Electron transfer reactions of tris(polypyridine)cobalt(III) complexes, [Co(N–N)₃]³⁺, with verdazyl radicals in acetonitrile solution†

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The kinetics and mechanisms of the reactions of 3-(4-X)-phenyl-1,5-diphenyl-verdazyl radicals where X = Cl, H, CH₃ and CH₃O with [Co(N–N)₃]³⁺, N–N = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) and 4,7-dimethyl-1,10-phenanthroline (4,7-Me₂phen), have been investigated in acetonitrile at 25 °C and ionic strength 0.05 mol dm⁻³ (^{n}C₄H₉)₄NPF₆ using stopped flow spectrophotometry. In all cases, transfer of one electron from the radical takes place resulting in the production of a Co(II) species and a verdazylium cation. The electron transfer occurs by an outer-sphere mechanism and the reactions appear to be consistent with Marcus theory. The self-exchange rate constants for the verdazyl–verdazylium cation have been estimated and are of the order of $3.4(\pm1.9) \times 10^7$ dm³ mol⁻¹ s⁻¹. This rate constant is consistent with the fact that the reactions of [Ru(bpy)₃]³⁺ with verdazyl radicals are too rapid to be investigated by stopped flow spectrophotometry.

Introduction

There are relatively few examples in the inorganic literature of reactions in which radicals have been used as electron transfer reagents in kinetic investigations.[1,2] In many of the reactions involving radicals, the radical species have been produced as radical-bridged intermediates or as transient intermediates by techniques such as pulse radiolysis, or by the production of transient ligands such as the nitrophenyl radical attached to a Co(III) complex.[3] In previous studies, it has been shown that the outer-sphere electron transfer reactions of [M(N–N)₃]³⁺ complexes (M = iron(III), ruthenium(III) or osmium(III); N–N = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) with substituted alkyl radicals were extremely rapid with second order rate constants exceeding 10⁶ dm³ mol⁻¹ s⁻¹.[4,5] Rollick and Kochi found that alkyl radicals are readily oxidised by the [M(N–N)₃]³⁺ complexes of iron(III), ruthenium(III), and osmium(III) (N–N = bpy, phen) in acetonitrile solution.[4] They identified two oxidative processes as (a) attack by the radical on the coordinated phenanthroline or bipyridine ligands, and (b) cation formation. The attack by the radical in process (a), termed an inner-sphere mechanism by the authors, was discussed in terms of steric effects on the rate constant k_L for this ligand substitution process. However, alkyl radicals are unstable entities and in the work described above were produced as transient species. It is clear that kinetic studies of the electron transfer reactions between inorganic complexes and stable radicals are relatively sparse.

Verdazyl radicals, the general structure of which is shown in Fig. 1, were discovered by Kuhn and Trischmann in 1964.[6] They are a class of extraordinary free radicals in which the stability is enhanced by an extensive symmetrical delocalisation of the unpaired electron. Five atoms including the 4 nitrogens participate in the delocalisation of spin density while the C₃ carbon (to which the R₄ substituent is attached) is generally accepted to be excluded from the conjugated system. This is clear
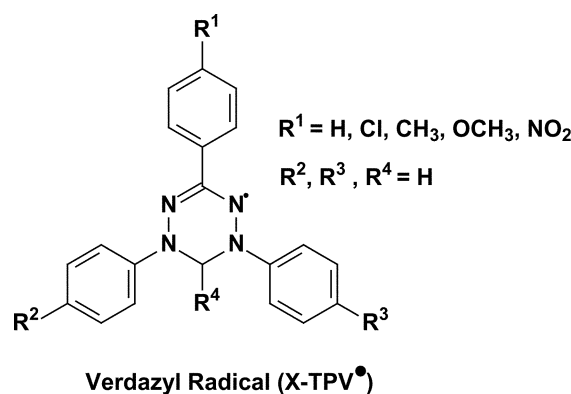

Fig. 1 Structure of verdazyl radicals.

from the EPR spectrum which shows nine peaks. In the parent compound, 1,3,5-triphenyl verdazyl radical (TPV·), R₁ = R₂ = R₃ = R₄ = H.

From the point of view of kinetic investigations of electron transfer reactions of inorganic complexes in solution, verdazyls have a number of distinct advantages as one-electron reducing reagents. These include: (a) verdazyls are stable both in the solid state and in solutions of dichloromethane and acetonitrile; (b) they are uncharged, thus greatly reducing the problems associated with ion-pairing in organic solvents; (c) the one-electron exchange in verdazyls is completely reversible at typical CV scan rates with $\Delta E_p = 59$ mV; (d) electron withdrawing/electron donating moieties can be introduced at the R₁ position of the verdazyl radical which alter the electrochemical properties; (e) the verdazyl radical (X-TPV·) has an extinction coefficient of *ca.* 4,000 dm³ mol⁻¹ cm⁻¹ between 720–730 nm while the oxidised form, the verdazylium cation (X-TPV⁺) has an extinction coefficient of *ca.* 12,000 dm³ mol⁻¹ cm⁻¹ between 540–580 nm dependent on substituents. This ensures that although electron transfer reactions tend to be relatively rapid and while low reactant concentrations must be used, the changes in absorbance accompanying electron transfer are large enough, even in dilute solutions, to be accurately measurable using stopped-flow spectrophotometry. The distinct colour change between the bottle-green verdazyl radical and the dark-blue/purple verdazylium cation in organic solutions facilitates the screening of potential reactions. However, despite these advantages, the potential of verdazyl radicals as electron transfer reagents remains relatively unexplored and relatively

