Perturbation Calculation from the Charge-Transfer Spectrum Data of Intervalence Site-Transfer D.C. Conductivity in Prussian Blue

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Summary Observed parameters from the charge-transfer spectrum of a thin film of Prussian Blue are employed in the Hush perturbation treatment yielding, from the tunnelling matrix and activation energy of thermal electron-transfer, an electron-transfer frequency which is equated with the so-called hopping frequency in conductivity, to obtain a calculated conductivity of $0\,43 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$, *cf* an observed conductivity, for the sample, of $1\,7 \times 10^{-7}$

THE parameters of charge-transfer (CT) spectra, *viz* the maximum molar absorptivity, ϵ_{max} at wavenumber $\bar{\nu}_{max}$ and the bandwidth at half the maximum absorptivity $\nu_{0\,5}$, can be directly related to the corresponding rate, k', for the thermal[1] electron-transfer using a theory based on Hush's perturbation treatment[2] for the high temperature limit of a harmonic oscillator system with weak electronic coupling between the transfer sites [3–7] Adopting Meyer's formulation[6] (see Allen[3] for detail), we obtain an expression for k' [equation (1)] where λ is a measure of the bond length

$$k' = (2\pi T_{da}^2/h)\,(\pi/kT\lambda)^{0\,5} \exp\{-(h\nu_{max})^2/4\lambda kT\} \qquad (1)$$

reorganisation energy,[2,3,4] T_{da} is the tunnelling matrix given by $(4\,24 \times 10^{-4}\epsilon_{max}\bar{\nu}_{0\,5}/\bar{\nu}_{max})^{0\,5}(h\nu_{max}/d)(gc)^{-1}$, d

being the distance between the transfer centres (Å, for this form of expression), and g and c the orbital occupancy and the donor co-ordination number, respectively.[8] Eminently reasonable rates were calculated from the spectra of dinuclear Ru complexes, but no experimental values were available for direct checks.[6] We now suggest that the phenomenological hopping-rate expression for intervalence electron-conductivity, σ, in solids[9] can provide the experimental thermal-transfer rates [equation (2)] where n is

$$\sigma = ne^2d^2\nu_t/kT \quad (2)$$

the number density of charge carriers. (This follows from the phenomenological expression for the diffusion coefficient of hopping species, the Stokes-Einstein expression for mobility, and the σ/mobility relation.[10]) The term ν_t in equation (2) is usually expressed as a function of a lattice frequency,[9,10] but it is the actual hopping frequency and thus is here directly identified with the transfer rate. Thus, ν_t, calculated from the observed conductivity, replaces the experimental k', for comparison with the rate calculated from spectroscopy. Alternatively, we may obtain ν_t from equation (1) and derive σ_{calc} from equation (2) to compare with σ_{obs}.

Prussian Blue (PB) is suitable material for study, but, while both spectra[10,11] and σ_{obs}[10,12] values are available, they do not refer to the same sample. To avoid problems arising from possible differences in composition, we have measured both optical and electrical properties on samples of PB deposited as a thin film on semi-transparent platinum on a microscope slide, thickness $1{\cdot}86 \times 10^{-6}$ cm.

Similar PB films have been prepared previously,[13] from aqueous $Fe^{III}Fe^{III}(CN)_6$ reduced by (presumably) the hydrogen dissolved in the Pt by extensive cathodisation. In order to determine the film thickness from the amount deposited we effected the reduction electrolytically *vs.* standard calomel electrode (S.C.E.) on non-cathodised Pt, with coulometric monitoring. The spectrum of the washed and dried PB film was recorded on a Beckman Acta MIV in the near i.r. With the film horizontal, a mercury drop on the scanned region of PB served as a second contact for conductimetry, which was ohmic over 4 V. All the information for σ_{calc} and σ_{obs} so obtained are given, together with the results, in the Table. The agreement is good and matches

TABLE. Experimental data for Prussian Blue allowing the calculation of conductivity, σ, from the charge-transfer spectrum

	This work	Lit.
$10^{-3}\bar{\nu}_{max}$/cm^{-1}	14·5 ± 0·2	14·1[a]
$10^{-3}\bar{\nu}_{0\cdot5}$/cm^{-1}	5·0	6·0
$10^{-4}\epsilon_{max}$/dm^3 mol^{-1} cm^{-1}	1·55 ± 0·1	0·98
Density/g cm^{-3} [b]	1·81	1·81
d/Å[b]	5·09	5·09
10^2T_{da}/eV	2·55 ± 0·02	1·15
E_{th}/eV[c]	0·58 ± 0·02[d]	0·50[d]
10^{-4} ν_t/s^{-1}	0·31 ± 0·15	5
$10^7\sigma_{calc}/\Omega^{-1}$ cm^{-1}	0·43 ± 0·24	7
$10^7\sigma_{obs}/\Omega^{-1}$ cm^{-1}	1·7 ± 0·02	*ca.* [1e]

[a] Ref. 11. [b] H. J. Baser, A. Ludi, W. Petter, and D. Schwarzenbach, *J. Chem. Soc., Chem. Commun.*, 1972, 1299. [c] Activation energy calculated for the exponential of equation (1). [d] Correspond to overall transfer energies E_0 [*cf.* Hush (ref. 2)] of 0·41 and *ca.* 0 eV, respectively. [e] Ref. 12

that claimed for the perhaps less directly derived electron-transfer reaction rate of the Ru species.[6] The literature data (Table) are similar and minor divergences in detail from our observations may be attributed to small differences of physical state and, possibly, composition. The apparently novel application of equation (2) has been supported by dielectric relaxation measurements in these laboratories.

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