The Marcus Inverted Region

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Many years ago, Marcus developed a quantitative model for predicting the rate constant for an outer-sphere electron transfer reaction [1]. The essence of the theory is based on the fact that the equilibrium nuclear configuration of a compound and its surrounding solvent molecules changes when it gains or loses an electron. For a transition metal complex, this configurational change involves changes in the vibrations and rotations of the solvent dipoles as well as changes in the metal-ligand and intraligand bond lengths and angles. Because the electron motion occurs on a time scale ($<10^{-15}$s) much faster that than of the nuclear motion(10^{-11}-10^{-13}s), the changes in the nuclear configuration result in an activation barrier to electron transfer.

Marcus found that the rate of electron transfer is given by equation 1 [1]

$$k = \kappa \rho Z \; \exp(-\Delta G^{\neq}/k_b T) \tag{1}$$

where, in a classical treatment of the nuclear motion,

$$\Delta G^{\neq} = w^r + \frac{\lambda}{4} \left(1 + \frac{\Delta G^O + w^P - w^r}{\lambda}\right)^2. \tag{2}$$

The transition coefficient κ is unity (since the reaction is assumed to be adiabatic); the factor ρ is approximately 1; Z is the bimolecular collision frequency; w^r is the work necessary to bring two charged reactants together and w^P is the corresponding term for the products; and λ is a term related to the reorganization of the inner and outer coordination spheres. The Marcus model has been found to predict the rate constants for many inorganic outer-sphere electron transfer reactions to within one or two orders of magnitude [2].

According to eqns. 1 and 2, at sufficiently high exoergicities (i.e., in the region where $|\Delta G^O + w^P - w^r|/\lambda > 1$), the rate of the reaction is expected to decrease with increasing driving force. Although Marcus predicted the possibility of this "inverted" region in 1960 [1d], experimental evidence for such behavior has only recently been obtained in fluid solution [3-6].

The first convincing experimental verification of the inverted region in fluid solution was reported by Closs and Miller in 1984 [3]. These workers prepared a series of molecules of the general structure A_x-Sp-Bi where Bi is biphenyl, Sp is a rigid saturated hydrocarbon spacer and A_x is one of eight different quinone or unsaturated hydrocarbon groups. Pulsed radiolysis was used to convert these molecules to the radical anions. The electrons were initially captured by either A_x or Bi with almost statistical probability. The rate at which this initial anion distribution attained equilibrium was obtained from optical absorption measurements. The data clearly show that the rate is initially enhanced with increasing exoergicity followed by an "inverted" region where the rates decrease with further increase in the driving force.

Wasielewski et al. [4] reported inverted rate behavior for intramolecular electron transfer reactions of a series of porphyrin molecules containing various quinone acceptor groups. The rates of formation and decay of the radical

pair states were obtained by laser flash photolysis methods. The rate constants for the radical ion recombination reaction were found to decrease over two orders of magnitude with increasing exoergicity. Similar results were obtained by Beddard et al. [5] for porphyrin molecules with quinone or methylviologen capping groups.

Very recently, inverted rate behavior has been observed for a series of bimolecular electron transfer reactions [6]. In these experiments, cyano-substituted anthracenes were used as the electron acceptors while naphthalene derivatives, diphenylacetylene and biphenyl were used as the electron donors. Quantum yield measurements were used to determine the rates of back electron transfer within photo-induced geminate radical ion pairs. The rate constants were found to decrease almost two orders of magnitude with increasingly negative ΔG^O values.

Although some experimental evidence of the inverted region has been reported for the quenching of polypyridineruthenium(II) $^*RuL_3^{2+}$ complexes by trivalent polypyridine ML_3^{3+} complexes (M = Cr, Os, Ru) [7] and for electron transfer reactions between metal-substituted cytochrome complexes [8], no unambiguous demonstration of the inverted region has been found for transition metal complexes. For some reactions involving metal-bipyridine complexes, it has been suggested that observation of inverted rate behavior is thwarted by alternate reaction pathways involving low-lying excited states [9].

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