

LETTERS

Electron Transfer Rates in Highly Exothermic Reactions on Semiconductor-Electrolyte Interfaces, and the Deuterium Isotope Effect

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Highly exothermic electron transfer rates were measured by semiconductor electrochemical techniques. Experiments demonstrate that the decreases in the electron transfer rates with the exothermicity of the reactions in so-called *abnormal regions* are much more moderate than the classical predictions, and that this is probably due to the effects of intramolecular vibrations such as C-H stretching and/or bending.

Introduction

Progress in charge transfer kinetics in condensed phases is mainly due to the theoretical works by Marcus,¹ Levich,² and Jortner.³ However, the kinetics of highly exothermic charge transfer remains to be clarified. Experimentally, impressive results were obtained by Rehm and Weller⁴ and Miller and his group.⁵ Those results show that in the highly exothermic region, in which the reaction free energy changes are more negative than its reorganization energy,

the electron transfer rates do not always obey classical predictions.

The experiments conducted so far had homogeneous conditions. The reaction free energy changes were controlled by the selection of proper donor and acceptor pairs. But, in our case, by the heterogeneous nature of the experiments, it is possible to continuously change the free energy of the electron transfer reactions with the electrode potential. So, the semiconductor electrochemical approach enables one to evaluate the electron transfer rate profile as a function of its free energy change.⁶

Experimental Section

Our experimental model was constructed with a ZnO electrode as the electron source and the monocation radical of normal and/or deuterium-substituted thianthrene as the electron acceptors. Normal thianthrene was purchased from a commercial source and deuterium-substituted

(1) Marcus, R. A. *J. Chem. Phys.* 1956, 24, 966. 1965, 24, 979. 1957, 26, 867, 872.

(2) Levich, V. G. In "Advances in Electrochemistry and Electrochemical Engineering"; Delahey, P., Ed.; Interscience: New York, 1966; Vol. 4, pp 249-372.

(3) (a) Jortner, J. *J. Chem. Phys.* 1975, 64, 4860. (b) Ulstrup, J.; Jortner, J. *Ibid.* 1975, 63, 4358. (c) Jortner, J. *J. Am. Chem. Soc.* 1980, 102, 6676. (d) Buhks, E.; Bixson, M.; Jortner, J. *J. Phys. Chem.* 1981, 85, 3763.

(4) (a) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* 1969, 73, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, 8, 259.

(5) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* 1979, 71, 4579.

(6) (a) Nakabayashi, S.; Fujishima, A.; Honda, K. *J. Electroanal. Chem.* 1982, 140, 223. (b) *J. Phys. Chem.* 1983, 87, 3487.

thianthrene was prepared by the recommended synthetic routes.⁷ These chemicals were purified at least 5 times by recrystallization from ethanol and final sublimation. The purities of these compounds were checked by the usual cyclic voltammetric measurements with a Pt electrode. The cation radicals were produced by preelectrolysis on a Pt electrode, and were found to be stable with lifetimes over 1 h under our experimental conditions. All electrochemical experiments were conducted in oxygen- and water-free acetonitrile-TBAP electrolyte.

The removal of water from the solvent was conducted by repeated vacuum distillation over the desiccant, P₄O₁₀. The removal of oxygen was carried out by freeze-pump-thaw cycles. All of these operations and the final preparations of the samples were performed under a vacuum line. The cell for electrochemical measurements was totally sealed from the ambient atmosphere.

A description of the system for measuring the electron transfer rate has been published previously.⁶ Essentially, the electrode potentials had been found to drop in the Helmholtz layer in the liquid phase in the potential region $E < -0.5$ vs. Ag. This confirms that changing the electrode potential in this region ($E < -0.5$ vs. Ag) makes it possible to vary the free energy change of the electron transfer reaction from the conduction band of ZnO to the electron acceptor in the liquid phase. To estimate the electron transfer rate, potential step chronoamperometry was employed in a time domain of about 1 ms. The time-dependent current profile had been found to obey the following equation⁶

$$i(t) = \frac{\Delta V}{R} \exp\left(-\frac{t}{RC}\right) + nFAk_0c_0^b \left[1 - 2k\left(\frac{t}{\pi D_0}\right)^{1/2} \right]$$

where the first term is the non-Faradaic one, and the second term is the linear-approximated Faradaic term for the irreversible electron transfer. ΔV , R , and C are the potential step height, resistance, and capacitance of the cell, respectively. k , c_0^b , and D_0 are the electron transfer rate constant, the bulk concentration, and the diffusion constant of the electron acceptors, respectively. Other symbols have the usual meanings.

