical in nature, have been enriched since then through semiclassical[3] and quantum[4] formulations. All the treatments emphasize the outstanding importance of the solvent in electron transfer reactions. Thus, the solvent influences both the pre-exponential and the exponential terms of the electron transfer rate constant.

When this parameter is written as:[5]

$$k_{et} = \kappa_{el} \upsilon_n e^{-\Delta G^{\neq}/RT} \quad (1)$$

κ_{el} is the electronic transmission coefficient, υ_n the nuclear frequency factor and $\Delta G^{\neq}$ the activation free energy, which is given by:

$$\Delta G^{\neq} = \frac{(\lambda + \Delta G^{o'})^2}{4\lambda} - H_{AB} \quad (2)$$

In this equation, λ is the reorganization free energy, $\Delta G^{o'}$ is the free energy of the electron transfer reaction and H_{AB} is the electronic coupling matrix element.[6]

In fact, the solvent influences all the parameters appearing in eqn (1).[7] However, except for extremely rapid processes, that is, processes in which dynamic solvent effects[8,9] are important,[10] the main influence of the solvent on the electron transfer reaction comes mainly from the effect of the solvent on λ and $\Delta G^{o'}$.

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For this reason, the study of the solvent effects on these free energies is of importance. However, this kind of study requires the selection of suitable experimental systems. The obvious selection in order to accomplish this task is to study intramolecular electron transfer processes, such as the reaction studied in this work. In this way, the kinetic data is directly k_{et}, as given in eqn (1). However, in order to avoid back electron transfer it is convenient to use binuclear complexes containing a cobalt(III) center. In this way once this center is reduced, the cobalt(II) complex resulting from this reduction decomposes rapidly in such a way that back electron transfer is precluded. Nevertheless, this fact makes it impossible to obtain the free energy of the reaction, $\Delta G^{o'}$, through conventional electrochemical measurements. Moreover, even if the redox potentials of the two centers in a binuclear complex could be measured, these measurements would give the comproportionation free energy, rather than the reaction free energy.[11] It should be mentioned that Haim[12] has developed a method to circumvent this problem. In other respects, this method cannot be applied in all cases, such as the one presented here, in which one of the centers is electrochemically irreversible.

For this reason we have used here a new procedure that permits us to get both λ and $\Delta G^{o'}$ for intramolecular electron transfer in binuclear complexes, even in the case of one of the centers being electrochemically irreversible. The method is based on the connection existing between the rate constant for thermal electron transfer processes and the corresponding optical spectra. This connection was established several years ago by Hush,[13] who obtained the equations for the reorganization and the reaction energies from spectra band energies (E_{op}) and spectra band widths ($\Delta\upsilon_{1/2}$).

These relationships can be seen by considering the schematic (one-dimensional) representation of the free energy surfaces for an electron transfer process depicted in Fig. 1. It is clear

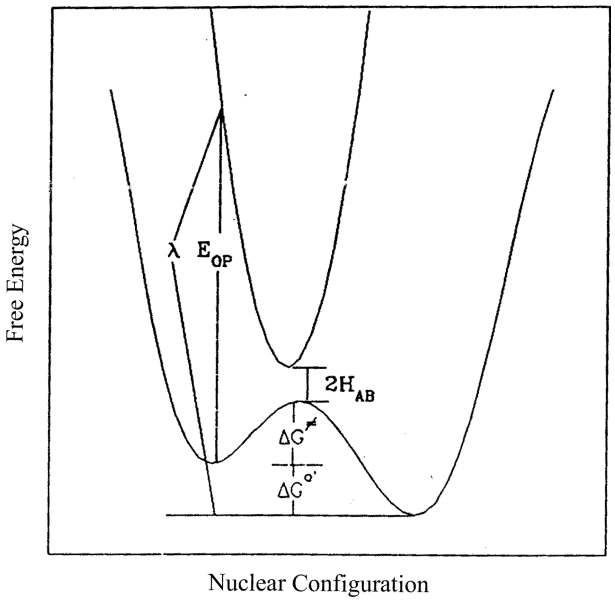

Fig. 1 Free energy surfaces for the reactant and product states showing the characteristic magnitudes for optical and thermal electron transfer.

from the figure that:

$$E_{op} = \lambda + \Delta G^{o'} \quad (3)$$

In such a way that:

$$\Delta G^{\neq} = \frac{E_{op}^2}{4\lambda} - H_{AB} \quad (4)$$

H_{AB} is given by:[13]

$$H_{AB}(cm^{-1}) = \frac{1.995 \times 10^{-2}}{R_{AB}} (\varepsilon_{max} \upsilon_{max} \Delta\upsilon_{1/2} b^{-1})^{1/2}$$
$$\Delta\upsilon_{1/2} = (2295\lambda)^{1/2} \text{ in } cm^{-1} \text{ at } 298\,K \quad (5)$$