† Electronic supplementary information (ESI) available: Fig. S1: Typical pre-trigger trace of raw data for reaction of pseudo-first order excess of [Co(bpy)₃](ClO₄)₃ (1.0 × 10⁻⁴ mol dm⁻³) with TPV· (1.0 × 10⁻⁵ mol dm⁻³) in acetonitrile and $I = 0.05$ mol dm⁻³ (^{n}C₄H₉)₄NPF₆ at 25 °C, $\lambda = 560$ nm. Fig. S2: Plot of the kinetic data for the reaction of 3-(4-X-phenyl)-1,5-diphenyl-verdazyl radical (X-TPV·) in pseudo-first order excess with 1.0 × 10⁻⁵ mol dm⁻³ [Co(4,7-Me₂phen)₃](ClO₄)₃ in acetonitrile and $I = 0.05$ mol dm⁻³ (^{n}C₄H₉)₄NPF₆ at 25 °C. See http://www.rsc.org/suppdata/dt/b4/b412569j/

little is known about their kinetic behaviour, for example there are no data to indicate whether they react by inner or outer-sphere mechanisms and a reliable self-exchange rate constant, k_{22}, for the verdazyl radical–verdazylium cation reaction has yet to be reported.

The reactions of 3-(4-X)-phenyl-1,5-diphenyl-verdazyl radicals where X = Cl, H, CH$_3$ and CH$_3$O with [Co(N–N)$_3$]$^{3+}$, N–N = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) and 4,7-dimethyl-1,10-phenanthroline (4,7-Me$_2$phen) reported in this paper are attractive as they offer a system that allows variations in the properties of the oxidants and reductants while still operating at moderate driving forces. This allows a test for adiabaticity using relationships between k_{12}, the rate constant for the cross reaction and K_{12}, the equilibrium constant for a set of closely related complexes.[3] Application of Marcus theory together with the known self-exchange rate constants (k_{11}) for the cobalt polypyridine complexes and the experimentally determined cross-reaction rate constants (k_{12}) may provide an insight into the magnitude of the rate constant for the verdazyl radical–verdazyl cation self exchange (k_{22}). Reliable values of this have not been previously reported.

Results

Cyclic voltammetry studies

The verdazyl radicals in general exhibited a chemically reversible one-electron oxidation to their corresponding verdazylium cations. Table 1 summarises the cyclic voltammetric data. By comparing the inductive influence of the different substituents, X, at the R$_1$ position of the verdazyls, the variations in reduction potential can be readily rationalised. Electron withdrawing groups promote the reduction potentials to more positive potentials, while electron donating groups have the opposite effect. Hence, $E°$ for the verdazyl radicals increases in the order CH$_3$O < CH$_3$ < H < Cl. This effect is also observed in the Co(III) complexes. When electron-donating methyl groups are added to the phenanthroline ligand, there is a decrease in $E°$ (Table 2).

Kinetics

When argon saturated acetonitrile solutions of the radicals were reacted with solutions of the Co(III) complexes, an absorbance change corresponding to a single exponential was observed. In all instances, an absorbance increase was observed in the region 540–580 nm which corresponded to that of the pure verdazylium cation. This clearly demonstrated that an electron transfer reaction occurred. The stoichiometry of the reactions was investigated by comparing the final absorbance obtained when the radical and the complex were reacted in a 1:1 ratio with that obtained when a solution of verdazyl radical having the same concentration was reacted with an excess of Cu(NO$_3$)$_2$ which is known to undergo a one-electron transfer with verdazyl radicals.

Table 1 Electrochemical data for 3-(4-X-phenyl)-1,5-diphenyl verdazyl radicals in acetonitrile and $I = 0.2$ mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$.

X	$E°$/V	ΔE_p/mV	I_{pa}/I_{pc}
CH$_3$O	0.168	59	1.04
CH$_3$	0.180	60	1.03
H	0.215	61	0.88
Cl	0.239	59	0.718

Table 2 Electrochemical data for the tris(polypyridine)cobalt(III) complexes, [Co(N–N)$_3$]$^{3+}$ in acetonitrile and $I = 0.2$ mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$.