The time-dependent current responses by the potential step perturbations were measured with a potentiostat and recorded in a transient memory for each electrode potential. From these results, electron transfer rates at different potentials were extracted by the curve-fitting procedures for the theoretical equation above.

Results and Discussion

The theory of electron transfer reactions in condensed media predicted by Marcus¹ was rearranged by Gerischer⁸ through the idea of the density of states in the liquid phase. The context permits the well-matched electronic model between the solid phase and the liquid phase. The heterogeneous electron transfer rate from the conduction band of ZnO to the electron acceptor in the liquid phase is confirmed to be represented as follows:⁸

$$k = Z \int_{-\infty}^{+\infty} \kappa(E) \rho(E) f(E) D(E, \lambda, E_{\text{red/ox}}) dE$$

where Z is the collision frequency of the reactant molecule upon the electrode surface, $\kappa(E)$, $\rho(E)$, and $f(E)$ are the adiabatic parameter, the density of states in the solid

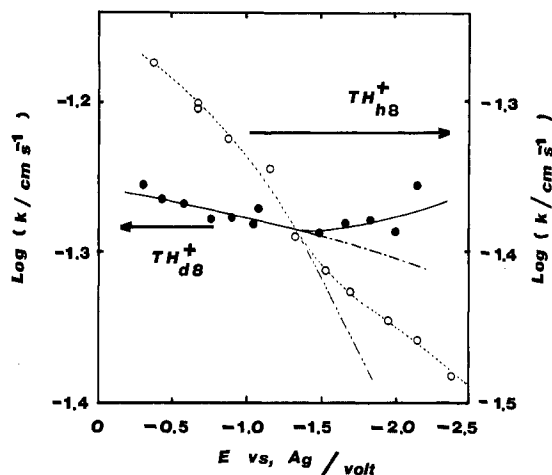


Figure 1. Plots of the logarithm of the rate constant for the reduction of the cation radicals of thianthrene and of deuterium-substituted thianthrene on a ZnO electrode vs. the electrode potential.

phase, and the Fermi function, respectively. $D(E, \lambda, E_{\text{red/ox}})$ is the line shape function of the density of states of the electron acceptor in the liquid phase, which will be the essential subject in the following discussion.

The flat-band potential of the ZnO single crystal electrode in contact with the ACN-TBAP electrolyte under our conditions had been found to be -0.3 V vs. Ag.⁶ The red/ox potentials of thianthrene/thianthrene monocation radical were found to be the same, $+1.25$ V vs. Ag, both for the normal and for the deuterium-substituted case. Then, the free energy change of the heterogeneous electron transfer reactions from the conduction band of the electrode to the acceptors is more exothermic than -1.55 eV ($-0.3 - 1.25/\text{eV}$), which is confirmed to be more exothermic than its reorganization energy (0.5 eV, approximately), i.e., these electron transfer reactions are considered to be in the abnormal region. Figure 1 shows the observed relationships between the rate of electron transfer to thianthrene and deuterium-substituted thianthrene monocation radicals and the electrode potentials. The rate decreases with the exothermicity of the reaction, where the exothermicity increases with the cathodic polarization of the electrode, were found to be clearly at variance with classical predictions. The observed rate decrease for normal thianthrene monocation radical was found to be about 30% with an electrode potential change from -0.5 to -1.5 V vs. Ag, where the free energy change of the reaction is supposed to be from -1.75 to -2.75 eV with a deviation of about 0.2 eV, which is attributed to the electron accumulation conditions on the electrode. And, the rate decrease was more moderate for the deuterium-substituted thianthrene monocation radical. These rate decreases are considered to be a few orders of magnitude smaller than that predicted by the classical theory.¹ However, these observed results show qualitative agreement with Rehm and Weller's experiments.⁴ It appears that the electron transfer rates in the abnormal region are quite incompatible with the basic postulate of classical theories,^{1,8} namely, that the electron transfer rates are dependent solely on the solvent reorganization energy which is represented by the dielectric properties of the solvent and the molecular volume of the reactant. As previously pointed out by Jortner,³ Levich,² and others,⁹

(7) Dougherty, G.; Hammond, P. D. *J. Am. Chem. Soc.* **1935**, *57*, 117.

(8) Gerischer, H. In "Advances in Electrochemistry and Electrochemical Engineering"; Delahey, P., Ed.; Interscience: New York, 1961; Vol. 1, pp 139-232.

(9) (a) Ulstrup, J. "Charge Transfer Processes in Condensed Media"; Springer-Verlag: New York, 1979, and references cited therein. (b) Kobayashi, K.; Aikawa, Y.; Sukigara, M. *J. Electroanal. Chem.* **1982**, *134*, 11.

