DALTON
FULL PAPER

Procedure for the determination of redox potentials of chemically (and electrochemically) irreversible inorganic redox couples from spectroscopic data

Francisco Sánchez, Pilar Pérez-Tejeda, Francisco Pérez and Manuel López-López *

Departamento de Química Física, Facultad de Química, Universidad de Sevilla,
c/Profesor García González s/n, 41012 Sevilla, Spain. E-mail: amurillo@cica.es

Received 8th June 1999, Accepted 5th July 1999

A procedure for the estimation of the redox potentials of chemically (or electrochemically) irreversible couples based on optical measurements and on the Marcus and Hush equations has been proposed and tested through the determination of redox potentials of different $Co(NH_3)_5L^{3+/2+}$ redox couples. The results are in agreement with the expectations based on the reactivity of these complexes.

Introduction

Many oxidants and reductants that are often used (such as $S_2O_8^{2-}$, most of the cobalt(III) complexes, *etc.*) are chemically or electrochemically irreversible. Consequently, classical electrochemical methods for the determination of redox potentials cannot be used for these compounds and in many cases these redox potentials are unknown. This raises a twofold problem: from the point of view of the interpretation of kinetic data corresponding to redox processes, in which these reactants participate, an analysis of the results, based on Marcus' equation,[1] is not possible because this analysis requires the use of the redox potentials of the oxidant and the reductant. On the other hand, if one wants to use this type of substance in a synthetic and/or industrial application, it is difficult to predict the reactivity unless each one is tested. Obviously, the situation could be altered if an alternative procedure for the determination of redox potentials was feasible. In the field of Organic Chemistry such a procedure has been developed by Saveant and coworkers[2a] and Antonello *et al.*[2b] based on the obtention of an electrochemically irreversible voltammogram, followed by convolution voltammetry analyses coupled to the double-layer correction. This procedure leads to reasonable estimates of the standard redox potentials for the dissociative electron transfer of dialkyl peroxides, according to the authors, having an uncertainty of about 0.1 V.

In this paper an alternative procedure to determine redox potentials for chemically or electrochemically irreversible couples is proposed based on the relation existing between optical data corresponding to MMCT bands and the redox energy for these processes. This relation was derived several years ago by Hush,[3] who obtained the equations for the reorganization energies, λ, and reaction free energies, $\Delta G^{\circ\prime}$, in terms of band energies, E_{op}, and widths, $\Delta\nu_{1/2}$, and for the electronic delocalization energies from the integrated band intensities. These relationships can be seen by considering the schematic (monodimensional) representation of the free energy surfaces for an electron transfer process depicted in Fig. 1. If the response of the solvent is assumed to be linear the free energy surfaces are parabolic. Indeed, it is frequently assumed, as Hush did, that the parabola of the reactant and product states have the same curvature. In this simple approach, eqn. (1) follows (see Fig. 1).[3–7,†] Eqn. (1) points to the possibility of using

$$E_{op} = \lambda + \Delta G^{\circ\prime} \qquad (1)$$

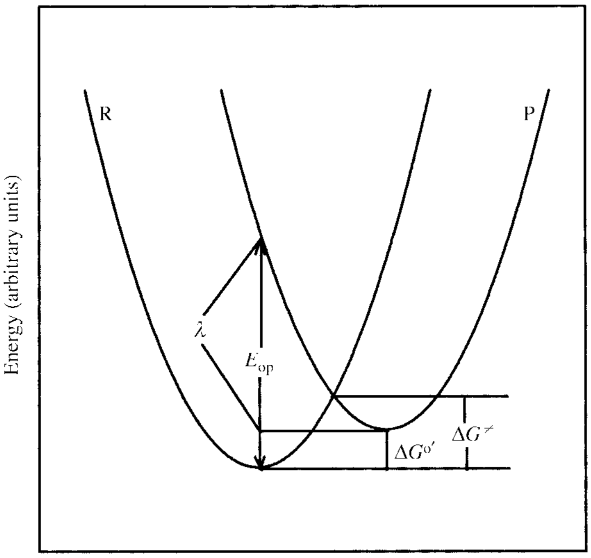


Fig. 1 Free energy surfaces (FES) showing the characteristic magnitudes for the optical (vertical transition) and thermal (movement of representative point along the reaction coordinate) electron transfer.