N–N	$E°$/V	ΔE_p/mV	I_{pa}/I_{pc}
bpy	0.345	66	1.16
phen	0.395	67	1.02
4,7-Me$_2$phen	0.218	74	1.16

In all cases, a 1:1 stoichiometry was obtained confirming the fact that the verdazyl radical acts as a one-electron reducing agent. Due to the rapidity of the reactions, the subsequent slower decomposition of the cobalt(II) complexes produced[7] did not interfere with the kinetic measurements. Reactions were also run in the presence of an excess of the ligand and the rate constants obtained were the same as those obtained in the absence of an excess within experimental error. Similarly, kinetic data obtained in the absence of ionic strength control showed little or no variation from those obtained in the presence of 0.05 mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$. The reported dependency of the [Co(phen)$_3$]$^{3+/2+}$ exchange rate on the nature of the counterion[8] was not observed at the low concentration of reactants used in the acetonitrile solutions. The kinetic data reported are those obtained when the ionic strength was controlled.

That the absorbance changes observed corresponded to a single reaction was confirmed by carrying out pre-trigger experiments and these clearly demonstrated that only a single exponential was involved. Fig. S1 (see ESI†) shows a typical example of the raw data obtained in these experiments. Table 3 summarises the kinetic data and gives the second-order rate constants for all the reactions studied. Figs. 2 and Fig. S2 (see ESI†) show typical plots of the kinetic data obtained for reactions run under pseudo-first-order conditions. The second order rate constants obtained under second-order conditions agreed well with those obtained when either the cobalt(III) complex or the radical was in pseudo-first-order excess and served to confirm the order of the reactions.
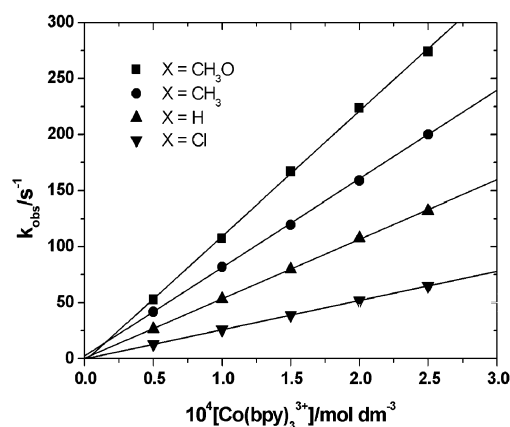

Fig. 2 Plot of the kinetic data for reaction of a pseudo-first order excess of [Co(bpy)$_3$](ClO$_4$)$_3$ with 1.0×10^{-5} mol dm^{-3} 3-(4-X-phenyl)-1,5-diphenyl-verdazyl radical (X-TPV$^•$) in acetonitrile and $I = 0.05$ mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$ at 25 °C.

Attempts at studying the electron transfer cross-reaction between the verdazyl radicals and [Ru(bpy)$_3$]$^{3+}$, which is known to only undergo electron transfer reactions *via* an outer-sphere mechanism,[1,2] were unsuccessful as the reactions proved too rapid ($t_{1/2} \ll 1$ ms) to be investigated using the stopped-flow technique.

Discussion

This work shows that stable radicals such as verdazyl can be used to effect one-electron transfer reactions in complexes of transition metal ions. The Co(III) complexes utilised here were selected on the basis of the fact that they are kinetically inert in terms of their ligand substitution reactions and also that their reduction potentials offered kinetic systems having relatively low driving forces. In addition, the lack of any free donor groups on the ligands together with the time-scale of the electron transfer reactions ensures that the electron transfer reactions are unambiguously outer-sphere and hence are amenable to theoretical treatment in terms of Marcus theory. Table 3 shows that the cross-reaction rate constants increase as the driving

Table 3 Kinetic and thermodynamic data for the reduction of the tris(polypyridine)cobalt(III) complexes ([Co(N–N)$_3$]$^{3+}$) by the verdazyl radicals (X-TPV$^{\bullet}$) in acetonitrile and $I = 0.05$ mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$ at 25 °C.

N–N	X-TPV$^{\bullet}$	$10^{-5}k_{12}$/dm^3 mol^{-1} s^{-1}	$\Delta E°$/V	K_{12}	$\log K_{12}$	$\log k_{12}$	k_{11}/dm^3 mol^{-1} s^{-1}	$10^{-7}k_{22}$/dm^3 mol^{-1} s^{-1}
bpy	X = CH$_3$O	9.84($\pm$0.02)	0.177	1000	3.00	5.99	5.7	3.9
phen	X = CH$_3$O	18.2($\pm$2.6)	0.227	7038	3.85	6.26	12.0	1.2
4,7-Me$_2$phen	X = CH$_3$O	0.792($\pm$0.012)	0.050	7.04	0.850	4.90	4.5^a	3.2
bpy	X = CH$_3$	7.65($\pm$0.06)	0.165	626	2.80	5.88	5.7	3.6
phen	X = CH$_3$	15.3($\pm$0.5)	0.215	4406	3.64	6.18	12.0	1.2
4,7-Me$_2$phen	X = CH$_3$	0.622($\pm$0.014)	0.038	4.41	0.644	4.79	4.5^a	3.1
bpy	X = H	5.37($\pm$0.05)	0.130	160	2.20	5.73	5.7	6.2
phen	X = H	10.1($\pm$0.90)	0.180	1124	3.05	6.00	12.0	1.8
4,7-Me$_2$phen	X = H	0.447($\pm$0.010)	0.003	1.12	0.051	4.65	4.5^a	6.2
bpy	X = Cl	2.60($\pm$0.01)	0.106	62.6	1.80	5.42	5.7	3.5
phen	X = Cl	5.45($\pm$0.50)	0.156	441	2.64	5.74	12.0	1.2
4,7-Me$_2$phen	X = Cl	0.270($\pm$0.001)	$-$0.021	0.441	$-$0.356	4.43	4.5^a	5.8

