A Novel Cross-reaction Relation for Redox Series

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Summary A modification of the simple Marcus cross-reaction relation, explicitly including fractions α of transition-state electron transfer different from one half, is shown to agree with observation for two redox series.

The observation[1] that rates for oxidations by eleven complexes $Co^{III}(am)_4LCl^{2+}$ of Fe^{2+}, V^{2+} and $Ru(NH_3)_6{}^{2+}$ yield the following correlations with non-unit slope, is in

$$\log k(V^{II}) = 0{\cdot}49 \log k(Fe^{II}) + 2{\cdot}68; \quad (1)$$

$$\log k(Ru^{II}) = 0{\cdot}83 \log k(Fe^{II}) + 5{\cdot}09 \quad (2)$$

contradiction of the simplest cross relation[2] for redox reactions in terms of self-exchange rates and equilibrium constants K. The rationalisation,[1] that the large K for Ru^{II} and even larger K for V^{II} reactions results in successive decreases in sensitivity of redox rate to effect of K is here made quantitative by identifying sensitivity with α the transition-state fraction of electron transfer. Thus $\alpha = 0{\cdot}5$ the usual value holds for K *ca.* unity and decreases for large K. We will infer α values (otherwise accessible only from putative wave mechanical calculation) from the observed slopes, and attempt calculation of the constant terms from them. The form resulting is $k_{12} = k_1^{1-\alpha} k_2^{\alpha} K_{12}^{\alpha}$, for reaction of species 1 with 2, which accords with the premise in regard to k_2 and K_{12}. For k_1 the exponent is chosen for dimensional consistency, and will introduce error which however can be minimised by choosing "1" as the species with the least self-exchange barrier, so invoking an erroneous fraction for only the lesser contribution to the total "12" activation barrier. (A comparable error is introduced in the usual cross-reaction relation by taking means of self-exchange energies.)

We apply this relation to the series noted: for reductants 1 and 2 (*e.g.* Fe^{II} and V^{II}) in reaction with a series of oxidants i,

$$k_{1i} = k_1^{1-\alpha_1},\ k_i^{\alpha}\ K_{1i}^{\alpha_1} \text{ and } k_{2i} = k_2^{1-\alpha_2}\, k_i^{\alpha_2}\, K_{2i}^{\alpha_2}$$

K_{Fei} being least, we set $\alpha_1 = \frac{1}{2}$ and eliminating the k_i, obtain equation (3). Comparison with (1) gives $\alpha_2 = 0{\cdot}245$,

$$\log k_{2i} = 2\alpha_2 \log k_{1i} + (1 - \alpha_2) \log k_2 - \alpha_2 \log k_1 + \alpha_2 \log (K_{2i}/K_{1i}) \qquad (3)$$

and use of the self-exchange[3] k for $Fe^{II,III}$ and for[4] $V^{II,III}$, with $K_{2i}/K_{1i} = K_{21}$ from electrode potentials,[5] leads directly to the value for the constant of 2·42, in excellent agreement with the observed 2·68. Use of the $Ru^{II,III}$ quantities[6] and the $\alpha_3 = 0{\cdot}415$ from comparison of (2) with (3) gives a calculated 5·84 to compare with 5·09.

The modified equation should have wide applicability, and its simplicity suggests that the systems tested follow the simplest of mechanisms, that is, outer-sphere.

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