---

† There has been some controversy about using eqn. (1) because it is written in terms of energy (E_{op}) and free energy (ΔG° and λ). It was pointed out that on the right hand side, instead of λ and ΔG°, the corresponding energetic magnitudes should appear. Nevertheless, Marcus and Sutin[1a] have convincingly argued that the parameters λ and $\Delta G^{\circ\prime}$ are better viewed as free energies. It can also be argued that λ depends on the optical and static dielectric constants of the medium and $\Delta G^{\circ\prime}$ mainly on the static dielectric constant. As the temperature coefficients of these dielectric parameters are low, the entropic terms in λ and $\Delta G^{\circ\prime}$ must also be low and they, indeed, compensate to some extent (see for example ref. 5). Finally, for an optical electron transfer, the nuclei are frozen, so the corresponding (electronic) entropy change would be $\Delta S = R \ln (\Omega^{exc}/\Omega^{g})$ where Ω is the spin multiplicity of the corresponding excited or ground state. Thus, the corresponding free energy term should be $\approx RT$, which is small in comparison to E_{op} and λ values. Consequently, λ and $\Delta G^{\circ\prime}$ can be taken as free energies. Indeed, in a dielectric continuum E_{op} and ΔG_{op} would, strictly speaking, be identical because it assumes a harmonic bath and the energies and free energy *differences* are the same for such a bath; the reaction field energies are also free energies of solvation.[6]

spectrally derived parameters to calculate the free energy of reaction, $\Delta G^{\circ\prime}$. Thus, E_{op} can be measured directly and λ obtained from the full width at half-height of the band, $\Delta\nu_{1/2}$, if the bandshape is assumed to be gaussian, eqn. (2).[3] Notice that

$$\lambda/\mathrm{cm}^{-1} = (\Delta\nu_{1/2})^2/2295 \text{ (at 298.2 K)} \qquad (2)$$

the determination of λ and $\Delta G^{\circ\prime}$ permits calculation of the activation free energy (and thus the rate constant, if the pre-exponential term can be calculated, see below) for the thermal electron transfer associated to the optical process, eqn. (3).

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{\circ\prime})^2}{4\lambda} = \frac{E_{op}{}^2}{4\lambda} \qquad (3)$$

However, the direct obtention of $\Delta G^{\circ\prime}$ from the band data (using eqn. (2) for estimating λ) is precluded from a practical point of view because of the phenomena of inhomogeneous broadening,[8–11] which causes an overestimation of the reorganization energy, λ.

In this paper a procedure to avoid the use of eqn. (2) is presented. It will be developed for the case of cobalt(III/II) complexes, which, as is well known, are chemically irreversible in such a way that redox potentials of these couples cannot be obtained by the conventional electrochemical method. It is worth pointing out that this case is especially difficult to handle because of the differences in the spin of cobalt(II) complexes produced in the optical and thermal electron transfer processes (see below).

It is worth pointing out that the results presented are related to those in a recently published paper of Lever and coworkers[12] on calculation of vertical ionization energies and electron affinities of ions in solution from MMCT bands. Indeed, from the procedure established in this paper, it would be possible, at first, to obtain ligand parameters relevant to the ligand influence on redox properties of complexes. From these parameters, redox potentials of new (electrochemically irreversible) couples could be obtained following Lever's method.[13,14]

Method and results (see Scheme 1)

In order to illustrate the procedure, the case of the $[Co(NH_3)_5(DMSO)]^{3+/2+}$ couple will be considered. It is not possible to determine the redox potential of this couple electrochemically because the cobalt(II) complex, resulting after an electron transfer to the cobalt(III) complex, suffers a rapid decomposition, eqn. (4). However, the stable species of

$$[Co(NH_3)_5(DMSO)]^{2+} \longrightarrow Co^{2+} + 5NH_3 + DMSO \qquad (4)$$

this couple, the cobalt(III) complex, forms with $Ru(CN)_6{}^{4-}$ an ion pair in which an MMCT band in water is observed; this band shows a maximum at 375.8 nm in water (ε_{max} = 179 dm^3 mol^{-1} cm^{-1}). Similarly, the $Ru(NH_3)_6{}^{3+}$ complex also forms an ion pair with $Ru(CN)_6{}^{4-}$, the MMCT band of which in water exhibits a maximum at 539 nm ($\varepsilon_{max} \approx$ 52 dm^3 mol^{-1} cm^{-1}).

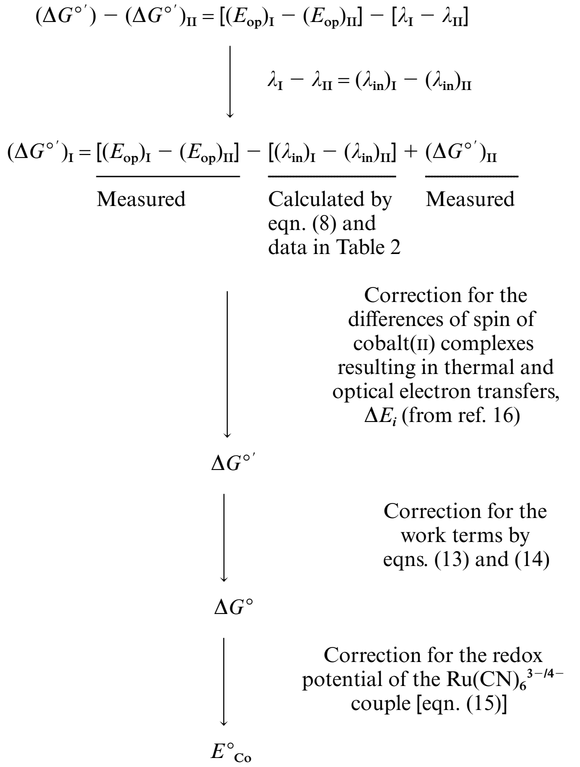
For these two optical electron transfer transitions, I and II, respectively, according to eqn. (1), we obtain eqn. (5) which