^{a} Calculated from Fig. 3.

force of the reactions as indicated by $\Delta E°$ increases. Reported self-exchange rate constants for [Co(bpy)$_3$]$^{3+}$, [Co(phen)$_3$]$^{3+}$ and [Co(4,7-Me$_2$phen)$_3$]$^{3+}$ are 5.7, 12.0 and 120 dm^3 mol^{-1} s^{-1}.[8,9] In the case of bpy and phen the cross-reaction rate constants reported here follow the pattern of the self exchange rate constants in that [Co(phen)$_3$]$^{3+}$ reacts more rapidly than [Co(bpy)$_3$]$^{3+}$. Based solely on the self exchange rate constants it would be expected that [Co(4,7-Me$_2$phen)$_3$]$^{3+}$ would react more rapidly with verdazyl radicals than either of the other complexes. This is clearly not the case. There is no obvious reason as to why the self exchange rate constant of [Co(4,7-Me$_2$phen)$_3$]$^{3+}$ should be an order of magnitude greater than that of [Co(phen)$_3$]$^{3+}$, considering that there is only a factor of two between the rates of the [Co(bpy)$_3$]$^{3+/2+}$ and [Co(phen)$_3$]$^{3+/2+}$ exchanges. It is clear that a discrepancy exists between the trend found for the rate constants of the cross reactions and the trend of the self-exchange rate constants.

Application of Marcus theory[10–12] provides a useful means for the theoretical prediction of self-exchange rate constants for adiabatic outer-sphere electron transfer reactions. This theory predicts a simple relationship between the cross-reaction rate constant k_{12} for the redox reaction, k_{11} and k_{22} the self-exchange rate constants for the reactants, and K_{12} the equilibrium constant for the reaction, eqn. (1) where

$$k_{12} = \left[\frac{(k_{11}k_{22}K_{12}f_{12})}{\kappa_{11}\kappa_{22}}\right]^{1/2} \kappa_{12}W_{12} \quad (1)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log\left(k_{11}k_{22}/Z^2\right)} \quad (2)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (3)$$

The individual electric work terms, w_{ij}, can be determined using eqn. (4) where a is the contact distance of the ions ($a = (r_1 + r_2)$), z_1 and z_2 are the charges on the reacting species, ε_o is the permittivity of a vacuum, ε is the bulk dielectric constant, $\chi = (2e_o^2 N_A I/\varepsilon_o \varepsilon k_B T)^{1/2}$ where e_o is the charge on a electron, N_A is Avogadro's constant, k_B is Boltzmann's constant, I is the ionic strength and T is the absolute temperature. In eqn. (2) Z is the collision frequency $\approx 10^{11}$ M^{-1} s^{-1}.

$$w_{ij} = z_i z_j e_o^2 N_A / 4\pi\varepsilon_o\varepsilon a(1 + \chi a) \quad (4)$$

With ionic radii of 0.7 nm for the cobalt complexes,[13] 0.85 nm for the verdazyl radicals,[14,15] $I = 0.05$ mol dm^{-3} and $\varepsilon = 37.5$ for acetonitrile at 25 °C, the work terms for the reactions are calculated to be: $w_{12} = 0$, $w_{21} = 1.8$ kJ mol^{-1}, $w_{11} = 6.38$ kJ mol^{-1} and $w_{22} = 0$.

Assuming that the reaction approaches adiabaticity such that $\kappa_{ij} \sim 1$, eqn. (1) can be written as eqn. (5).

$$2\log k_{12} - \log f_{12} - 2\log W_{12} - \log k_{11} = \log k_{22} + \log K_{12} \quad (5)$$