In this equation, υ_{max} is the wave number corresponding to the absorption band maximum, E_{op} (in cm^{-1}), ε_{max} is the absorption coefficient at this wave number in mol^{-1} dm^3 cm^{-1} and $\Delta\upsilon_{1/2}$ is the full width at half-height of the band (in cm^{-1}). The degeneracy term, b, is equal to 2.0 and it accounts for the possibility of optical transition from either of two equivalent donor orbitals of the Fe(II) center (d_{xz} or d_{yz}) and R_{AB} is the geometric distance between the redox sites in Å.

From eqn (4)–(5), the results are:

$$\Delta G^{\neq}(cm^{-1}) = \frac{E_{op}^2}{4\lambda} - d(\varepsilon_{max} E_{op} b^{-1})^{1/2} (2295\lambda)^{1/4}$$
$$d = \frac{1.995 \times 10^{-2}}{R_{AB}} \quad (6)$$

Thus, having $\Delta G^{\neq}$ from kinetic data and E_{op} from optical data of the MMCT band, it is possible to calculate λ from eqn (6) by using an iterative numerical procedure and then $\Delta G^{o\prime}$ from eqn (3).

Using this approach we have obtained the free energies for the following reaction:

$$[Fe^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(h.s.)(NH_3)_5] \quad (7)$$

where (l.s.) and (h.s.) refer to the spin state (low and high, respectively) of the cobalt center in the reactant and product states.

It is worth pointing out that intramolecular electron transfers in binuclear and polynuclear complexes are of interest on their own. In fact, numerous recent reviews dealing with electronic and energetic factors of relevance to thermal and optical electron transfer processes have appeared, offering an overview of experimental, theoretical and computational methods of probing these systems.[14] Interest in this kind of process arises from their multiple potential applications.[15]

Finally, the study of the reaction in eqn (7) has additional interest for us: we have previously considered the kinetics of the reaction:[16]

$$[Fe(CN)_6]^{4-} + [Co(NH_3)_5pz]^{3+} \rightarrow [Fe(CN)_6]^{3-} + [Co(NH_3)_5pz]^{2+} \rightarrow Co^{2+} + 5NH_3 + pz \quad (8)$$

in the same reaction media considered here. In this way the comparison of reactions (7) and (8) will permit us to study the influence of the coupling between the Fe(II) and Co(III) centers through the pyrazine ligand on the kinetics of the electron transfer process.

Experimental

Materials

The complexes $[Fe(CN)_5H_2O]^{3-}$, $[Co(NH_3)_5pz]^{3+}$ and $[Ru(CN)_5H_2O]^{3-}$ were prepared and purified following the procedures described in the literature.[17–19] The co-solvents (methanol, ethylene glycol and *tert*-butyl alcohol) were commercial products and were used as received. Water was obtained from a Millipore Milli Q water system, its conductivity being less than 10^{-6} S m^{-1}. It was deoxygenated before use.

Kinetic measurements

In order to follow the reaction in eqn (7), the binuclear complex was prepared "*in situ*" using solutions of $[Fe(CN)_5H_2O]^{3-}$ and $[Co(NH_3)_5pz]^{3+}$:

$$[Fe(CN)_5H_2O]^{3-} + [Co(NH_3)_5pz]^{3+} \rightarrow [Fe^{II}(CN)_5pzCo^{III}(NH_3)_5] \quad (9)$$

As this reaction is rapid in relation to the subsequent electron transfer reaction (eqn (7)), their kinetics are well separated, in such a way that they can be followed without mutual interference.

Kinetic runs were carried out in a stopped flow spectrophotometer from Hi-Tech, monitoring the absorbance changes at 620 nm, which is the wavelength corresponding to the maximum absorbance of the binuclear complex. The concentrations of the precursor reactants, $[Fe(CN)_5H_2O]^{3-}$ and $[Co(NH_3)_5pz]^{3+}$, after mixing, were 5×10^{-5} mol dm^{-3} and 5×10^{-4} mol dm^{-3}, respectively. In preliminary experiments we checked that these concentrations ensured complete formation of the binuclear complex.