$$(\Delta G^{\circ\prime})_{I} - (\Delta G^{\circ\prime})_{II} = [(E_{op})_{I} - (E_{op})_{II}] - [\lambda_{I} - \lambda_{II}] \qquad (5)$$

permits calculation of $(\Delta G^{\circ\prime})_{I}$ if the other parameters are known. In the present case $(E_{op})_{I}$ is the energy of the maximum of the optical electron transfer band within the ion pair $[Co(NH_3)_5(DMSO)]^{3+}\cdot Ru(CN)_6{}^{4-}$, $(E_{op})_{I}$ = 303 kJ mol^{-1}, and $(E_{op})_{II}$ the corresponding one for the $Ru(NH_3)_6{}^{3+}\cdot Ru(CN)_6{}^{4-}$ ion pair, $(E_{op})_{II}$ = 207 kJ mol^{-1} (both after spin–orbit correction ‡,[15,16]) in water. Given that $[Co(NH_3)_5(DMSO)]^{3+}$ and $Ru(NH_3)_6{}^{3+}$ complexes have similar radii and that their distances of closest approach to the $Ru(CN)_6{}^{4-}$ ion are identical (≈8 Å assuming that the cobalt(III) complex approaches the Ru^{II} from the side of the ammonia ligands[16]), the same solvent reorganization free energy (λ_{out}) and work term [eqn. (14)] values are expected for both electron transfer processes. However, the values of the internal reorganization free energies (λ_{in}) are different for the electron transfer processes corresponding to the ion pairs $[Co(NH_3)_5(DMSO)]^{3+}\cdot Ru(CN)_6{}^{4-}$ and $Ru(NH_3)_6{}^{3+}\cdot Ru(CN)_6{}^{4-}$ and, consequently, the values of λ are also different. So, eqns. (6) and (7) follow. The value of $(\Delta G^{\circ\prime})_{II}$ can be obtained [see eqns. (13) and (14)] from redox potentials of $Ru(NH_3)_6{}^{3+/2+}$ and $Ru(CN)_6{}^{3-/4-}$ couples (E° $Ru(NH_3)_6{}^{3+/2+}$ = 0.098 and E° $Ru(CN)_6{}^{3-/4-}$ = 0.919 V in water at ionic strength 0.069 mol dm^{-3}) and the corresponding work terms, w_p and w_r (see below), for the ion pair $Ru(NH_3)_6{}^{3+}\cdot Ru(CN)_6{}^{4-}$ ($w_p - w_r$ = 7.85 kJ mol^{-1}

$$\lambda_{I} - \lambda_{II} = (\lambda_{in})_{I} - (\lambda_{in})_{II} \qquad (6)$$

$$(\Delta G^{\circ\prime})_{I} = [(E_{op})_{I} - (E_{op})_{II}] - [(\lambda_{in})_{I} - (\lambda_{in})_{II}] + (\Delta G^{\circ\prime})_{II} \qquad (7)$$



Scheme 1 Representation of the steps for determination of redox potentials from optical data.

---

‡ These values of E_{op} are corrected for the spin–orbit coupling of the $M^{III}(CN)_6{}^{3-}$ (M = Fe or Ru) in the excited state, $E_{op} = E_{op}{}^{exp} - \lambda_{so}$. The λ_{so} parameter represents the correction for the spin–orbit coupling: in the octahedral symmetry, the d^5 T state of the metal is split by spin–orbit coupling into a higher degenerate E state and a lower A state, the energy separation of these states being $\frac{3}{2}\lambda_{so}$, where λ_{so} is the spin–orbit coupling parameter (see ref. 15). Owing to the existence of two excited states, the experimental charge transfer band is the sum of two bands, corresponding to transitions from the ground state to the E and A states. These bands are at $\lambda_{so}/2$ (higher) and λ_{so} (lower) energies, respectively, than the maximum absorption observed in the composite band. The values of λ_{so} used were 15 and 5 kJ mol^{-1} for $Ru(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{3-}$ complexes, respectively (see refs. 15 and 16).

