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Outer-sphere Electron Transfer in the Systems Tris(Naphthoquinoneoximato) Iron(III)/Oximes or Metal Dithizonates

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Mixing the solutions of tris(naphthoquinoneoximato) iron(III) with the solutions of various oximes in different solvents produces colour changes attributable to outer-sphere transitions from the oximes to the iron(III) naphthoquinoneoximate complex. The interaction of tris(naphthoquinoneoximato) iron(III) is also observed with the complexes of dithizonate, where a charge transfer (CT) band is recorded upon mixing solutions of the iron complex and $Ni(HDz)_2$, $Cu(HDz)_2$, and $Zn(HDz)_2$. A detailed analysis of the outer-sphere absorption bands leads to some important conclusions. The Hush theory is adopted to deduce optical and thermodynamic parameters.

INTRODUCTION

The properties of mixed-valence complexes[1] have been used as a probe of the donor-acceptor interactions that are of interest in the electron-transfer field[1, 2]. An example of such mixed-valence complexes, for which low energy absorption bands are recorded, which are correlated with intervalence (IT) transitions, is illustrated in the following equation[3]:

$$[(bpy)_2ClRu^{II}(pyr)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow{Ea} [(bpy)_2ClRu^{III}(pyr)Ru^{II}Cl(bpy)_2]^{3+}$$

(bpy = 2,2-bipyridine; pyr = pyrazine).

In systems of moderate donor-acceptor electronic coupling, the position and intensities of donor-acceptor (or intervalence) charge transfer bands yield information about the energetic barriers to electron transfer and the magnitude of the donor-acceptor coupling element, respectively[4].

One issue of importance to evolve from the work on mixed valence ions is the possibility of extensions of the basic ideas and formalisms in a more general way to charge transfer processes in chemical systems. Such a transition can be observed in outer-sphere systems, *e.g.* ion pairs, which allow the ideas developed for mixed-valence dimers to be extended to charge transfer in outer-sphere cases[5–7]. In this article we are embarked on studying some intermolecular outer-sphere electron transfer in systems containing tris (naphthoquinoneoximato) iron(III) and oximes.

RESULTS AND DISCUSSION

Upon mixing an ethanolic solution of tris(naphthoquinoneoximato)-iron(III), Fe(nqo)$_3$ with an ethanolic solution of acetoxime a green coloration develops, which is caused by the new band appearing at 737 nm. The same colour development was observed in other solvents, namely acetone, dimethylformamide, and dimethyl sulphoxide, with new bands located at 677, 726 and 711 nm, respectively, which clearly indicates the dependence of this band on the solvent used. The spectrum of this system in dimethyl sulphoxide is depicted in Fig. 1. The new band, which has no counterpart in the spectra of the individual components, is apparently a charge transfer band originating from an electronic transfer from a highest occupied orbital in the oxime to a lowest unoccupied orbital at the iron(III) ion. This suggestion comes from observations on similar systems[8].

The yellow brownish colour produced when the two solutions of Fe(nqo)$_3$ and benzoinoxime in dimethyl sulphoxide are mixed together is manifested by the