Eqn. (5) predicts that a plot of the left hand side against log K_{12} should be linear with a slope of 1.0 if the Marcus theory is obeyed. Fig. 3 shows such a plot using the kinetic data in Table 3 and the calculated work terms for the reactions of the four verdazyls with [Co(bpy)$_3$]$^{3+}$ and [Co(phen)$_3$]$^{3+}$. This plot can be constructed as there is only a factor of two between the [Co(bpy)$_3$]$^{3+/2+}$ and [Co(phen)$_3$]$^{3+/2+}$ self-exchange rate constants and it is assumed that there would be small variations between the self-exchanges of the verdazyl radicals. The average value of k_{11}, 8.85 dm^3 mol^{-1} s^{-1} was used in the construction of Fig. 3. It is clear that a relatively good linear relationship is obtained. The slope of the plot is 0.89($\pm$0.07) and the intercept 7.66($\pm$0.20) gives an average value of 4.6×10^7 dm^3 mol^{-1} s^{-1} for the verdazyl radical–verdazylium ion self exchange rate constant, k_{22}.
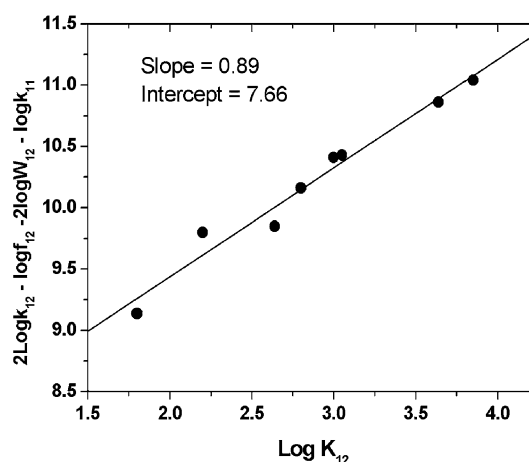
Fig. 3 Plot of (2log k_{12} − log f_{12} − 2log W_{12} − log k_{11}) against log K_{12} for reaction of [Co(bpy)$_3$]$^{3+}$ and [Co(phen)$_3$]$^{3+}$ with verdazyl radicals in acetonitrile and $I = 0.05$ mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$ at 25 °C.

Eqn. (1) allows k_{11} to be evaluated once k_{22}, k_{12} and K_{12} are known. Using this approach and the value of k_{22} derived from Fig. 3, values of the self-exchange rate constant of [Co(4,7-Me$_2$phen)$_3$]$^{3+/2+}$ were calculated to be 3.16, 3.10, 6.15, 5.74 dm^3 mol^{-1} s^{-1} for X = CH$_3$O, CH$_3$, H and Cl respectively. This gives an average value of 4.5($\pm$1.6) dm^3 mol^{-1} s^{-1} for the self exchange rate of [Co(4,7-Me$_2$phen)$_3$]$^{3+/2+}$. This is consistent with the self exchange rates of the other two complexes. The difference between this and the previously reported value[8] of 120 dm^3 mol^{-1} s^{-1} may be due to the difference in the media as it has been reported that the self-exchange rate constant of this complex is particularly sensitive to media effect.[16]

Using the average value of 4.5 dm^3 mol^{-1} s^{-1} for the self-exchange of [Co(4,7-Me$_2$phen)$_3$]$^{3+/2+}$ in acetonitrile, the rates of the self-exchanges for the tris(polypyridine)cobalt complexes
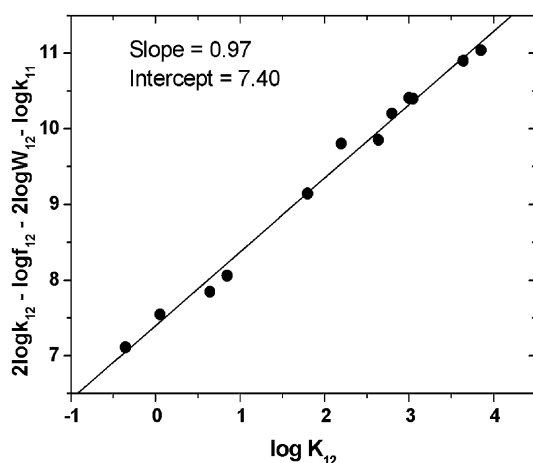
Fig. 4 Plot of $(2\log k_{12} - \log f_{12} - 2\log W_{12} - \log k_{11})$ against $\log K_{12}$ for reaction of $[Co(bpy)_3]^{3+}$, $[Co(phen)_3]^{3+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ with verdazyl radicals in acetonitrile and $I = 0.05$ mol dm^{-3} ($^nC_4H_9)_4NPF_6$ at 25 °C.

increases in the order $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+} < [Co(bpy)_3]^{3+/2+} < [Co(phen)_3]^{3+/2+}$, the same order as the rates for the cross-reactions with the verdazyl radicals. Combining these results, Fig. 4 can be constructed using the kinetic data in Table 3 and the work terms for all three cobalt(III) complexes and all four radicals. The plot is linear and excellent correlation is found between $(2\log k_{12} - \log f_{12} - 2\log W_{12} - \log k_{11})$ and $\log K_{12}$ as predicted by Marcus theory, slope = 0.97 (± 0.03), intercept = 7.40 (± 0.07). Thus, the reactions proceed by outer-sphere electron transfer. Inserting the data from Table 3 into eqn. (1) allows the calculation of the self-exchange rate constants of the individual verdazyl radicals. An average value of $3.4(\pm 1.9) \times 10^7$ dm^3 mol^{-1} s^{-1} is obtained for the verdazyl radical–verdazylium cation self-exchange rate constant.

The value calculated for the self-exchange rate constant of $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ using these results differs from a previously reported value.[8] However, analysis of the data in Fig. 3 from which this complex is excluded gives results for the self exchange rate constants of the verdazyl radicals that do not differ significantly from results derived from Fig. 4 which includes results for all three cobalt complexes. Therefore inclusion or exclusion of the $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ results provide values for the verdazyl self exchange that are clearly well within the generally accepted uncertainty of the Marcus approach to outer-sphere electron exchange.