The water–co-solvent mixtures were prepared by weight. The bulk static dielectric constants of these solutions at

298.2 K were 78.5 (pure water), 76.0, 74.0, 70.0, 66.0, 64.0 and 60.0. The suitable molar fractions of the organic component in the mixtures corresponding to these values of dielectric constant were taken from the literature,[20] and they are include in Tables 1–4.

Spectra

In order to obtain the MMCT bands corresponding to the optical transition in the mixed valence complex $[Fe^{II}(CN)_5pzCo^{III}(NH_3)_5]$ in the different reaction media at 298.2 K we used a HP-8452A Diode Array spectrophotometer coupled to a manual mixing system from Hi-Tech. The binuclear complex was prepared *in situ* by mixing equal volumes of $[Fe(CN)_5H_2O]^{3-}$ and $[Co(NH_3)_5pz]^{3+}$ solutions at the concentration 1.2×10^{-4} mol dm^{-3}.

It is interesting to mention that the band does not correspond exactly to the same electron transfer as the thermal process, but to the process:

$$[Fe^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(l.s.)(NH_3)_5] \quad (10)$$

that is, the spin of the cobalt center is conserved in the optical transition. Thus, the energy corresponding to the maximum of the band needs to be corrected before using it in eqn (3)–(6). These corrections include: (i) correction for the spin–orbit coupling in the iron center,[21,22] (ii) corrections for the differences of the cobalt center spin in optical and thermal electron transfer.[22] The procedure followed in order to perform these corrections is described in detail by López-López *et al.*[23]

Results and discussion

Tables 1 and 2 contain the results of the experiments. Table 1 shows the rate constant (k_{et}) corresponding to the electron transfer studied here (eqn (7)) and Table 2 contains E_{op} values, which are the energies of the band maxima corresponding to the process in eqn (10). In order to obtain E_{op}^{corr} we did not use the experimental E_{op} values, but the values of this energy resulting from the fit of these experimental values to:[24]

$$E_{op} = \frac{E_{op}^{w} + KE_{op}^{s}x}{1 + Kx} \quad (11)$$

where x represents the ratio between the mole fractions of the methanol and water.

These energies were corrected as previously mentioned in such a way that E_{op}^{corr} values are obtained (see Table 2). Thus, E_{op}^{corr} values correspond to the optical process equivalent to the thermal process in eqn (7), which are the values to be used in eqn (3)–(6) in order to obtain information on the parameters controlling the electron transfer process.

In order to advance in this direction, it is necessary to derive $\Delta G^{\neq}$ from k_{et}. The pre-exponetial term in k_{et} is of the order of the (average) vibratory frequency promoting the activation of the binuclear complex, except for strong non-adiabatic processes. Thus, a value of 10^{12}–10^{13} s^{-1} seems to be a reasonable one and in our calculations, a value of 6.62×10^{12} s^{-1} was used. This value corresponds to the value of the pre-exponential term in the equation of the rate constant given by the classical Transition State Theory (k_BT/h) at our working temperature. In this way $\Delta G^{\neq}$ can be obtained for k_{et} as follows:

$$\Delta G^{\neq} = -RT \ln \frac{k_{et}}{6.62 \times 10^{12}} \quad (12)$$

Table 1 Rate constants (k_{et}) for the intramolecular process $[Fe^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(h.s.)(NH_3)_5]$ in several solvents at 298.2 K

Solvent	Mole fraction of organic solvent	D^a	$10^2\ k_{et}/s^{-1}$
Water	0.000	78.5	5.3
Water–methanol	0.034	76	7.6
	0.064	74	11.0
	0.126	70	19.0
	0.191	66	25.6
	0.248	64	31.4
Water–ethylene glycol	0.029	76	7.2
	0.054	74	9.4
	0.117	70	12.6
	0.211	66	19.7
	0.267	64	20.6
	0.409	60	33.2
Water–*tert*-butyl alcohol	0.007	76	6.3
	0.013	74	8.3
	0.027	70	11.7
	0.042	66	13.9
	0.049	64	14.8
	0.066	60	16.1

[a] Bulk static dielectric constant.

