Rates of Electron Transfer within Outer-sphere Precursor Complexes in the System Penta-ammine(dimethyl sulphoxide)cobalt(III) and Substituted Pentacyanoferrates(II) †

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The kinetics of outer-sphere electron-transfer reactions between $[Co(NH_3)_5(dmso)]^{3+}$ (dmso = dimethyl sulphoxide) and a series of $[Fe(CN)_5L]^{3-}$ complexes (L = imidazole, ammonia, pyridine, pyrazine, isonicotinamide, or pyrazine-2-carboxamide) have been investigated as a function of the ligand L. The formation constants of the precursor $[Co(NH_3)_5(dmso)]^{3+} || [Fe(CN)_5L]^{3-}$ complexes are nearly constant in the series (400—550 $dm^3 mol^{-1}$), and practically temperature independent in the range 10—35 °C (ΔH *ca.* 0, ΔS = 50—55 J $K^{-1} mol^{-1}$). The rates of electron transfer in the precursor complexes show a systematic increase from the pyrazinamide to the imidazole complex, with a linear dependence of $\ln(k_{et})$ against $\Delta E^\ominus$, as predicted theoretically. This increase in rate is paralleled by a decrease in the activation enthalpies from 109 to 92 kJ mol^{-1}, the activation entropies remaining nearly constant at 71—75 J $K^{-1} mol^{-1}$.

OUTER-SPHERE electron-transfer reactions are usually described[1] by a sequence of three elementary steps

$$\text{Oxid} + \text{Red} \xrightleftharpoons{K_\text{P}} \text{Oxid}||\text{Red} \qquad (1)$$

$$\text{Oxid}||\text{Red} \xrightleftharpoons{k_\text{et}} \text{Oxid}^-||\text{Red}^+ \qquad (2)$$

$$\text{Oxid}^-||\text{Red}^+ \xrightleftharpoons{1/K_\text{S}} \text{Oxid}^- + \text{Red}^+ \qquad (3)$$

corresponding to a diffusion-controlled association of the reactants (1), electron transfer (2), and a rapid dissociation of the products (3), respectively. The associated species in equations (1) and (3) are also known as precursor (P) and successor (S) complexes. For most systems, the composite rate law (4) reduces to a simple

$$\text{Rate} = \frac{K_\text{p}k_\text{et}[\text{Oxid}][\text{Red}]}{1 + K_\text{p}[\text{Oxid}]} \qquad (4)$$

second-order rate law, since $K_\text{p}[\text{Oxid}] \ll 1$. Consequently, the observed rate constants cannot be ascribed to a pure electron-transfer process, since they reflect the barrier to bringing the reactants together as well as the electron transfer itself.

To evaluate the rates of electron transfer, high concentrations of the reactants are required in order to shift the equilibrium (1) in the direction of the precursor complex. However, this evaluation is seldom possible because K_p, the association constant for the precursor complex, is usually very small, or because the rates can become too fast with increasing concentrations of the reactants to be measured by the available techniques.

The few examples of outer-sphere reactions in which it was possible to resolve the observed rate constant into its elementary components have been described by Haim and his co-workers for the hexacyanoferrate(II)–penta-ammineaquacobalt(III)[2] and –penta-ammine(pyridine)-cobalt(III)[3] systems. Recently, we reported[4] a related study but involving the aqua- and ammine-pentacyanoferrate(II) ions and the penta-ammine(dimethyl sulphoxide)cobalt(III) complex.

The complex $[Co(NH_3)_5(dmso)]^{3+}$ (dmso = dimethyl sulphoxide) was found to be appropriate for a systematic study because it has a high positive charge, and it is more easily reducible than most of the substituted penta-amminecobalt(III) complexes, *e.g.* with ammonia or pyridine. By using a series of $[Fe(CN)_5L]^{3-}$ complexes (L = imidazole, ammonia, pyridine, isonicotinamide, pyrazine, or pyrazine-2-carboxamide), we now extend our previous work[4] to show the dependence of the intramolecular electron-transfer rates on the driving forces ($\Delta E^\ominus$) of outer-sphere electron-transfer reactions.