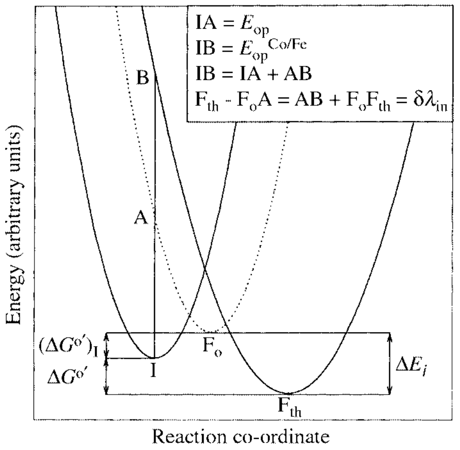


Fig. 2 Schematic representation of the parameters of thermal (——) and optical (····) electron transfer processes in the ion pairs $[Co(NH_3)_5(DMSO)]^{3+}\cdot Fe(CN)_6^{4-}$: I is the initial state at equilibrium for both optical and thermal electron transfers, F_o the final state at equilibrium for the optical transfer, $[Co(NH_3)_5(DMSO)]^{2+}$(low-spin)$\cdot Fe(CN)_6^{3-}$, and F_{th} that for the thermal electron transfer $[Co(NH_3)_5(DMSO)]^{2+}$(high-spin)$\cdot Fe(CN)_6^{3-}$. As indicated the energies of the vertical transitions corresponding to the optical and thermal electron transfer processes, E_{op} and $E_{op}^{Co/Fe}$, are given by the distances between IA and IB, respectively. The free energy changes for the optical and thermal electron transfer reactions are also given, $(\Delta G^{\circ\prime})_I$ and $\Delta G^{\circ\prime}$, respectively. Finally ΔE_i represents the difference between the free energies of thermally equilibrated high-spin and low-spin cobalt(II) complexes.

in water). On the other hand, the values of λ_{in} can be calculated. In this paper the classical eqn. (8a) for this parameter has been used,[1b,4] but more exact equations can be used if necessary.[7] In eqn. (8), f_i^r and f_i^p are the stretching (or breathing) force

$$\lambda_{in} = \frac{1}{2}\sum_i f_i(\Delta d_i)^2 \qquad (8a)$$

$$f_i = 2f_i^r f_i^p / f_i^r + f_i^p \qquad (8b)$$

constants for the *i*th metal–ligand bond in the reactant and product states, respectively, Δd_i is the change in the equilibrium value of the *i*th metal–ligand bond after electron transfer. The sum includes all the metal–ligand bonds. The values of f_i and Δd_i, necessary for this calculation, are given in Table 2. So, it is possible to obtain $(\Delta G^{\circ\prime})_I$ for the electron transfer in the ion pair $[Co(NH_3)_5(DMSO)]^{3+}\cdot Ru(CN)_6^{4-}$ in water.

In order to obtain the redox potential of interest for the cobalt couple it is necessary to correct $(\Delta G^{\circ\prime})_I$. This need arises since the cobalt(II) product of the thermal electron transfer is a high-spin species[16,17] whereas in the optical electron transfer a low spin cobalt(II) species appears. Therefore, the thermal and optical electron transfers correspond to different processes, (9) and (10). Fig. 2 represents both electron transfer processes.

Thermal

$$[Co(NH_3)_5(DMSO)]^{3+}\text{ (low spin)}\cdot Ru(CN)_6^{4-} \longrightarrow [Co(NH_3)_5(DMSO)]^{2+}\text{ (high spin)}\cdot Ru(CN)_6^{3-} \qquad (9)$$

Optical

$$[Co(NH_3)_5(DMSO)]^{3+}\text{ (low spin)}\cdot Ru(CN)_6^{4-} \longrightarrow [Co(NH_3)_5(DMSO)]^{2+}\text{ (low spin)}\cdot Ru(CN)_6^{3-} \qquad (10)$$

The free energy change, $\Delta G^{\circ\prime}$ for the thermal electron transfer was obtained by using eqn. (11) (see Fig. 2). Here, ΔE_i

$$\Delta G^{\circ\prime} = (\Delta G^{\circ\prime})_I + \Delta E_i \qquad (11)$$

represents the difference between free energies of thermally equilibrated high-spin and low-spin cobalt(II) complexes. A value of -79.5 kJ mol^{-1} was taken for this magnitude according to the data of Brunschwig *et al.*[16] The resulting value of $\Delta G^{\circ\prime}$ is given in Table 1.

On the other hand, $\Delta G^{\circ\prime}$ is not the variation of free energy in which we are interested in order to obtain the redox potential of the $Co^{3+/2+}$ couple, that is the free energy of reaction, ΔG°. This free energy corresponds to the process (12), while the

$$\text{Separate reactants}_{\text{ground state}} \xrightarrow{\Delta G^\circ} \text{Separate products}_{\text{ground state}} \qquad (12)$$

magnitude which appears in eqn. (11), $\Delta G^{\circ\prime}$, is the variation of free energy when the reactants and products are in contact (that is, when they form the precursor complex and the successor complex, respectively, in the terminology used in the context of Marcus' theory). However, both magnitudes are connected by eqn. (13). Here, w_r is the work corresponding to the

$$\Delta G^{\circ\prime} = \Delta G^\circ + w_p - w_r \qquad (13)$$

precursor complex formation from the separate reactants and w_p is the equivalent for the successor complex formation from separate products. These work terms can be calculated by using the Eigen–Fuoss treatment,[18] eqn. (14) where z_i and z_j are the

$$w = z_i z_j e^2 N_A / D_s r(1 + \kappa r) \qquad (14)$$

charges of the two reactants, considered with their signs, *r* is the distance of closest approach and κ is the inverse Debye length. For the ion pairs Co^{III}/Ru^{II} and Co^{II}/Ru^{III} the work term $(w_p - w_r)$ is equal to 7.85 kJ mol^{-1}.