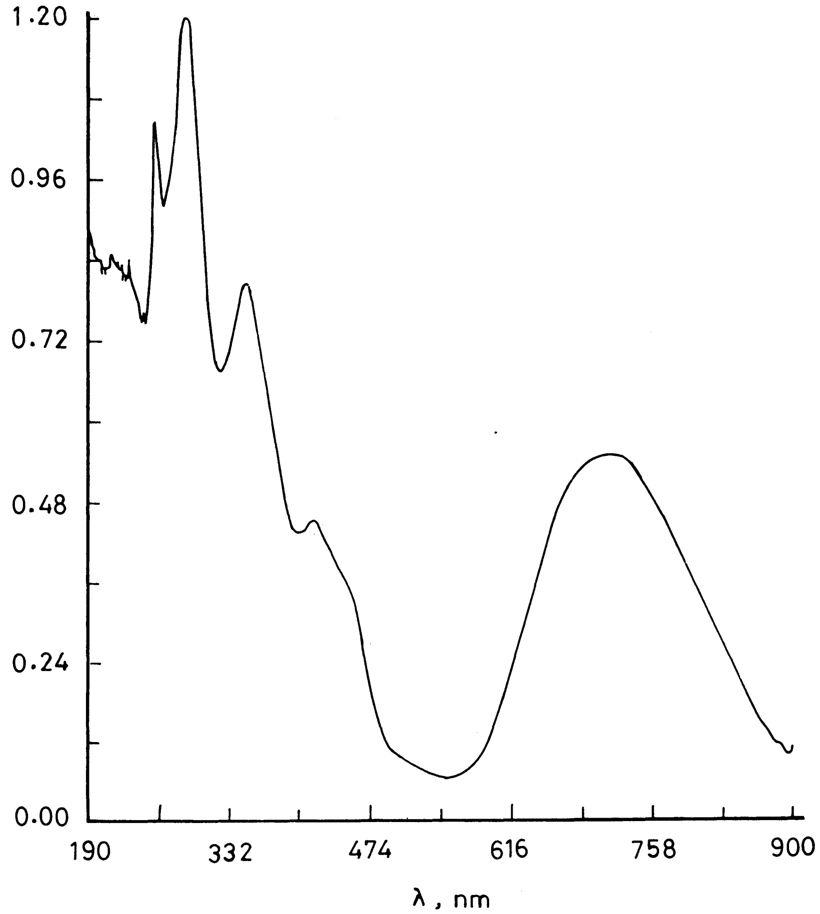

Fig. 1 The spectrum of the system Fe(nqo)$_3$/acetoxime in dimethylsulphoxide

appearance of a new band at 672 nm. The position of the outer-sphere optical charge transfer band resulted from the interaction of the iron complex and cyclohexanone-oxime is again (as in the acetoxime system) affected by changing the solvent. The CT band occurs at 672, 707, 719 and 749 nm in acetone, acetonitrile, ethanol, and tetrahydrofuran, respectively. Further, the systems $Fe(nqo)_3$/diacetylmonoxime, $Fe(nqo)_3$/furaldoxime and $Fe(nqo)_3$/salicylaldoxime in dimethyl sulphoxide exhibit their CT bands at 711, 710, and 710 nm respectively.

It is of interest to note that the previous interaction is also possible between $Fe(nqo)_3$ and coordinated ligands. Upon mixing solutions of $Ni(HDz)_2$, $Cu(HDz)_2$ and $Zn(HDz)_2$ (where HDz = dithizonate anion) in dimethyl sulphoxide with dimethyl sulphoxide solutions of $Fe(nqo)_3$, a green coloration is developed with a new absorption at 706, 715, and 709 nm respectively. It is suggested that this new band is attributed to an outer-sphere ligand to metal charge transfer from the coordinated dithizonate to the trivalent iron of $Fe(nqo)_3$.

Analysis of the CT bands

The recorded optical outer-sphere charge transfer bands are in the range 672–749 nm. The bandwidth at half-maximum calculated from the whole band are in the 2685–4171 cm^{-1} range. The relation between optical and thermal electron transfer is suggested by Hush theory[4]. According to this theory the energy of the optical transition at the absorption maximum, E_{op}, is related to the internal energy difference between two thermally equilibrated redox isomeric states, ΔE, and the reorganizational energy χ by the following equation:

$$E_{op} = \chi + \Delta E$$

The halfwidth of the CT band ($\Delta v_{1/2}$) and the activation energy, E_a, for thermal electron transfer are given by the following relations:

$$\chi = 3.606(\Delta v^{1/2})$$

$$E_a = E_{op}/4\chi$$

χ can be expressed as the sum of a term arising from localised (metal-ligand) vibrational modes, χ_{inner}, and a term arising from lattice vibrational modes of the solvent system, χ_{outer}.

$$E_{op} - \Delta E = \chi_{inner} + \chi_{outer}$$

Table 1 includes the values of E_{op}, ΔE, E_a, χ and $\Delta v^{1/2}$ of some systems in dimethyl sulphoxide.

In all the studied systems one can observe that the E_a (thermal activation barrier to electron transfer) and ΔE (internal energy difference) values are nearly the same. A qualitative potential energy diagram for the system $Fe(nqo)_3$/acetoxime in dimethylformamide is drawn in Fig. 2 deduced by comparison with systems, which behave similarly[6].

Further, for the interaction of $Ni(HDz)_2$, $Cu(HDz)_2$ and $Zn(HDz)_2$ with $Fe(nqo)_3$, it is clear from the values of E_{op} and (more pronounced) from those of

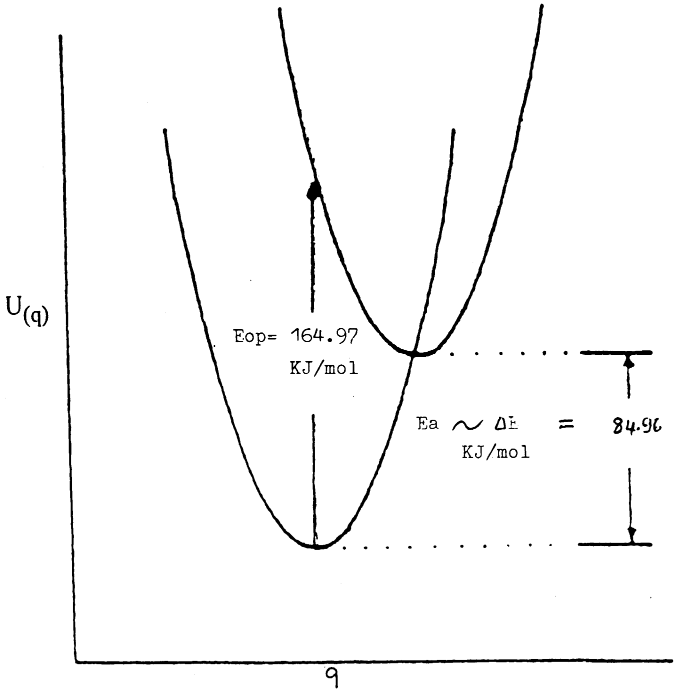

Fig. 2 Qualitative potential energy diagram for the system $Fe(nqo)_3$/acetoxime in dimethylformamide

E_a (Table 1) that the metal ion affects the CT band energy as well as the thermal activation barrier to electron transfer.