EXPERIMENTAL

The complex $[Co(NH_3)_5(dmso)][ClO_4]_3 \cdot 2H_2O$ was prepared and recrystallized according to the procedure of Piriz Mac-Coll and Beyer.[5] Solutions of the cobalt(III) complex were prepared by dissolving the solid in argon-saturated water at the appropriate ionic strength (lithium perchlorate) and pH (acetate buffer, 10^{-2} mol dm^{-3}). Only freshly prepared solutions were used in this work, to minimize the effects of the slow aquation[6] of the cobalt(III) complex. Solutions of the pentacyanoferrate(II) complexes of imidazole, pyridine, isonicotinamide, pyrazine, and pyrazine-2-carboxamide were prepared from the ammine-pentacyanoferrate(II) complex[7] in the presence of at least a 10-fold excess of the heterocyclic ligand (Aldrich). Distilled deionized water, previously saturated with argon, was used to prepare the solutions.

The spectra of the reactants and products were recorded on a Cary 14 spectrophotometer, which was also used in the kinetics of the slow reactions between $[Co(NH_3)_5(dmso)]^{3+}$ and the pentacyanoferrate(II) complexes of isonicotinamide, pyrazine, and pyrazine-2-carboxamide. Analysis of the products was carried out spectrophotometrically, after the separation of the cobalt species with Dowex 50W-X4 ionic exchange resin. Complete conversion of the reactants into the corresponding pentacyanoferrate(III) complex has been observed in all the cases.

The kinetics of the fast reactions between $[Co(NH_3)_5(dmso)]^{3+}$ and the pentacyanoferrate(II) complexes of imidazole, ammonia, and pyridine were investigated using a Durrum D-110 stopped-flow spectrophotometer, equipped with a Kel-F flow system.

A Chemtrix model 205 polarograph coupled with a Beckmann Expandomatic SS-2 potentiometer and a Tektronix model 564-B oscilloscope was employed in the cyclic-voltammetry measurements of the $[Fe(CN)_5L]$ complexes. All the measurements were carried out under similar conditions to the kinetics experiments: pH 4.6, 0.100 mol dm^{-3} lithium

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perchlorate, argon atmosphere. Platinum wires were used as auxiliary and working electrodes *versus* a NaCl-saturated calomel electrode. Reversible cyclic voltammograms were obtained at sweep rates from 50 to 500 mV s^{-1}, with typical peak separations in the range 58—69 mV.

RESULTS AND DISCUSSION

The reaction between the $[Co(NH_3)_5(dmso)]^{3+}$ ion and the pentacyanoferrate(II) complexes of pyridine, isonicotinamide, pyrazine, and pyrazine-2-carboxamide was monitored spectrophotometrically, following the disappearance of the strong charge-transfer bands[7] centred at 362, 439, 458, and 492 nm, respectively. The absorption bands of the oxidized $[Fe(CN)_5L]^{2-}$ complexes, at 400—420 or 350—370 nm, were also used for this purpose, particularly in the case of the ammine[4] and imidazole complexes. Typical first-order behaviour was observed for the kinetics, during at least two half-lives. Under the conditions employed in this work, $[Fe(CN)_5L^{3-}] = 2 \times 10^{-5}$—$5 \times 10^{-5}$ mol dm^{-3}, $[Co(NH_3)_5(dmso)^{3+}] = 1 \times 10^{-3}$—$6 \times 10^{-3}$ mol dm^{-3}, $I = 0.100$ mol dm^{-3} (lithium perchlorate), pH 4.6 (acetate buffer, 10^{-2} mol dm^{-3}), no evidence of precipitation[2,3] was found.

TABLE 1

Rate constants of outer-sphere electron-transfer reactions between $[Co(NH_3)_5(dmso)]^{3+}$ and $[Fe(CN)_5L]^{3-}$ complexes[a]

