Homogeneous *versus* heterogeneous electron-transfer processes in solution: a 'fifty percent rule' for volumes of activation

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Ac voltammetry at pressures up to 200 MPa shows that volumes of activation for heterogeneous electron transfer in three aqueous couples {$[Fe(CN)_6]^{3-/4-}$, $[Co(sep)]^{3+/2+}$ and $[Co(en)_3]^{3+/2+}$} are numerically about 50% of those for homogeneous (bimolecular) electron transfer in these same couples, with the same algebraic sign, as predicted by an extension of Marcus theory.

Marcus[1] has proposed that the free energy ΔG_{el}^* of activation for electron transfer in a couple $ML_n^{(z+1)+/z+}$ at an electrode should be approximately one-half that (ΔG_{ex}^*) for homogeneous (bimolecular) electron transfer in the same couple in solution,† if an adiabatic outer-sphere mechanism is operative [eqn. (1)]

$$\Delta G_{el}^* \approx \tfrac{1}{2}\Delta G_{ex}^* \qquad (1)$$

Since free energies of activation ΔG_i^* are measurable (indeed, have meaning) only in terms of the corresponding rate constants k_i [eqn. (2)],

$$k_i = Z_i \exp(-\Delta G_i^*/RT) \qquad (2)$$

the expectation† is that

$$k_{el}/Z_{el} \approx (k_{ex}/Z_{ex})^{\frac{1}{2}} \qquad (3)$$

Unfortunately, the pre-exponential factors Z_{el} and Z_{ex} are not clearly definable,‡ and indeed have different dimensions (traditionally, cm s^{-1} and $dm^3\ mol^{-1}\ s^{-1}$, respectively), so that eqns. (1) and (3) are difficult to test experimentally.[2] If, however, Z_{el} and Z_{ex} are assumed to be independent of (or vary in the same way with) pressure P to within experimental uncertainty, then Marcus' prediction may be tested through the experimental *volumes* of activation $\Delta V_i^\ddagger$ [$= -RT(\partial \ln k_i/\partial P)_T$], since eqn. (3) then implies that:

$$\Delta V_{el}^\ddagger \approx \tfrac{1}{2}\Delta V_{ex}^\ddagger \qquad (4)$$

with consistency of dimensions. For homogeneous electron-transfer reactions,[3] the pressure dependence of Z_{ex} is small, contributing only *ca.* +1 $cm^3\ mol^{-1}$ to $\Delta V_{ex}^\ddagger$, and it may be confidently expected that the pressure effect on Z_{el} will be no greater than this.

We report here successful tests of eqn. (4) for three aqueous outer-sphere self-exchange couples for which $\Delta V_{ex}^\ddagger$ is respectively strongly positive {$[Fe(CN)_6]^{3-/4-}$},[4] strongly negative {$[Co(en)_3]^{3+/2+}$},[5] and mildly negative {$[Co(sep)]^{3+/2+}$}.[6]§ In principle, it is possible to obtain $\Delta V_{el}^\ddagger$ values from the pressure dependences of peak–peak separations (δE_p) in dc cyclic voltammograms (CV) for quasi-reversible redox couples.[7] In practice, however, δE_p is too poorly reproducible and shows too small a pressure dependence, particularly for couples close to reversibility.[4,8] We have therefore used ac voltammetry (ACV) to measure k_{el} as a function of pressure to 200 MPa—this appears to be the first high-pressure application of ACV. The high-pressure electrochemical cell described previously[8] was reconstructed with a Pt wire working electrode and a longer counter electrode of Au wire (both 0.5 mm diameter, and cleaned with H_2SO_4–H_2SO_5 followed by sonication in water), and a reference electrode (AgCl-coated Ag wire in 4 mol dm^{-3} KCl) in a tube with electrical connection to the test solution through a Vycor frit mounted in a free piston.[9] Solutions were deoxygenated with N_2 before the cell was closed. The system was left for 45 min after each change of pressure to reequilibrate to the thermostated jacket temperature (25.0 ± 0.05 °C).