Once the value of the free energy change, ΔG°, is obtained, it is a straightforward matter to calculate the redox potential of the acceptor couple, $[Co(NH_3)_5(DMSO)]^{3+}$ (low spin)–$[Co(NH_3)_5(DMSO)]^{2+}$ (high spin) using eqn. (15) because the

$$\Delta G^\circ = -nF[E^\circ(\text{Acceptor couple}) - E^\circ(\text{Donor couple})] \qquad (15)$$

redox potential of the donor couple, $Ru(CN)_6^{3-/4-}$, is known. The value of the redox potential thus obtained is given in Table 1.

By the same procedure the redox potentials of $[Co(NH_3)_5(py)]^{3+}$ (low spin)–$[Co(NH_3)_5(py)]^{2+}$ (high spin), $[Co(NH_3)_4(pzCO_2)]^{2+}$ (low spin)–$[Co(NH_3)_4(pzCO_2)]^{+}$ (high spin) ($pyCO_2$ = pyrazinecarboxylate) and $Co(NH_3)_6^{3+}$ (low spin)–$Co(NH_3)_6^{2+}$ (high spin) were also obtained by using the data in Tables 1 and 2. The values obtained also appear in Table 1.

Discussion

In order to check our procedure it is not possible to compare the values of E° of cobalt complexes in Table 1 with other experimental values of these potentials because the latter are not available. As a consequence this check must be done by an indirect procedure. In the present case this was the calculation of the free energy of activation, $\Delta G^\ddagger$, for electron transfer reactions where these compounds participate as oxidants. The data used correspond to thermal electron transfer reactions between these complexes and $Fe(CN)_6^{4-}$.[19–21] The values of electron transfer rate constant for these processes are shown in Table 3. From these data, of course, it is possible to obtain $\Delta G^\ddagger$ for these processes: in accordance with theories on electron transfer reactions, the rate constant for an electron transfer process can be formulated as[1b,22] in eqn. (16). Here κ_{el},

Table 1 Energy for the optical electron transfer processes (Co^{III}(low spin)·$M(CN)_6^{4-} \longrightarrow Co^{II}$(low spin)·$M(CN)_6^{3-}$), $(E_{op})_I$, free energies of the thermal electron transfer processes (Co^{III}(low spin)·$M(CN)_6^{4-} \longrightarrow Co^{II}$(high spin)·$M(CN)_6^{3-}$), $\Delta G^{\circ\prime}$ and formal standard redox potentials *versus* NHE for the couples Co^{III}(low spin)–Co^{II}(high spin), E°_{Co} at 298.2 K ($I = 0.069$ mol dm^{-3})

Ion pair	$(E_{op})_I{}^a$/kJ mol^{-1}	$\Delta G^{\circ\prime}$/kJ mol^{-1}	Couple	E°_{Co}/V
$[Co(NH_3)_5(DMSO)]^{3+}\cdot Ru(CN)_6^{4-}$	303^b	47.7	$[Co(NH_3)_5(DMSO)]^{3+/2+}$	0.50
$[Co(NH_3)_5(py)]^{3+}\cdot Fe(CN)_6^{4-}$	264^c	17.5	$[Co(NH_3)_5(py)]^{3+/2+}$	0.35
$[Co(NH_3)_4(pzCO_2)]^{2+}\cdot Ru(CN)_6^{4-}$	295^d	50.9	$[Co(NH_3)_4(pzCO_2)]^{2+/+}$	0.46
$Co(NH_3)_6^{3+}\cdot Ru(CN)_6^{4-}$	317^e	77.4	$Co(NH_3)_6^{3+/2+}$	0.19

[a] Corrected for the spin–orbit coupling as described in footnote ‡. [b] Ref. 20. [c] Ref. 25. [d] Ref. 19. [e] Ref. 23.

Table 2 Force constants for the reactant and product states and changes in the equilibrium values of the *i*th metal–ligand bond length after electron transfer for several metal–ligand bonds