L	$10^3\,[Co(NH_3)_5(dmso)^{3+}]$/mol dm^{-3}	$k_{obs.}$[b]/s^{-1} T_1	T_2	T_3
Imidazole	1.00	1.52×10^{-1}	7.9×10^{-1}	2.76
	2.00	2.27×10^{-1}	1.26	4.01
	3.00	2.65×10^{-1}	1.44	4.84
	4.00	2.86×10^{-1}	1.56	5.20
	5.20	3.10×10^{-1}	1.82	5.70
	6.00	3.22×10^{-1}	1.92	5.80
Pyridine	1.00	9.5×10^{-3}	4.92×10^{-2}	1.66×10^{-1}
	2.00	1.26×10^{-2}	6.8×10^{-2}	2.62×10^{-1}
	3.00	1.55×10^{-2}	9.0×10^{-2}	$3.19 \times 10^{1-}$
	4.00	1.71×10^{-2}	9.8×10^{-2}	3.44×10^{-1}
	2.00	1.77×10^{-2}	1.07×10^{-1}	3.59×10^{-1}
	6.00	2.14×10^{-2}	1.12×10^{-1}	3.86×10^{-1}
Isonicotinamide	1.00	3.10×10^{-3}	1.86×10^{-2}	5.6×10^{-2}
	2.00	4.63×10^{-3}	2.57×10^{-2}	9.0×10^{-2}
	3.00	5.4×10^{-3}	2.99×10^{-2}	1.06×10^{-1}
	4.00	6.1×10^{-3}	3.19×10^{-2}	1.15×10^{-1}
	5.00	6.8×10^{-3}	3.75×10^{-2}	1.26×10^{-1}
	6.00	7.0×10^{-3}	3.73×10^{-2}	1.30×10^{-1}
Pyrazine	1.00	5.2×10^{-4}	2.37×10^{-3}	9.0×10^{-3}
	2.00	7.9×10^{-4}	3.79×10^{-3}	1.29×10^{-2}
	3.00	9.6×10^{-4}	4.53×10^{-3}	1.69×10^{-2}
	4.00	1.04×10^{-3}	5.4×10^{-3}	1.86×10^{-2}
	5.00	1.17×10^{-3}	5.8×10^{-3}	1.93×10^{-2}
	6.00	1.27×10^{-3}	6.0×10^{-3}	2.16×10^{-2}
Pyrazine-2-carboxamide	1.00	2.65×10^{-4}	1.68×10^{-3}	6.1×10^{-3}
	2.00	4.14×10^{-4}	2.45×10^{-3}	8.4×10^{-3}
	3.00	4.58×10^{-4}	2.86×10^{-3}	1.06×10^{-2}
	4.00	4.90×10^{-4}	3.21×10^{-3}	1.19×10^{-2}
	5.00	5.3×10^{-4}	3.45×10^{-3}	1.21×10^{-2}
	6.00	5.6×10^{-4}	3.70×10^{-3}	1.32×10^{-2}

[a] pH 4.6 (acetate buffer, 10^{-2} mol dm^{-3}), $I = 0.100$ mol dm^{-3} lithium perchlorate, $[Fe(CN)_5L^{3-}] = 2 \times 10^{-5}$—$5 \times 10^{-5}$ mol dm^{-3}. The rates are averages from duplicate measurements. [b] $T_1 = 11.6$, 12.9, 12.7, 14.9, and 13.3 (± 0.2) °C, $T_2 = 25.0 \pm 0.2$ °C, and $T_3 = 33.8$, 33.6, 33.5, 33.8, and 34.0 (± 0.2) °C for the imidazole, pyridine, isonicotinamide, pyrazine, and pyrazine-2-carboxamide complexes, respectively.

The dependence of the rate constants on the concentration of the reactants was investigated at three temperatures for each $[Fe(CN)_5L]^{3-}$ complex. The observed rate constants (Table 1) showed a remarkable deviation from a second-order rate law with respect to the concentration of the $[Co(NH_3)_5(dmso)]^{3+}$ complex, yielding typical saturation behaviour. This type of behaviour corresponds exactly to that predicted for an electron-transfer reaction preceded by an association step [*cf.* equations (1) and (2)]:

$$[Fe(CN)_5L]^{3-} + [Co(NH_3)_5(dmso)]^{3+} \overset{K_p}{\rightleftharpoons} [Fe(CN)_5L]^{3-}\|[Co(NH_3)_5(dmso)]^{3+} \quad (5)$$

$$[Fe(CN)_5L]^{3-}\|[Co(NH_3)_5(dmso)]^{3+} \xrightarrow{k_{et}} [Fe(CN)_5L]^{2-} + Co^{2+} + [NH_4]^+ + dmso \quad (6)$$

Thus, applying equation (4), the observed rate constant becomes (7). Equation (7), in its inverse form (8),

$$k_{obs.} = \frac{K_p k_{et}[Co(NH_3)_5(dmso)^{3+}]}{1 + K_p[Co(NH_3)_5(dmso)^{3+}]} \quad (7)$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_{et}} + \frac{1}{k_{et}K_p[Co(NH_3)_5(dmso)^{3+}]} \quad (8)$$

provides a useful way of determining k_{et} and K_p. Linear plots of $1/k_{obs}$ against $1/[Co(NH_3)_5(dmso)^{3+}]$ were obtained for all the substituted pentacyanoferrate(II) complexes. From the intercept and gradient of each plot the limiting rates of electron transfer and the association constants of the precursor complexes were evaluated. A summary of the k_{et} and K_p values for the imidazole, pyridine, isonicotinamide, pyrazine, and pyrazine-2-carboxamide complexes, including the activation and thermodynamic parameters, is shown in Table 2.