At each pressure, the working electrode was thoroughly cleaned by potential cycling at least three times to the H_2 evolution point. This is the key to successful ACV measurements at high pressure, as it removes trace contaminants and provides a reproducible electrode surface after each pressurization. A normal CV was also recorded at 50 mV s^{-1} to obtain the half-wave potential $E_{\frac{1}{2}}$, and the uncompensated resistance R_u was determined at 8 kHz and a potential at least 300 mV more positive than $E_{\frac{1}{2}}$.[10] ACVs were then collected at three frequencies f with a 7 mV ac voltage amplitude superimposed onto a dc voltage ramp swept at 5 mV s^{-1}, using EG&G PARC

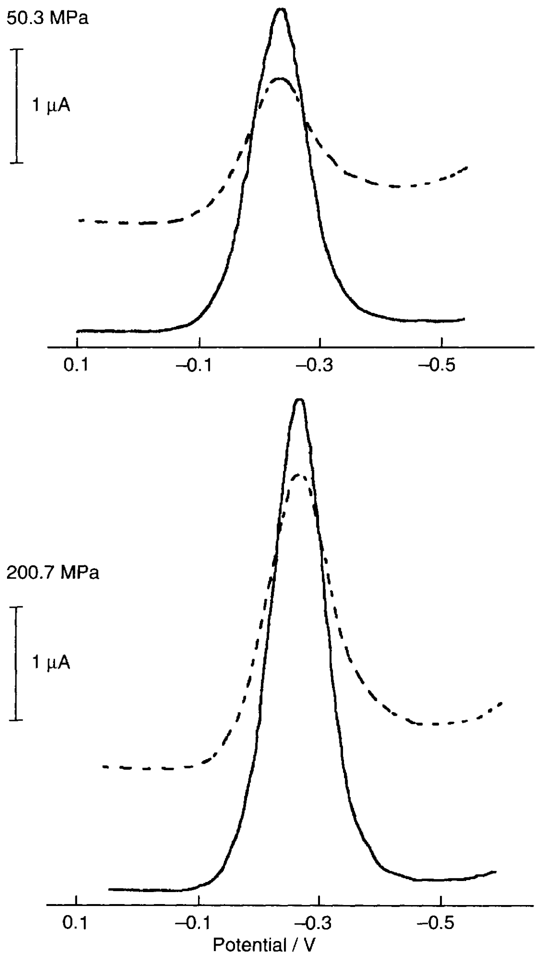

Fig. 1 Ac voltammograms at f = 100 Hz for $[Co(en)_3]Cl_3$ (2.0 mmol dm^{-3}) with excess en (0.2 mol dm^{-3}) in aqueous KCl (0.5 mol dm^{-3}) on a Pt electrode relative to AgCl/Ag in 4.0 mol dm^{-3} KCl, at two pressures and 25.0 °C. Solid curves: in-phase current. Broken lines: 90° out-of-phase current.

equipment (Model 173 Potentiostat, Model 124A Lock-in-Amplifer with a built-in Model 117 Differential Preamplifier, Model 174 Universal Programmer, and Model RE0074 X–Y Recorder). The maximum in-phase and 90° out-of-phase faradaic currents were obtained from the total peak currents after correction for R_u and the double-layer capacitance, and the phase angle ϕ was used to obtain k_{el} from the standard eqn. (5):[10,11]

$$[\cot \phi]_{max} = 1 + (2D_O{}^{\beta}D_R{}^{\alpha}\omega)^{\frac{1}{2}}/(\alpha^{-\alpha}\beta^{-\beta}k_{el}) \qquad (5)$$