TABLE 1
SPECTROSCOPIC AND THERMODYNAMIC DATA FOR SOME $Fe(nqo)_3$/OXIMES OR METAL DITHIZONATES[a]

Oximes or $M(HDz)_2$	E_{op} KJ/mol	ΔE KJ/mol	E_a KJ/mol	χ KJ/mol	$\Delta v^{1/2}$ cm^{-1}
Benzoinoxime	177.52	—	—	—	—
Diacetylmono-oxime	167.86	98.41	101.43	69.45	3613
Furaldoxime	168.82	99.37	102.59	69.45	3655
Salicylaldoxime	168.82	103.22	108.61	65.60	3578
$Ni(HDz)_2$	168.82	130.24	184.70	38.58	2685
$Cu(HDz)_2$	166.90	118.66	144.33	48.24	3010
$Zn(HDz)_2$	167.86	98.41	102.50	69.45	3686

[a]in dimethyl sulphoxide

Moreover, the effect of steric hindrance on the CT band is also apparent from the E_{op} and E_a data of some systems. For the system $Fe(nqo)_3$/salicylaldoxime, the values of E_{op} (168.82 KJ/mole) and E_a (108.61 KJ/mole) are higher than those of $Fe(nqo)_3$/acetoxime, $E_{op} = 167.86$ KJ/mole, $E_a = 92.41$ KJ/mole (in dimethyl

TABLE 2

SPECTROSCOPIC AND THERMODYNAMIC DATA OF $Fe(nqo)_3$/ACETOXIME AND $Fe(nqo)_3$/CYCLOHEXANONEOXIME IN DIFFERENT SOLVENTS.

Solvent	$1/D_{op}-1/D_s$	$Fe(nqo)_3$/acetoxime					$Fe(nqo)_3$/cyclohexanoneoxime				
		E_{op} KJ/mol	ΔE KJ/mol	E_a KJ/mol	χ KJ/mol	$\Delta v^{1/2}$ cm^{-1}	E_{op} KJ/mol	ΔE KJ/mol	E_a KJ/mol	χ KJ/mol	$\Delta v^{1/2}$ cm^{-1}
Ethanol	0.50	162.09	—	—	—	—	165.93	—	—	—	—
Acetonitrile	0.52	—	—	—	—	—	165.93	92.63	93.90	73.30	3733
Tetrahydrofuran	0.37	—	—	—	—	—	159.20	—	—	—	—
Acetone	0.50	176.56	82.96	83.26	93.60	4171	177.53	—	—	—	—
Dimethyl formamide	0.46	164.97	84.89	84.96	80.08	3850	—	—	—	—	—
Dimethyl sulphoxide	0.44	167.86	91.63	92.41	76.23	3776	—	—	—	—	—

sulphoxide). The effect is also apparent when comparing E_{op} for the system $Fe(nqo)_3$/acetoxime (167.86 KJ/mole) with that of $Fe(nqo)_3$/benzoinoxime (173.63 KJ/mole) (in dimethyl sulphoxide).

The same trend is found for the two systems $Fe(nqo)_3$/cyclohexanone-oxime ($E_{op} = 164.01$ KJ/mole) and $Fe(nqo)_3$/acetoxime ($E_{op} = 162.08$ KJ/mole) in ethanol or in acetone (E_{op} for the former system = 177.40 KJ/mole, E_{op} for the latter = 173.67 KJ/mole). This effect is consistent with the fact that the energies of the intervalence-transfer absorptions are functions of the distance between the electron donor and acceptor sites[7]. In the above cases the interaction within the systems containing the bulky salicylaldoxime, cyclohexanoneoxime and benzoinoxime is supposed to occur at greater distance as compared with the acetoxime system. Using the dielectric continuum model, χ_{outer} is predicted to vary with $(1/D_{op}-1/D_s)$, where D_{op} and D_s are the optical and static dielectric constants of the solvent, respectively[4]. Some spectroscopic and thermodynamic data are calculated for the system $Fe(nqo)_3$/acetoxime in different solvents, which are tabulated in Table 2. Plotting χ against $(1/D_{op}-1/D_s)$ gives a linear relationship for the solvents acetone, dimethyl formamide, and dimethyl sulphoxide. The linearity of the plot shows that good argeement exists between experiment and theory, which may reinforce the validity of Hush theory in this case.

EXPERIMENTAL

All chemicals used in this work were of analytical grades. α-Benzoinoxime (Riedel-De Haen AG), diacetylmonoxime(BDH), 2-furaldoxime (Eastman Organic Chemicals), dithizone and naphthoquinoneoxime (BDH) were purchased and used without further purification. Acetoxime, cyclohexanoneoxime, salicylaldoxime[9], tris(naphthoquinoneoximato) iron(III)[10], bis(dithizonato) nickel(II), copper(II), and zinc(II)[11] were prepared according to recommended procedures.

The electronic spectra were recorded on a Varian UV-visible DMS 100S spectrophotometer.

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