The association constants for the outer-sphere precursor complexes are nearly the same in this series, *i.e.* *ca.* 500 dm^3 mol^{-1}, and are practically temperature independent in the range 10—35 °C. The formation of the associated species is determined exclusively by the favourable ΔS, since $\Delta H \sim 0$. Such a pattern is typical of ionic association in solution,[8] where the desolvation process which takes place as the ions of opposite charge come together is the factor mainly responsible for the positive ΔS.

The Eigen–Fuoss[9] equation (9) has been frequently

$$K = (4\pi Na^3/3\,000)\exp[-U(a)/kT] \qquad (9)$$

$$\text{where } U(a) = \frac{Z_1Z_2e^2}{Da(1 + \kappa a)}$$

$$\text{and } \kappa = (8\pi Ne^2I/1\,000DkT)^{\frac{1}{2}}$$

used to estimate the association constant of ion pairs in solution. The theoretical values calculated for K_p using equation (9) show initially a dramatic dependence on the distance a between the reactants, which decreases rapidly as the separation increases. This is illustrated in Figure 1, for $|Z_1| = |Z_2| = 3$. Agreement between the theoretical and experimental values of K_p is attained only when the distance $a = 6$ Å. This distance is *ca.* 1 Å smaller than that estimated for the closest approach between the amminecobalt(III) and cyanoiron complexes.[2] The difference, which could be regarded as small, is actually critical since in the vicinity of $a = 6$ Å (Figure 1) a variation of 1 Å is enough to change K_p by a factor of greater than two. Besides this problem of accuracy, the lack of agreement between the theoretical and experimental values of K_p can also be due to specific interactions (*e.g.* charge-transfer, hydrogen bonding, *etc.*) not included in equation (9).

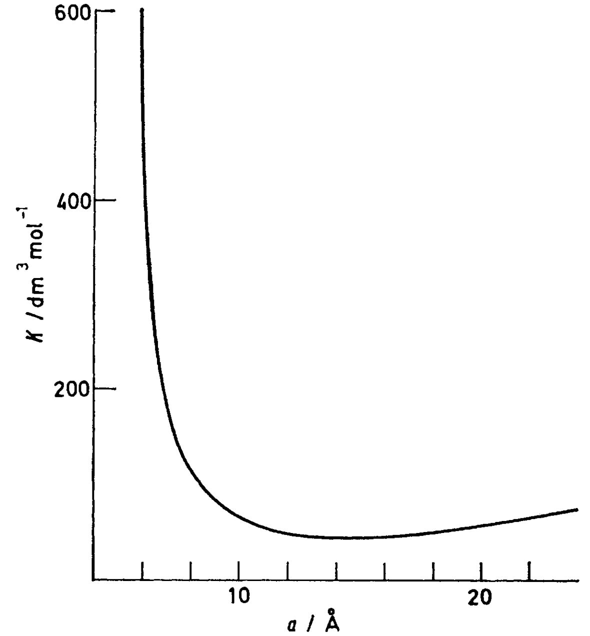

FIGURE 1 Variation of the theoretical association constants with the distance a for $|Z_1| = |Z_2| = 3$, 25.0 °C, and $I = 0.100$ mol dm^{-3}

TABLE 2

Kinetic and thermodynamic parameters for the outer-sphere reactions between $[Co(NH_3)_5(dmso)]^{3+}$ and $[Fe(CN)_5L]^{3-}$ complexes

