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Solvent Effects in the Electroreduction of Ferrocene at Pt in the Temperature Range 200-300 K

by

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Kinetic parameters for the electrooxidation of ferrocene have been obtained at low temperatures down to 193 °K at a Pt ultramicroelectrode (diameter, 25 μm) in three alcohol solvents, namely, methanol, ethanol, and n-propanol. In addition, data are reported in nine aprotic solvents at 285 °K. Kinetic data for this system show a strong dependence on the solvent's longitudinal relaxation time. The data obtained in the alcohol solvents are analyzed in detail to demonstrate the importance of faster relaxation processes in these solvents in determining the kinetic parameters.

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Solvent Effects in the Electrooxidation of Ferrocene at Pt in the Temperature Range 200-300 °K

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The effect of the solvent in the kinetics of simple electrode reactions has been the subject of considerable interest in recent years [1]. In the case of electron transfer reactions, one recognizes two ways in which the solvent influences the rate constant, namely, through its influence on the outer sphere contribution to the activation barrier, ΔG^*_{os} and through its dynamical role in affecting the pre-exponential factor. Weaver and coworkers [2, 3] have shown that the metallocenes are particularly good systems to examine solvent effects on electron transfer reactions for several reasons: they are neutral or have unit charge in the redox couple; they have low inner sphere reorganizational energies; and they can be considered spherical to a first approximation. the present study is concerned with ferrocene, a molecule which is oxidized at fairly positive potentials with respect to other metallocenes studied in this context [2]. The goal of this work was to examine the effect of the solvent over a wide range of temperature and in a number of solvents.

The kinetic data were obtained using either cyclic voltammetry or a.c. admittance measurements depending on the magnitude of the rate constant. The working electrode was an ultramicroelectrode made from a Pt wire with a radius of 12.5 μm which was sealed in a soft glass capillary. The tip of the capillary was prepared by polishing with extra fine carborundum paper followed by 0.3 μm alumina. The counter electrode was also Pt, and the Ag/Ag^+ system was used as reference. Constant temperatures down to -55 °C were obtained using a methanol bath in a Dewar flask whose temperature was controlled with an immersion cooler. For measurements at lower temperatures, the cell was cooled with liquid nitrogen and then slowly warmed up to the desired temperature. During the warming period, the solution was stirred and the temperature monitored using an internal thermometer. It was possible to keep the temperature in the cell constant to within 1 °C for several minutes by varying its height above the boiling liquid nitrogen in a Dewar flask in a similar manner to that used in NMR experiments.

Kinetic data were obtained in nine different aprotic solvents at 285 °K. The standard rate constant varied from a high of 2.6 cm s^{-1} in acetonitrile to a low of 0.14 cm s^{-1} in tetrahydrofuran. Values of the apparent transfer coefficient were all close to 0.5. We emphasize that the data reported here are more precise than those usually reported in the range in question, because of the fact that they were acquired at ultramicroelectrodes for which problems with uncompensated resistance are negligible.

A plot of the logarithm of the standard rate constant against the logarithm of the longitudinal relaxation time for the solvent is shown in Figure 1. A good linear relationship is obtained whose slope is very close to unity. This result suggests that the heterogeneous oxidation of ferrocene can be considered an adiabatic process. The scatter about the best straight line is attributed to variation in ΔG^*_{os} with solvent nature.

Kinetic data obtained in methanol, ethanol, and 1-propanol as a function of temperature are shown in Fig. 2. As one would expect on the basis of the solvent dynamical effect, the rate constant at a given temperature decreases with the molecular weight of the alcohol. When the data at 285 °K are compared with those obtained in aprotic solvents it is clear that the solvent dynamical effect in the alcohols is controlled by higher frequency relaxation processes in so far as electron transfer is concerned. From the slopes of the plots in Fig. 2, one estimates experimental enthalpies of activation equal to 9.7, 9.6, and 12.4 kJ mol^{-1} in methanol, ethanol, and 1-propanol, respectively. For a process in which solvent dynamical effects are important, the experimental enthalpy of activation, ΔH^*_{ex} is related to the true enthalpy of activation, ΔH^* by the equation [4]

$$\Delta H^*_{ex} = \Delta H^* + \alpha \Delta H_\tau \qquad (1)$$

where ΔH_τ is the enthalpy associated with the temperature dependence of the longitudinal relaxation time, and α, a coefficient related to the degree of reaction adiabaticity [5]. On the basis of dielectric relaxation data in the alcohols [6], ΔH_τ for the second relaxation process in the alcohols is less than ΔH^*_{ex} whereas ΔH_τ for the first relaxation process is greater. It follows that dynamical solvent effects related to the first relaxation process in the alcohols do not influence the rate of electron transfer if the coefficient α is unity as suggested by the data at 285 °K.

The above data are analyzed further to extract the Gibbs energy and entropy of activation for the electrooxidation of ferrocene. The results are compared with those reported earlier [7] for homogeneous electron transfer for this system and related ones. The significance of these data are discussed with respect to current theoretical developments in this area.

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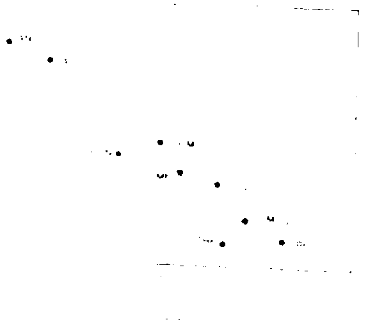

Figure 1. Plot of the logarithm of the standard rate constant for the electrooxidation of ferrocene at Pt against the logarithm of the solvents' longitudinal relaxation time for nine different aprotic solvents.

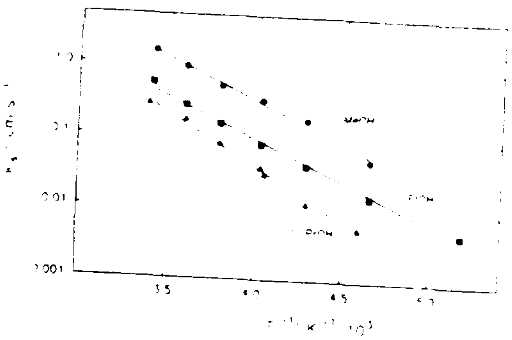

Figure 2. Plot of the logarithm of the standard rate constant for the electrooxidation of ferrocene at Pt against the reciprocal of the Kelvin temperature for data obtained in methanol (●), ethanol (■), and 1-propanol (▲).

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