Table 2 Values of energies associated with the processes $[Ru^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Ru^{III}(CN)_5pzCo^{II}(l.s.)(NH_3)_5]$, ($E_{op}$), and $[Fe^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(h.s.)(NH_3)_5]$, ($E_{op}^{corr}$)[a], in several solvents at 298.2 K

Solvent	Mole fraction of organic solvent	E_{op}/ kJ mol^{-1}	E_{op}^{corr}/ kJ mol^{-1}
Water	0.000	220.1	246.2
Water–methanol	0.034	220.2	246.6
	0.064	220.7	246.9
	0.126	220.9	247.1
	0.191	220.7	247.3
	0.248	221.3	247.4
	0.362	221.4	247.6
Water–ethylene glycol	0.029	220.2	246.3
	0.054	220.1	246.5
	0.117	220.6	246.7
	0.211	220.7	246.9
	0.267	220.9	247.0
	0.409	220.9	247.2
Water–*tert*-butyl alcohol	0.007	221.1	247.2
	0.013	221.3	247.7
	0.027	222.1	248.3
	0.042	222.7	248.3
	0.049	222.5	248.9
	0.066	222.9	249.0

[a] E_{op}^{corr} values have been calculated using the following equation: $E_{op}^{corr} = E_{op} - \lambda_{so} - \Delta E_i + \delta\lambda_i$, where λ_{so} is the spin–orbit correction for a Fe(III) center in an excited state (5.38 kJ mol^{-1}),[21,22] ΔE_i is the difference between free energies of thermally equilibrated high and low spin cobalt(II) centers (79.5 kJ mol^{-1})[22] and $\delta\lambda_i$ is the inner shell reorganization free energy owing to the differences in the spins of Co(II) centers (111.1 kJ mol^{-1}).[30]

Table 3 Reorganization (λ) and reaction ($\Delta G^{o\prime}$) free energies corresponding to the process $[Fe^{II}(CN)_5pzCo^{III}(l.s.)(NH_3)_5] \rightarrow [Fe^{III}(CN)_5pzCo^{II}(h.s.)(NH_3)_5]$ in different solvents at 298.2 K ($\gamma \equiv$ Pekar factor)

Solvent	Mole fraction of organic solvent	γ	λ/kJ mol^{-1}	$\Delta G^{o\prime}$/ kJ mol^{-1}
Water	0.00	0.5505	167	80
Water–methanol	0.034	0.5486	169	78
	0.064	0.5472	171	76
	0.126	0.5445	174	74
	0.191	0.5419	175	72
	0.248	0.5406	176	71
Water–ethylene glycol	0.029	0.5421	168	78
	0.054	0.5369	169	77
	0.117	0.5253	171	76
	0.211	0.5139	173	73
	0.267	0.5086	174	73
	0.409	0.4991	176	70
Water–*tert*-butyl alcohol	0.007	0.5474	169	79
	0.013	0.5459	171	77
	0.027	0.5401	173	75
	0.042	0.5364	174	75
	0.049	0.5347	175	74
	0.066	0.5295	175	74

Once, $\Delta G^{\neq}$ has been obtained, it is easy to get λ through eqn (6), with $\varepsilon_{max} = 1600$ mol^{-1} dm^3 cm^{-1} and $R_{AB} = 6.8$ Å,[22] then,$\Delta G^{o\prime}$ can be calculated using eqn (3). The values of these parameters are shown in Table 3.

It is important to realize that the values of the pre-exponential factor are not critical for the calculation of λ and $\Delta G^{o\prime}$, because a value higher (or lower) than the real one by a factor of 10 would produce only an error of about 5% in $\Delta G^{\neq}$.

The results shown in Table 3 deserve some comments. First of all, $\Delta G^{o\prime}$ has a positive sign which could imply that, in the binuclear complex, the equilibrium would be displaced towards the reactant state. Thus, after the electron transfer, dissociation of the cobalt center is the cause of the complete disappearance of the reactant state in the binuclear complex.

A second comment concerns the value of λ appearing in Table 3. These values include a solvent contribution (λ_s) and an internal contribution (λ_i), arising from the internal reorganization of the donor and the acceptor. The latter is usually considered as independent of the reaction media. Consequently, as the solvent reorganization free energy is proportional to Pekar's factor, $\gamma = (1/n^2) - (1/D)$, and this factor decreases as the molar fraction of the co-solvent is increased (see Table 3), both λ_s and λ would decrease when the amount of the co-solvent in the reaction mixture is increased. However, the λ values shown in Table 3 change in the opposite sense.

In order to explain the increase of λ values, it is important to realize that our data correspond to solvent mixtures instead of neat solvents. In these mixtures, when the electron transfer occurs, both reactants change their charges, and consequently, a modification of the composition of their solvation shells is expected (this modification, of course, is absent in neat solvents). This change in the composition of the solvation shells will produce an extra solvent reorganization, caused by a translational movement of some solvent molecules, because at the transition state the positions of the molecules of the two solvent components (and not only the solvent polarization) must be intermediate between the positions corresponding to the (preferential) solvation of the precursor and successor complexes. It is important to note that the cause of the extra component in λ is not the preferential solvation itself, but the changes in this preferential solvation in the activation process, which implies a movement of solvent molecules in the activation step.