L	$(T_1{}^a)$	$(T_2{}^a)$	$(T_3{}^a)$	ΔH^b	ΔS^b
Imidazole					
k_{et}/s^{-1}	$(4.2 \pm 0.1) \times 10^{-1}$	2.6 ± 0.2	7.6 ± 0.2	92 ± 2	71 ± 8
K_p/dm^3 mol^{-1}	$(5.3 \pm 0.3) \times 10^2$	$(4.5 \pm 0.5) \times 10^2$	$(5.7 \pm 0.3) \times 10^2$	*ca.* 0	52 ± 8
Ammonia^c					
k_{et}/s^{-1}	$(2.7 \pm 0.3) \times 10^{-1}$	1.3 ± 0.1	3.0 ± 0.1	94 ± 2	71.8
K_p/dm^3 mol^{-1}	$(5.3 \pm 0.6) \times 10^2$	$(4.2 \pm 0.5) \times 10^2$	$(5.2 \pm 0.3) \times 10^2$	*ca.* 0	52 ± 8
Pyridine					
k_{et}/s^{-1}	$(2.7 \pm 0.3) \times 10^{-2}$	$(1.5 \pm 0.2) \times 10^{-1}$	$(5.1 \pm 0.3) \times 10^{-1}$	100 ± 2	75 ± 8
K_p/dm^3 mol^{-1}	$(5.6 \pm 1.3) \times 10^2$	$(4.9 \pm 0.7) \times 10^2$	$(4.6 \pm 0.4) \times 10^2$	*ca.* 0	51 ± 10
Isonicotinamide					
k_{et}/s^{-1}	$(9.2 \pm 0.4) \times 10^{-3}$	$(5.0 \pm 0.5) \times 10^{-2}$	$(1.8 \pm 0.1) \times 10^{-1}$	102 ± 7	71 ± 24
K_p/dm^3 mol^{-1}	$(5.0 \pm 0.3) \times 10^2$	$(6.0 \pm 1.1) \times 10^2$	$(4.6 \pm 0.4) \times 10^2$	*ca.* 0	52 ± 10
Pyrazine					
k_{ct}/s^{-1}	$(1.7 \pm 0.1) \times 10^{-3}$	$(8.9 \pm 0.4) \times 10^{-3}$	$(2.9 \pm 0.3) \times 10^{-2}$	108 ± 6	75 ± 20
K_p/dm^3 mol^{-1}	$(4.5 \pm 0.3) \times 10^{-2}$	$(3.6 \pm 0.2) \times 10^2$	$(4.5 \pm 0.5) \times 10^2$	*ca.* 0	50 ± 8
Pyrazine-2-carboxamide					
k_{et}/s^{-1}	$(7.2 \pm 0.1) \times 10^{-4}$	$(4.7 \pm 0.1) \times 10^{-3}$	$(1.7 \pm 0.1) \times 10^{-4}$	109 ± 2	75 ± 8
K_p/dm^3 mol^{-1}	$(5.9 \pm 0.8) \times 10^2$	$(5.6 \pm 0.3) \times 10^2$	$(5.7 \pm 0.7) \times 10^2$	*ca.* 0	53 ± 4

[a] $T_1 = 11.6$, 13.8, 12.9, 12.7, 14.9, and 13.3 (± 0.2) °C, $T_2 = 25.0 \pm 0.2$ °C, and $T_3 = 33.8$, 32.0, 33.6, 33.5, 33.8, and 34.0 (± 0.2) °C, for the imidazole, ammine, pyridine, isonicotinamide, pyrazine, and pyrazine-2-carboxamide complexes, respectively. [b] Activation ($\Delta H^‡$ and $\Delta S^‡$) and thermodynamic parameters (ΔH and ΔS) in kJ mol^{-1} and J K^{-1} mol^{-1}, respectively. [c] Recalculated from ref. 5 including standard deviations from regression analysis.

The strong dependence of the limiting rates, k_{et}, on the nature of the ligand L in the $[Fe(CN)_5L]^{3-}$ complexes illustrates an interesting aspect of the role of non-bridging ligands[10] in electron-transfer reactions. Unsaturated ligands such as pyridine,[7] pyrazine,[7] and dimethyl sulphoxide[11] are known to stabilize the lower oxidation states of the pentacyanoferrates through back-bonding interactions with the filled metal d_π orbitals. This effect increases the oxidation potentials of the complexes,[12] changing the free energies of the electron-transfer reactions.