Given the discussion outlined above and the apparent conformity of the reactions with Marcus theory, the inability to obtain kinetic data for the reactions with $[Ru(bpy)_3]^{3+}$ is not surprising.

Given that the self exchange rate constant[17] for $[Ru(bpy)_3]^{3+/2+}$ is 4.2×10^8 dm^3 mol^{-1} s the second order rate constants for reaction of $[Ru(bpy)_3]^{3+}$ with verdazyl radicals ($\Delta E° \sim 1.09$ V) should be close to the diffusion controlled limit and would clearly not be amenable to investigation by stopped-flow spectrophotometry.

For a long time, there existed uncertainties as to whether Co$^{III/II}$ exchange proceeded by an adiabatic[18–26] or a non-adiabatic[27–29] process. The nonadiabatic pathway would involve electron transfer between ground-state high-spin Co^{II} and ground-state low-spin Co^{III} with a large multiplicity change. The adiabatic pathway, which is the explanation now favoured[30,31], involves a fast[32] but unfavourable ground-state high-spin to excited-state low-spin Co^{II} pre-equilibrium (any accompanying geometrical distortions e.g. Jahn–Teller type contributing to the Franck–Condon energy barrier to electron transfer) with adiabatic electron transfer between the low-spin Co^{II} and Co^{III} species.

Some cross-reactions of Co^{III} and Co^{II} complexes have been reported to be mildly nonadiabatic and an apparent dependence of the nonadiabaticity on the driving force for electron transfer has been noted.[7,21,33–36] A decrease in driving force leads to an increase in the electronic interaction between the reactant and product states as the excited-state energy decreases.[24] Table 3 illustrates that the systems studied here operate at moderate driving forces. Given the slopes of the plots in Figs. 3 and 4, it must be concluded that the reactions investigated here are broadly adiabatic in nature.

Table 4 lists the rate constants for the self-exchange reactions of a number of radicals. They span approximately four orders of magnitude between the fastest, TCNQ/TCNQ$^•$, and the slowest, the ascorbate system. The verdazyl radicals fall between the two extremes and the values reported here appear reasonable in the light of this.

Conclusion

The kinetics of the reactions of a series of verdazyl radicals with cobalt(III) complexes have been successfully investigated using stopped-flow spectrophotometry in acetonitrile solution. The reactions involve transfer of a single electron from the radical to the cobalt(III) complex. The reactions are outer-sphere and are consistent with Marcus theory. For the first time, an estimate of the self-exchange rate constant of verdazyl radicals has been calculated.

Experimental

Preparation of radicals and Co(III) complexes. CAUTION: perchlorate salts of metal complexes are potentially explosive, as are the verdazyl radicals, which contain a ring of four

Table 4 Self exchange rate constants for a number of radicals.

Couple	$10^{-8} k_{ex}$/dm^3 mol^{-1} s^{-1}	T/K	Solvent	Ref.
NB/NB$^{•-}$	2.84 ± 0.3	296	NB	40
TMPPD/TMPPD$^{•+}$	11.7 ± 0.8	293	CH$_3$CN	41,42
TCNQ/TCNQ$^{•-}$	47.3 ± 1.1	298	CH$_3$CN	43
TCNE/TCNE$^{•-}$	25.3 ± 1.7	298	CH$_3$CN	43
Vitamin K$_3$/K$_3^{•-}$	28.5 ± 2.1	303	EtOH	44
1-Nitronaphthalene/ 1-nitronaphthalene$^{•-}$	3.1 ± 0.3	300	DMF	45
DDQ/DDQ$^{•-}$	29.2 ± 0.3	293	CH$_3$CN	46
HA$^-$/HA$^•$	0.0016	298	H$_2$O	47
H$_2$cat/H$_2$cat$^{+•}$	≈ 0.6	298	H$_2$O	48
H$_2$quin/H$_2$quin$^{+•}$	≈ 0.6	298	H$_2$O	48
Various organic radicals	$\approx 0.5^a$	298	H$_2$O	49
Verdazyl$^+$/verdazyl$^•$	0.34	298	CH$_3$CN	This work

^{a} This is an average value for a series of organic radicals.
NB = nitrobenzene; TMPPD = $N,N,N'N'$-tetramethyl-p-phenylenediamine; TCNQ = tetracyanoquinonedimethane; TCNE = tetracyanoethylene; vitamin K$_3$ = 2-methyl-1,4-naphthoquinone; DDQ = 2,3-dicyano-5,6-dichloro-p-benzoquinone; HA$^-$ = ascorbic acid; H$_2$cat = catechol; H$_2$quin = quinol.

nitrogen atoms in their structure. Therefore, these compounds were prepared in small quantities.

The substituted verdazyl radicals are named 3-(4-X)-phenyl-1,5-diphenyl-verdazyl radicals (X-TPV$^{\bullet}$), X = H, Cl, CH$_3$ and CH$_3$O

1,3,5-triphenyl verdazyl radical and 1,5-diphenyl-3-(p-X-phenyl)-verdazyl radicals. These radicals were prepared from their corresponding formazans by reaction with 37% aqueous formaldehyde and KHSO$_4$, following the procedure of Kuhn and Trischmann.[6] The crystals were purified by recrystallisation from distilled methanol and dried over silica gel in vacuum.