It is worth pointing out that this component of the reorganization energy has been observed by some of the present authors in previous works[16,25] as well as by other authors. Thus, Curtis *et al.*[26] suggested this extra contribution from the result obtained through thermodynamic (redox) measurements corresponding to some inorganic complexes in solvent mixtures. A similar conclusion was reached by Hupp *et al.*[27] from the study of the spectra of some complexes in solvent mixtures. Moreover, the existence of this extra component of the solvent reorganization energy in solvent mixtures has been predicted theoretically by Matyushov[28] and corroborated by computer simulations.[29]

An interesting point for us has to do with the comparison between the kinetic data of the reaction studied in this work and those previously obtained for the reaction shown in eqn (8). In order to compare these results, data obtained for the intramolecular reaction are given in Table 4. First of all, it is interesting to note that reaction 8 is more rapid than reaction 7, which is somewhat surprising. According to the Marcus–Hush treatment, λ should be greater for the intermolecular process (eqn 8) and the pyrazine, acting as a bridging ligand, would produce a better electronic connection between donor and acceptor centers in the intramolecular reaction (eqn (7)). In fact, an estimation of H_{AB} from eqn (5) for both reactions gives $H_{AB}^{intra} \approx 10.8$ kJ mol^{-1} (903 cm^{-1}) and $H_{AB}^{inter} \approx 5.6$ kJ mol^{-1} (468.2 cm^{-1}),[16] which confirms this point of view. Parameters used in eqn (5) for the intramolecular process in

Table 4 Rate constants (k_{et}), reorganization energy (λ) and reaction free energy ($\Delta G^{o\prime}$) for the intermolecular process: $[Fe^{II}(CN)_6]^{4-} + [Co^{III}(l.s.)(NH_3)_5pz]^{3+} \rightarrow [Fe^{II}(CN)_6]^{3-} + [Co^{II}(h.s.)(NH_3)_5pz]^{2+}$ in several solvents at 298.2 K

Solvent	Mole fraction of organic solvent	k_{et}/s^{-1}	λ/ kJ mol^{-1}	$\Delta G^{o\prime}$/ kJ mol^{-1}
Water	0.00	0.17	284	13
Water–methanol	0.034	0.28	291	7
	0.064	0.36	291	6
	0.126	0.52	291	4
	0.191	0.82	290	2
	0.248	1.10	290	1
Water–ethylene glycol	0.029	0.26	287	10
	0.054	0.34	286	9
	0.117	0.57	285	7
	0.211	0.79	286	5
	0.267	1.13	284	4
	0.409	1.25	286	2
Water–*tert*-butyl alcohol	0.007	0.25	290	8
	0.013	0.27	289	8
	0.027	0.34	290	7
	0.042	0.43	288	6
	0.049	0.48	287	6
	0.066	0.52	286	6

water are: $\varepsilon_{max} = 1600\ mol^{-1}\ dm^3\ cm^{-1}$, $\upsilon_{max} = 20\ 589\ cm^{-1}$, $\Delta\upsilon_{1/2} = 5655\ cm^{-1}$ and $R_{AB} = 6.8$ Å.[22] A comparison of λ values in Tables 3 and 4 also corroborate the prediction of the Marcus–Hush treatment.

It is clear from data shown in Tables 3 and 4 that the cause of the greater rate for the intermolecular process, as compared with the intramolecular one, is the higher free energy of the intramolecular reaction. *Thus, the coupling of the donor and acceptor centers produces a more favorable electronic connection but a more unfavorable driving force*. This fact is relevant in the molecular electronic field because the interest is normally focused on the electronic conductivity of the participant medium between the donor and the acceptor, which is the electronic bridge. But, this property is not the only one to be considered because the bridge can also produce changes in the driving force that can overwhelm the effect of the conductivity.

In conclusion, a method to obtain the main parameters of electron transfer reactions, namely λ and $\Delta G^{o\prime}$, has been presented. The method is based on the connection between optical and thermal electron transfer processes and has been applied to the study of an intramolecular electron transfer reaction in which $\Delta G^{o\prime}$ can not be directly obtained by using any other approach. Furthermore, comparison of the data presented in this work with those previously obtained for the intermolecular process shown in eqn (8) allows us to conclude that an increase in the electronic conductivity between the donor and the acceptor centers involved in the reaction does not necessarily produce an increase of the electron transfer rate, because the increase of the conductivity can be accompanied by an unfavorable change in the driving force.

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