The relation between the free-energy change, $\Delta G^{\ominus}{}_{12}$, and the free energy of activation, $\Delta G^{*}{}_{12}$, of an outer-sphere electron-transfer reaction is given[13] by equation (10)

$$\Delta G^{*}{}_{12} = \frac{\Delta G^{*}{}_{11} + \Delta G^{*}{}_{22}}{2} + \frac{\Delta G^{\ominus}{}_{12}}{2} \qquad (10)$$

provided that $(\Delta G^{\ominus}{}_{12})^2 \ll 8(\Delta G^{*}{}_{11} + \Delta G^{*}{}_{22})$. In this expression, the subscript 12 refers to the cross reaction, and 11 or 22 to the exchange reactions. The activation free energies arise essentially from the reorganization of the inner and outer shells of the reactants, and are directly related to the limiting (intramolecular) electron-transfer rates, by[13] $k_{\text{et}} = pZ \,.\, \exp(\Delta G^{*}{}_{12}/RT)$. Under adiabatic conditions, p, the probability of electron transfer in the activated complex, is equal to 1. The activation parameters expressed in this way are not exactly

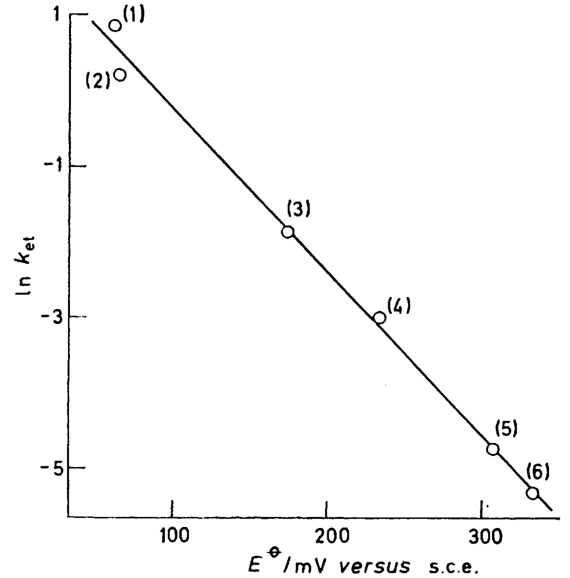

FIGURE 2 Plot of ln k_{et} against the oxidation potentials of the $[\text{Fe(CN)}_5\text{L}]^{3-}$ complexes at $I = 0.100$ mol dm^{-3} (lithium perchlorate), pH 4.7, and 25 °C. L = Imidazole (1), ammine (2), pyridine (3), pyridine-4-carboxamide (4), pyrazine (5), and pyrazine-2-carboxamide (6)

$$kr = p \,.\, \frac{kT}{h} \,.\, e^{-\Delta G^{\ddagger}/RT} \qquad (11)$$

the same as those calculated normally from temperature-dependence data, because the Eyring expression (11) from transition-state theory is different from the equation assumed in the Marcus derivations.

By assuming that Z, the collision frequency, is proportional to $T^{\frac{1}{2}}$, the following conversions have been proposed:[14]

$$\Delta G^{\ddagger} = \Delta G^{*} - RT\ln(hZ/kT) \qquad (12)$$

$$\Delta S^{\ddagger} = \Delta S^{*} + R\ln(hZ/kT) - \tfrac{1}{2}R \qquad (13)$$

$$\Delta H^{\ddagger} = \Delta H^{*} - \tfrac{1}{2}RT \qquad (14)$$

Since $\Delta G^{\ominus}{}_{12} = -nF(E^{\ominus}{}_{11} - E^{\ominus}{}_{22})$, a plot of ln k_{et} against $E^{\ominus}{}_{22}$, the oxidation potentials of the $[\text{Fe(CN)}_5\text{L}]^{3-}$ complexes, should be linear, under the assumption that the intrinsic barriers $(\Delta G^{*}{}_{11} + \Delta G^{*}{}_{22})/2$ are constant or proportional to $\Delta G^{\ominus}{}_{12}$. The theoretical gradient is predicted to be 0.50 (nF/RT), where n, R, F, and T have the conventional meaning. The existence of such a linear correlation can be seen in Figure 2. The calculated gradient of $0.57(nF/RT)$ is in reasonable agreement with that predicted theoretically. Comparison of the activation parameters collected in Table 2 shows that the trends in $\Delta G^{*}{}_{12}$ or k_{et} are determined essentially by $\Delta H^{\ddagger}$. The activation entropies associated with the electron-transfer step are always positive, but constant in the series. Since the electron is passing from a negative ion to a positive one the formal reduction of the net charges in the activated complex should be preceded by a desolvation process, responsible for the positive $\Delta S^{\ddagger}$.

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