1,3,5-triphenyl verdazyl radical (TPV$^{\bullet}$). Found: C, 76.42, H, 5.37, N, 18.07. Calc. For C$_{20}$H$_{17}$N$_4$: C, 76.65, H, 5.47, N, 17.88% (λ_{max} = 720 nm, ε_{max} = 4,330 dm^3 mol^{-1} cm^{-1})

1,5-diphenyl-3-(p-tolu-phenyl)-verdazyl radical (CH$_3$-TPV$^{\bullet}$). Found: C, 76.75, H, 5.69, N, 16.99. Calc. for C$_{21}$H$_{19}$N$_4$: C, 77.04, H, 5.85, N, 17.11% (λ_{max} = 720 nm, ε_{max} = 4,064 dm^3 mol^{-1} cm^{-1})

1,5-diphenyl-3-(p-methoxy-phenyl)-verdazyl radical (CH$_3$O-TPV$^{\bullet}$). Found: C, 73.51, H, 5.58, N, 15.91. Calc. for C$_{21}$H$_{19}$N$_4$O: C, 73.45, H, 5.58, N, 16.32% (λ_{max} = 730 nm, ε_{max} = 3,107 dm^3 mol^{-1} cm^{-1})

1,5-diphenyl-3-(p-chloro-phenyl)-verdazyl radical (Cl-TPV$^{\bullet}$). Found: C, 69.23, H, 4.82, N, 16.15. Calc. For C$_{20}$H$_{16}$N$_4$Cl: C, 69.06, H, 4.64, N, 16.11% (λ_{max} = 720 nm, ε_{max} = 3,375 dm^3 mol^{-1} cm^{-1})

[Co(bpy)$_3$](ClO$_4$)$_3 \cdot$3H$_2$O. was prepared as previously described[37] and yellow, needle-like crystals were obtained on recrystallisation.

[Co(phen)$_3$](ClO$_4$)$_3 \cdot$3H$_2$O and [Co(4,7-Me$_2$phen)$_3$](ClO$_4$)$_3 \cdot$3H$_2$O. were synthesised in the same fashion as for [Co(bpy)$_3$](ClO$_4$)$_3 \cdot$3H$_2$O, using 1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline respectively in place of 2,2'-dipyridyl.

Cyclic voltammetry studies

Cyclic voltammetry data were obtained with a Bioanalytical Systems, Inc. CV-50W potentiostat using a three electrode system, consisting of a glassy carbon working electrode (3.0 mm diameter), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The cell used was a Bioanalytical Systems, Inc. VC-2 glass vial with a fitted top equipped with four holes to accommodate the three electrodes and a gas purging tube. The glassy carbon working electrode surface was polished with 0.05 micron gamma alumina powder (from CH Instruments Inc. electrode polishing kit) ensuring a clean and uniform electrode surface and rinsed thoroughly with distilled water and acetonitrile. The cell was filled with freshly prepared 5 × 10^{-4} mol dm^{-3} acetonitrile solutions of the compound to be analysed containing 0.2 mol dm^{-3} (^{n}C$_4$H$_9$)$_4$NPF$_6$. The system was deoxygenated before measurements were taken by purging with argon for 10 min. Electrochemical behaviour was examined at low scan rates over a potential range (−0.1 to 0.7 V).

Kinetics

Kinetic measurements were carried out in acetonitrile, which had been purified by distillation over calcium hydride. All solutions were saturated with argon. The reactions were monitored by observing the increase in absorbance due to formation of the verdazylium cation between 560 and 600 nm depending on the radical involved. Kinetic data were acquired with a HI-TECH SF20 stopped flow spectrophotometer. This was interfaced to a PC using an ADC-216 16-bit device supplied by PICO Technology Limited and a custom Windows based interface.[38] Pseudo first order rate constants were calculated using the OLIS

KINFIT routines (OLIS, Bogart, GA, USA). Errors in individual rate constants as reported by the program were of the order of 1%. Spectral data were obtained with a HP8453 diode array spectrophotometer. Reactions that were too rapid to investigate under pseudo-first-order conditions were investigated under second order conditions using equivalent concentrations of the reactants and repeated over a concentration range of 1.0×10^{-5}–5×10^{-5} mol dm^{-3}. In this instance, rate constants were evaluated using a three parameter fit as previously described.[39] Where the reactions were run under pseudo-first-order conditions, the reactions were found to be first order with either reactant in excess.