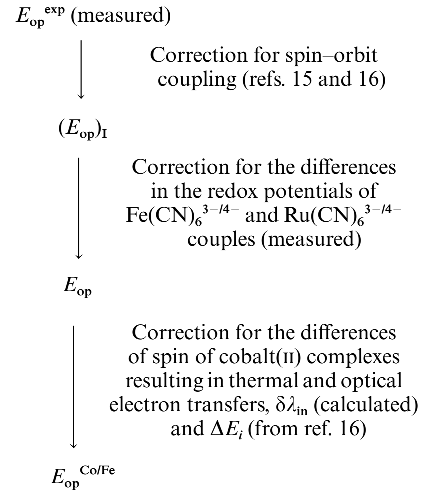
Bond	$10^{-5} f_k{}^a$/dyn cm^{-1}	$10^{-5} f_k{}^r$/dyn cm^{-1}	$10^{-5} f_k{}^p$/dyn cm^{-1}	Δd_k/Å
$Co^{III/II}$–NH_3	1.70^b	2.45^c	1.3^b	0.22^c
	1.86^d		1.5^d	0.12^c
$Co^{III/II}$–DMSO	7.6^b	11.6^e	5.7^{b,f}	0.17^g
	8.4^d		6.6^{d,h}	0.09^i
$Co^{III/II}$–py (pz)^j	1.9^b	2.89^e	1.41^{b,k}	0.27^i
	2.1^d		1.63^d	0.15^l
$Co^{III/II}$–OCO^m	1.96^b	2.54^g	1.60^{b,c,g}	0.17^g
	2.14^d		1.85^{d,h}	0.09^i
$Ru^{III/II}$–NH_3	2.2^c	—	—	0.04^c
$Ru^{II/III}$–CN	2.0^c	—	—	0.01^c
$Fe^{II/III}$–CN^c	2.0^c	—	—	0.01^c

[a] Calculated by using eqn. (8). [b] Corresponding to a high-spin cobalt(II) complex. [c] Ref. 16. [d] Corresponding to a low-spin cobalt(II) complex. [e] Estimated from the relation $\omega_{II} = 0.7\omega_{III}$ from ref. 26, where $\omega_{II/III}$ is the frequency of the metal–ligand corresponding to the complexes of Co^{II} and Co^{III}, respectively. [f] Ref. 26. [g] Ref. 27. [h] Calculated from the assumption that the relation of force constants for the bonds Co^{II} (low spin)–L and Co^{II} (high spin)–L is the same as that for the bonds Co^{II} (low spin)–NH_3 and Co^{II} (high spin)–NH_3 from ref. 16. [i] Estimated, $0.545\Delta d_k(Co^{II}$(high spin)) from ref. 13, which is satisfied for the bond Co–NH_3, also for the bond Co–L. [j] Force constants for the bond Co–pz have been considered the same as those for the bond Co–py. [k] Ref. 28. [l] Ref. 29. [m] Force constants and change in the equilibrium value of the bond Co–OCO after electron transfer have been considered the same as those for the bond Co–OH_2.

$$k_{et} = \kappa_{el} \nu_n \exp(-\Delta G^\ddagger/RT) \qquad (16)$$

ν_n and $\Delta G^\ddagger$ are the electronic transmission coefficient, the nuclear frequency factor and the free energy of activation, respectively. The value of $\Delta G^\ddagger$ has been obtained by using eqn. (16) with a preexponential factor $\kappa_{el}\nu_n = 6.2 \times 10^{12}$ s^{-1}. It corresponds to an adiabatic process ($\kappa_{el} = 1$)§ and a value of ν_n of the order corresponding to a vibrational frequency. As the vibrational modes have a frequency ranging from 10^{12} (solvent) to 10^{13} s^{-1} (internal), we have used 6.2×10^{12} s^{-1}, which is the average of these values and in fact corresponds also to the k_BT/h value of Transition State Theory at 298.2 K. The values of $\Delta G^\ddagger$ thus obtained appear as $\Delta G^\ddagger_{exp}$ in Table 3.

On the other hand it is possible to estimate directly these free energies of activation from optical ($E_{op}{}^{Co/Fe}$) and thermodynamic ($\Delta G^{\circ\prime}{}_{Co/Fe}$) data using eqn. (3). The values of these parameters were estimated in the following way: $\Delta G^{\circ\prime}{}_{Co/Fe}$ from the estimated value of the redox potential for the cobalt couple and the measured redox potential of the $Fe(CN)_6^{3-/4-}$ couple, and correction of work terms [eqn. (13)]. On the other hand, $E_{op}{}^{Co/Fe}$ were obtained from the corresponding experimental values for the Co/Ru ion pairs and the following corrections (see Scheme 2).



Scheme 2 Correction of $E_{op}{}^{exp}$ to obtain $E_{op}{}^{Co/Fe}$ for the electron transfer processes.

$$E_{op} = (E_{op})_I + F[E^\circ(Fe(CN)_6^{3-/4-}) - E^\circ(Ru(CN)_6^{3-/4-})] \qquad (17)$$

(a) The difference in redox potential of $Fe(CN)_6^{3-/4-}$ and $Ru(CN)_6^{3-/4-}$ couples in order to obtain the maximum energy of the MMCT band corresponding to the ion pair $[Co(NH_3)_5(DMSO)]^{3+}\cdot Fe(CN)_6^{4-}$, eqn. (17). (b) The difference between free energies of thermally equilibrated high-spin and low-spin cobalt(II) complexes, ΔE_i, and the inner-shell reorganization free energy difference between the thermal and optical processes, owing to the differences in the spin of Co^{II}, $\delta\lambda_{in}$ (see Fig. 2 and eqn. (11)); eqn. (18).