Here, $\omega = 2\pi f$, D_O and D_R are the diffusion coefficients for the oxidized and reduced species (from CV measurements, assuming $D_O = D_R$), and α and β ($= 1 - \alpha$) are the transfer coefficients for the reduction and oxidation processes, respectively. It was found, from the ACV peak potential E_{dc}, that $\alpha = \beta = 0.50 \pm 0.02$ for $[Fe(CN)_6]^{3-/4-}$ and $[Co(sep)]^{3+/2+}$

$$E_{dc} = E_{\frac{1}{2}} + (RT/nF) \ln (\alpha/\beta) \qquad (6)$$

while $\alpha = 0.44 \pm 0.02$ for $[Co(en)_3]^{3+/2+}$. Typical ACV results are shown in Fig. 1, in which a pressure-induced increase in the out-of-phase current relative to the in-phase current, and hence also in k_{el}, is obvious and readily quantifiable. Plots of ln k_{el} *vs.* p were linear within the experimental uncertainty, and so the $\Delta V_{el}^{\ddagger}$ values given in Table 1 are effectively independent of pressure over the range 0.1–200 MPa.

Comparison of $\Delta V_{el}^{\ddagger}$ values with $\Delta V_{ex}^{\ddagger}$ data previously obtained[4–6] (Table 1) leads to the following conclusions. (*a*) Eqn. (4) is valid, within the experimental uncertainty, regardless of the sign and magnitude of $\Delta V_{ex}^{\ddagger}$; in short, $\Delta V_{el}^{\ddagger}$ is about 50% of $\Delta V_{ex}^{\ddagger}$. (*b*) By extension of (*a*), the Marcus relationship between k_{el} and k_{ex} [eqn. (3)] is verified.[†] (*c*) Although the experimental $|\Delta V_{ex}^{\ddagger}|$ values for $[Fe(CN)_6]^{3-/4-}$ (with K^+ counter ion) and $[Co(en)_3]^{3+/2+}$ couples are anomalously large in terms of an extension of the Marcus–Hush theory of k_{ex},[3] eqn. (4) is clearly applicable to experimental $\Delta V_{ex}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$ values of outer-sphere electron transfer processes regardless of theoretical anomalies. (*d*) Measurements of $\Delta V_{el}^{\ddagger}$ can provide estimates of $\Delta V_{ex}^{\ddagger}$ with acceptable accuracy when $\Delta V_{ex}^{\ddagger}$ is not directly measurable—*e.g.* for fast exchanges in which paramagnetism of both partners precludes NMR measurements of k_{ex}.

Table 1 Rate constants and volumes of activation for electron transfer at a Pt electrode at 25.0 °C

Couple	[KCl]/ mol dm^{-3}	k_{el} (0.1 MPa)/ cm s^{-1}	$\Delta V_{el}^{\ddagger}$/ cm^3 mol^{-1}	$\Delta V_{ex}^{\ddagger}$/ cm^3 mol^{-1}
$[Fe(CN)_6]^{3-/4-}$	0.5	0.068	11.6 ± 1.8	21.8 ± 1.7
	0.2	0.043[a]	9.6 ± 2.0	
$[Co(sep)]^{3+/2+}$	0.5	0.099	−2.7 ± 1.3	−6.4 ± 0.2
$[Co(en)_3]^{3+/2+}$	0.5[b]	0.033	−8.6 ± 0.1	−15.5 ± 1.0[b,c]

[a] *cf.* [K^+] dependence of k_{el} and k_{ex} noted in refs. 4 and 12. [b] Excess en present to suppress dissociation of $[Co(en)_3]^{2+}$. [c] Mean value, 0.1–200 MPa at 65 °C in 0.5 mol dm^{-3} $NaClO_4$.

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Footnotes

[†] It is assumed there that the $M^{(z+1)+}$–M^{z+} separation in the homogeneous electron transfers is twice the average distance from the M centres to the electrode surface in the corresponding electrode reaction. If, for example, a layer of adsorbed solvent on the electrode intervenes, then $k_{el}/Z_{el} < (k_{ex}/Z_{ex})^{\frac{1}{2}}$ (ref. 1), but the success of eqn. (4) vindicates the assumption and implies that this is not the case.

[‡] Marcus' $\Delta G_{ex}{}^{*}$ is not necessarily identical with $\Delta G_{ex}^{\ddagger}$, the Eyring free energy of activation obtained by replacing Z_{ex} with $k_bT\kappa/h$, where κ is the transmission coefficient.

[§] en = 1,2-diaminoethane; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

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