Acknowledgements

References

1 A. G. Lappin, in *Redox Mechanisms in Inorganic Chemistry*, ed. D. J. Burgess, Ellis Horwood Ltd., New York, 1994.
2 M. L. Tobe and J. Burgess, *Inorganic Reaction Mechanisms*, Addison Wesley Longman Ltd., Harlow, 1999.
3 R. G. Wilkins, Oxidation–Reduction Reactions, in *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, ed., New York, 1991.
4 K. L. Rollick and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 1319.
5 J. Grodkowski, P. Neta, C. J. Schlesener and J. K. Kochi, *J. Phys. Chem.*, 1985, **89**, 4373.
6 R. Kuhn and H. Trischmann, *Monatsh. Chem.*, 1964, **95**, 457.
7 Y. Fu, A. S. Cole and T. W. Swaddle, *J. Am. Chem. Soc.*, 1999, **121**, 10410.
8 R. M. L. Warren, A. G. Lappin, B. D. Mehta and H. M. Neumann, *Inorg. Chem.*, 1990, **29**, 4185.
9 R. M. L. Warren, A. G. Lappin and A. Tatehata, *Inorg. Chem.*, 1992, **31**, 1566.
10 R. A. Marcus, *Discuss. Faraday Soc.*, 1960, **29**, 21.
11 R. A. Marcus, *Can. J. Chem*, 1959, **37**, 155.
12 R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853.
13 A. Haim and N. Sutin, *Inorg. Chem*, 1976, **15**, 476.
14 D. E. Williams, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1973, **B29**, 96.
15 N. Azuma, K. Tsutsui, Y. Miura and T. Higuchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 3274.
16 A. G. Lappin, Personal Communication, 2004.
17 R. C. Young, R. Keene and T. J. Meyer, *J. Am. Chem. Soc.*, 1977, **99**, 2468.
18 B. S. Brunschwig, C. Creutz, D. H. Macartney, T.-K. Sham and N. Sutin, *Faraday Discuss. Chem. Soc.*, 1982, **74**, 113.
19 J. F. Endicott, T. Ramasami, D. C. Gaswick, R. Tamilarasan, M. J. Heeg, G. R. Brubaker and S. C. Pyke, *J. Am. Chem. Soc.*, 1983, **105**, 5301.
20 T. Ramasami and J. F. Endicott, *Inorg. Chem.*, 1984, **23**, 3324.
21 T. Ramasami and J. F. Endicott, *J. Am. Chem. Soc.*, 1985, **107**, 389.
22 D. H. Macartney and N. Sutin, *Inorg. Chem.*, 1983, **22**, 3530.
23 D. J. Szalda, D. H. Macartney and N. Sutin, *Inorg. Chem.*, 1984, **23**, 3473.
24 C.-Y. Mok, A. W. Zanella, C. Creutz and N. Sutin, *Inorg. Chem.*, 1984, **23**, 2891.
25 J. K. Beattie and H. Elsbernd, *Inorg. Chim. Acta*, 1995, **240**, 641.
26 R. D. Shalders and T. W. Swaddle, *Inorg. Chem.*, 1995, **34**, 4815.
27 D. Sandrini, M. T. Gandolfi, M. Maestri, F. Bolletta and V. Balzani, *Inorg. Chem.*, 1984, **23**, 3017.
28 W. H. Jolley, D. R. Stranks and T. W. Swaddle, *Inorg. Chem.*, 1990, **29**, 385.
29 M. R. Grace and T. W. Swaddle, *Inorg. Chem.*, 1993, **32**, 5597.
30 T. W. Swaddle, *Can. J. Chem.*, 1996, **74**, 631.
31 Y. Fu and T. W. Swaddle, *J. Am. Chem. Soc.*, 1997, **119**, 7137.
32 J. K. Beattie, *Adv. Inorg. Chem.*, 1988, **32**, 2.
33 K. Zahir, J. H. Espenson and A. Bakac, *Inorg. Chem.*, 1988, **27**, 3144.
34 M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1977, **99**, 5615.
35 F. J. Endicott and T. Ramasami, *J. Phys. Chem.*, 1986, **90**, 3740.
36 U. Furholz and A. Haim, *J. Phys. Chem.*, 1986, **90**, 3686.
37 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
38 M. J. Hynes, Inorganic Reaction Mechanisms Meeting, Athens, Greece, 2004.

39 M. J. Hynes, *Proc. R. Ir. Acad.*, 1989, **89B**, 435.
40 G. Grampp, Y. A. Khan and H. Larsen, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2555.
41 G. Grampp and W. Jaenicke, *Ber. Bunsen-Ges. Phys. Chem.*, 1984, **88**, 325.
42 G. Grampp and W. Jaenicke, *Ber. Bunsen-Ges. Phys. Chem.*, 1984, **88**, 335.
43 G. Grampp and W. Jaenicke, *Ber. Bunsen-Ges. Phys. Chem.*, 1991, **95**, 904.
44 G. Grampp and G. Stiegler, *J. Magn. Reson.*, 1986, **70**, 1.
45 G. von Coll, PhD Thesis, University of Erlangen, Germany, 1986..
46 G. Grampp, S. Landgraf and K. Rasmussen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1897.
47 A. Wanat, R. van Eldik and G. Stochel, *J. Chem. Soc., Dalton Trans.*, 1998, 2497.
48 E. Mentasti, E. Pelizzetti and C. Baiocchi, *J. Chem. Soc., Dalton Trans.*, 1977, 132.
49 D. Meisel, *Chem. Phys. Lett.*, 1975, **34**, 263.