$$E_{op}{}^{Co/Fe} = E_{op} + \Delta E_i + \delta\lambda_{in} \qquad (18)$$

A value of −79.5 kJ mol^{-1} was taken for ΔE_i according to the data of Brunschwig *et al.*[16] and a value of 127.8 kJ mol^{-1} was calculated for $\delta\lambda_{in}$ using the force

---

§ The adiabatic character of the reaction follows from the values of the molar absorption coefficients at the band maxima, ε_{max}, and the equations H_{ab}/cm^{-1} = $^1/r \times 2.05 \times 10^{-2}(\varepsilon_{max}\nu_{max}\nu_{1/2})^{1/2}$ and $4.6 \times 10^{-3} H_{ab}{}^2 (\nu_{max})^{-1/2} > 1$, where H_{ab} is the coupling energy, r the distance separating the redox sites in Å, ν_{max} and $\Delta\nu_{1/2}$ are the energy at band maximum and the full width at half-height of the band, respectively.

Table 3 Electron transfer rate constants, k_{et}, values of $E_{op}{}^{Co/Fe}$ and $\Delta G^{\circ\prime}$, and calculated and experimental free energies of activation, $\Delta G^{\ddagger}{}_{calc}$ and $\Delta G^{\ddagger}{}_{exp}$, for the thermal electron transfer process within $Co^{III}/Fe(CN)_6{}^{4-}$ in water at 298.2 K

$10^2\ k_{et}{}^{a}/s^{-1}$	$E_{op}{}^{Co/Fe\ b}$/kJ mol^{-1}	$\Delta G^{\circ\prime\ c}$/kJ mol^{-1}	$\Delta G^{\ddagger}{}_{calc}{}^{d}$/kJ mol^{-1}	$\Delta G^{\ddagger}{}_{exp}{}^{e}$/ kJ mol^{-1}
		$[Co(NH_3)_5(DMSO)]^{3+}\cdot Fe(CN)_6{}^{4-}$		
24.8	306.0	2.4	77.1	76.5
		$[Co(NH_3)_5(py)]^{3+}\cdot Fe(CN)_6{}^{4-}$		
1.5	321.2	18.2	85.1	83.4
		$[Co(NH_3)_4(pzCO_2)]^{2+}\cdot Fe(CN)_6{}^{4-}$		
7.0	310.3	7.3	79.5	79.6

[a] Refs. 19–21. [b] Obtained by using the procedure described in Scheme 2. [c] Obtained from the redox potentials of Table 1 corrected for the ionic strength effects (from 0.069 mol dm^{-3} to the ionic strength used in the kinetic measurements) and the redox potentials of the $Fe(CN)_6{}^{3-/4-}$ couple (ref. 20) by using eqn. (13). [d] Determined by eqn. (3). [e] Obtained by eqn. (16).

constants and bond lengths from Table 2. Notice that eqn. (18) follows from Fig. 2 using simple geometrical considerations.

The values of $E_{op}{}^{Co/Fe}$ and $\Delta G^{\circ\prime}{}_{Co/Fe}$ calculated in this way as well as those of the activation free energy, $\Delta G^{\ddagger}{}_{calc}$, are given in Table 3. As can be seen there is a good agreement between $\Delta G^{\ddagger}{}_{calc}$ and $\Delta G^{\ddagger}{}_{exp}$, which supports our results on redox potentials. Notice that although a difference of about 2 kJ mol^{-1} in $\Delta G^{\ddagger}$ would imply a difference in k_{et} of a factor close to e, this difference implies only a difference of about 0.02 V in redox potentials.

The reliability of the method receives further support from the plot of ln k_{et} for the above mentioned processes *versus* $\Delta G^{\circ\prime}$ (Table 3).¶ As is well known, for cases in which $\Delta G^{\circ\prime 2} \ll \lambda$ (as happens in the examples considered here) this plot must be a straight line having a slope of -0.20 kJ^{-1} mol. In fact a good linear plot is found ($r = 0.988$) which has a slope of -0.17 ± 0.02 kJ^{-1} mol, close to the theoretical value, and an intercept $(\ln(\kappa_{el}\nu_n) - (\lambda/4RT))$ of -1.16. As $\lambda \approx 303$ kJ mol^{-1} ($E_{op}{}^{Co/Fe} - \Delta G^{\circ\prime}$, Table 3), this intercept corresponds to a pre-exponential term of 6.05×10^{12} s^{-1}. Notice that this value confirms our hypothesis (used in the calculation of $\Delta G^{\ddagger}{}_{exp}$) that the reactions are adiabatic.

