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Dynamic Solvent Effects in Alcohol Solutions for Electron Transfer Reactions Involving the
Metalloenes

by

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Prepared for Presentation

at

The Electrochemical Society Meeting
Montreal, Canada, May 1990

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Kinetic data for simple electron transfer reactions, both homogeneous and heterogeneous, are examined for ferrocene, cobaltocene and other metallocenes in both aprotic and protic alcoholic solvents. Attention is focussed on the solvent dynamical effect for the pre-exponential factor of the electron transfer rate constant. It is shown that this effect, which has heretofore been considered anomalous in the alcohols, can be understood on the basis of the parameters for the second dielectric relaxation process, that is, by assuming that the reactant and product are chiefly solvated by solvent monomers, not by hydrogen bonded clusters.

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Dynamic Solvent Effects in Alcohol Solutions for Electron Transfer Reactions Involving the Metallocenes

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The role of the solvent in determining the rate of electron transfer reactions, both homogeneous and heterogeneous, has been the subject of intense interest in recent years [1-6]. As a result, it is now recognized that the solvent affects the rate constant for simple electron transfer reactions in at least two ways. On the basis of Marcus theory [7], the magnitude of the outer sphere contribution to the free energy of activation ΔG^* depends on the dielectric properties of the solvent. In addition, for adiabatic reactions in which the outer sphere contribution to ΔG^* is much larger than that due to inner sphere reorganization, the pre-exponential factor depends on the dynamical properties of the solvent [8]. As a result, for electron transfer reactions in which the inner sphere contribution to the free energy of activation, ΔG_{is}^* , is solvent independent, the electron transfer rate constant may be expressed by the equation

$$k_T = A \tau_L^{-\alpha} e^{-\Delta G_{is}^*/RT} e^{-\gamma} \quad (1)$$

where A is the solvent independent part of the pre-exponential factor, τ_L , the longitudinal relaxation time, α , a fraction varying between 0 and 1, γ , the solvent permittivity parameter, and g , a collection of constants together with the size-distance parameter for the reacting system [6]. Equation (1) has been shown to apply for a wide variety of kinetic data obtained in aprotic solvents for both homogeneous and heterogeneous electron transfer reactions [6].

The important parameter determining the solvent dependence of the pre-exponential factor is the longitudinal relaxation time τ_L . In the case of a simple Debye solvent it is defined as

$$\tau_L = \frac{\epsilon_\infty}{\epsilon_s} \tau_D \quad (2)$$

where ϵ_∞ is the high frequency value of the dielectric constant, ϵ_s , the static dielectric constant, and τ_D , the Debye relaxation time. The majority of aprotic solvents, with the possible exception of propylene carbonate [9], behave as simple Debye solvents so that τ_L can be estimated from dielectric relaxation data provided these data are available in the GHz frequency range or higher. In the case of the alcohols, the dielectric dispersion data are much more complex, exhibiting three relaxation regions which are attributed to the breaking and forming of hydrogen bonds in clusters, the rotational diffusion of monomers, and rotation of the -OH group in the monomer, in the low frequency range, microwave frequency range, and high frequency range, respectively [10]. Sumi and Marcus [11] argued that, when the reactant and product of the redox couple are predominantly solvated by alcohol clusters, and solvent clusters predominate with respect to solvent monomers, the longitudinal relaxation time is defined in alcohols by the relationship

$$\tau_L = \frac{\epsilon_{op}}{\epsilon_s} \tau_{D1} \quad (3)$$

where ϵ_{op} is the dielectric constant at optical frequencies (square of the refractive index), and τ_{D1} , the Debye relaxation time associated with the first dispersion region. On the other hand, if the reacting couple are predominantly solvated by alcohol monomers, then it is appropriate to define the longitudinal relaxation time using the equation [12,13]

$$\tau_L = \frac{\epsilon_{ir}}{\epsilon_{mw}} \tau_{D2} \quad (4)$$

where τ_{D2} is the Debye relaxation time for the second dispersion region, ϵ_{ir} , the infrared value of the dielectric constant and ϵ_{mw} , the microwave value. Values of τ_L calculated by equation (4) are at least an order of magnitude smaller than those calculated by equation (3). As a result, if the reactant is surrounded mainly by alcohol monomers, the frequency of formation of the pre-encounter complex for electron transfer is significantly higher in alcohols than previously assumed, the predicted value of the rate constants being much higher.

In the present paper, electron transfer kinetic data for ferrocene, cobaltocene, and other metallocene compounds in both aprotic and alcohol solvents [3-5] are re-examined with respect to the above question. It is shown that the anomalously fast rate constants observed in the alcohols are indeed normal with respect to those found in aprotic solvents if the longitudinal relaxation time is estimated on the basis of equation (4). The significance of these observations with respect to the solvent dependence of electron transfer processes and other rapid processes depending on solvent structure is discussed.

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