In order to check our approach further we have obtained the redox potential for the couple $Co(NH_3)_6{}^{3+/2+}$ using the data for the MMCT band within the ion pair $Co(NH_3)_6{}^{3+}\cdot Ru(CN)_6{}^{4-}$.[23] By the previous procedure a value of $E^{\circ} = 0.19$ V is obtained in a reasonable agreement with the published value for this redox potential E° $Co(NH_3)_6{}^{3+/2+} = 0.11$ V.[24] Notice that, according to this result, the error in our procedure is of the same order as those of Savéant's method.[2a]

In conclusion, the possibility of using an optical method to determine redox potentials of chemically or electrochemically irreversible systems has been shown. The procedure to obtain redox potentials is of interest because, as was indicated in the Introduction, these data are necessary in relation to both theoretical (interpretation of results) and applied synthetic purposes.

Acknowledgements

This work was financed by the Dirección General de Investigación Científica y Técnica (PB-95-0535) and the Consejería de Educación y Ciencia de la Junta de Andalucía.

References

1 R. A. Marcus and N. Sutin (*a*) *Comments Inorg. Chem.*, 1986, **5**, 119; (*b*) *Biochim. Biophys. Acta*, 1985, **811**, 265.
2 (*a*) C. P. Andrieux, J.-M. Savéant and C. Tardy, *J. Am. Chem. Soc.*, 1998, **120**, 4167; (*b*) S. Antonello, M. Masumeci, D. D. M. Wayner and F. Maran, *J. Am. Chem. Soc.*, 1997, **119**, 9541; (*c*) S. Antonello and F. Maran, *J. Am. Chem. Soc.*, 1998, **120**, 5713.
3 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391.
4 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155 and refs. therein.
5 Y. Doong and J. T. Hupp, *Inorg. Chem.*, 1992, **31**, 332.
6 J. S. Bader, C. M. Cortis and B. J. Berne, *J. Phys. Chem.*, 1997, **106**, 2372.
7 P. Chen and T. J. Meyer, *Chem. Rev.*, 1998, **98**, 1439.
8 D. W. Oxtoby, *Adv. Chem. Phys.*, 1979, **40**, 1.
9 J. Jonas, *Acc. Chem. Res.*, 1984, **17**, 74.
10 R. F. Loring and S. Mukamel, *J. Chem. Phys.*, 1985, **83**, 2116.
11 R. D. Cannon, *Adv. Inorg. Chem. Radiochem.*, 1988, **21**, 179.
12 S. I. Gorelsky, V. Yn. Kotov and A. B. P. Lever, *Inorg. Chem.*, 1998, **37**, 4584.
13 A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 1271.
14 E. S. Dodsworth and A. B. P. Lever, *Chem. Phys. Lett.*, 1985, **119**, 61.
15 J. C. Curtis and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 1562.
16 B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.*, 1986, **90**, 3657.
17 M. D. Newton, *J. Phys. Chem.*, 1991, **95**, 30; *Inorganic Reactions and Methods*, ed. J. J. Zuckerman, VCH, London, 1985, vol. 15, p. 51.
18 C. M. Fuoss, *J. Am. Chem. Soc.*, 1958, **80**, 5059; M. Z. Eigen, *Phys. Chem.* (*Wiesbaden*), 1954, **1**, 176.
19 P. Pérez-Tejeda, J. Benko, M. López, M. Galán, P. López, M. Domínguez, M. L. Moyá and F. Sánchez, *J. Chem. Soc.*, *Faraday Trans.*, 1996, **92**, 1155.
20 M. López-López, P. Pérez-Tejeda, P. López-Cornejo and F. Sánchez, *Chem. Phys.*, in the press.
21 A. J. Miralles, R. E. Armstrong and A. Haim, *J. Am. Chem. Soc.*, 1977, **99**, 1416.
22 V. G. Levich, *Adv. Electrochem. Eng.*, 1966, **4**, 249; R. R. Dogonadze, *Reaction of Molecules at Electrodes*, ed. N. S. Hush, Wiley-Interscience, New York, 1971, ch. 3, p. 135.
23 A. Haim, *Comments Inorg. Chem.*, 1985, **4**, 113.
24 A. Vogler, A. H. Osman and H. Kunkely, *Coord. Chem. Rev.*, 1985, **64**, 159.
25 A. J. Miralles, A. P. Szecsy and A. Haim, *Inorg. Chem.*, 1982, **21**, 697.
26 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 3rd edn., 1978, p. 345.
27 Z. Zhou and S. U. M. Khan, *J. Phys. Chem.*, 1989, **93**, 5292.
28 R. Robin, J. H. Clark and C. S. Williams, *Inorg. Chem.*, 1965, **4**, 350.
29 P. Thuéry, J. Zarembowitch, A. Michalowicz and O. Kahn, *Inorg. Chem.*, 1987, **26**, 851; J. M. Malin, D. A. Ryan and T. V. O'Halloran, *J. Am. Chem. Soc.*, 1978, **100**, 297.

Paper 9/04616J

¶ The linear dependence of ln k_{et} *versus* $\Delta G^{\circ\prime}$ corresponds to the equation $\ln k_{et} = \ln(\kappa_{el}\nu_n) - (\Delta G^{\circ\prime}/2RT) - \lambda/4RT$.