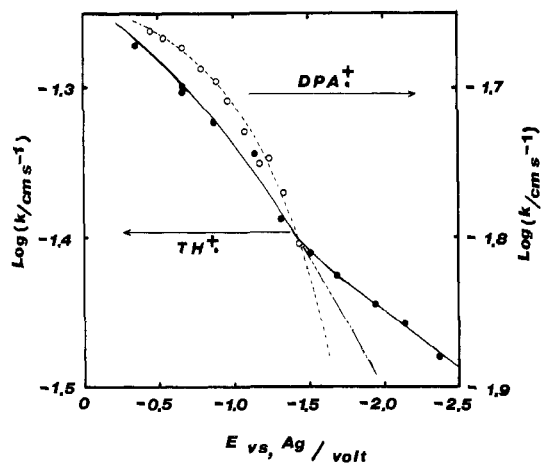


Figure 2. Plots of the logarithm of the rate constant for the reduction of the cation radicals of thianthrene and of 9,10-diphenylanthracene on a ZnO electrode vs. the electrode potential.

it must be considered that the intramolecular vibrational effects of the reactants are indispensable in abnormal electron transfer reactions; the decreases of the electron transfer rate in abnormal region are expected to be moderated by the vibrational excited products. Figure 1 suggests that C-H stretching or bending is one of the major contributions to these intramolecular vibrational effects, since the rate decreases are quite different between the normal and the deuterium-substituted thianthrene monocation radicals.

The rate decrease profiles in Figure 1 were found to be changed in the region more cathodic than -1.5 V vs. Ag. This may be caused by another electron transfer path being open at -1.5 V vs. Ag, which is assigned to electron transfer from the valence band of the ZnO electrode to the electron acceptors in the liquid phase, since at this potential the overlap between the acceptor density of states in the liquid phase and the donor density of states in the valence band of the electrode is expected to start, energetically.

Figure 2 shows the comparison between the normal thianthrene monocation radical and the 9,10-diphenylanthracene monocation radical, which had been measured by the same experimental procedures and reported previously.⁶ These two redox couples have the same redox potential and their solvent reorganization energies are

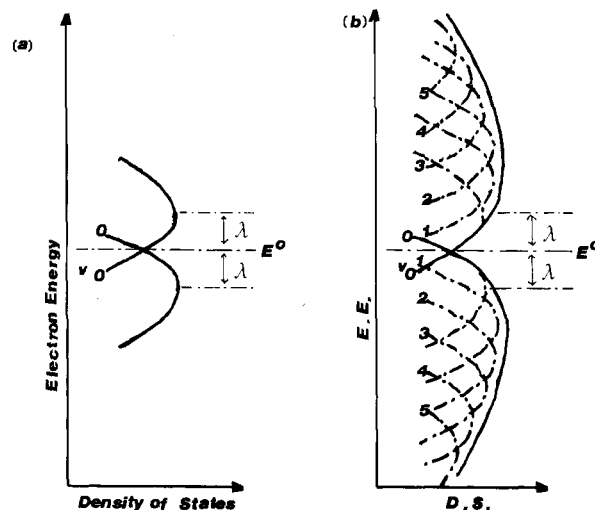


Figure 3. Schematic representations of the correlation between classical model (a) and vibronic model (b). (a) Upper solid branch shows the acceptor line shape function, and lower solid branch shows the donor line shape function. (b) Upper solid branch shows the acceptor line shape function, and lower solid branch shows the donor line shape function. Dashed lines (parabolas) show the line shape functions for each molecular vibrational state (v). Solid lines show the thermally averaged summation of each parabola (i.e., each molecular vibrational state).

assumed to be similar. The rate decrease profiles between the two seem to be the same in the region more anodic than -1.5 V vs. Ag. This leads to the conclusion that the vibrational modes of the two phenyl groups attached to the anthracene structure have little effect on the electron transfer rate in the abnormal region although, as is well-known, the molecular conformation of the thianthrene structure is slightly different from anthracene.¹⁰

Conclusion

Through the above discussion, intramolecular vibrations, such as C-H vibrations, are considered to play a decisive role in electron transfer kinetics in the *abnormal region*. To include these effects, Figure 3a, which is equivalent to the classical theory, must be corrected to Figure 3b, which shows the slow rate decreases in the *abnormal region* through the intramolecular vibrational assisted line shape function of the density of states in the liquid phase. We suppose that Figure 3b must be indispensable for the semiconductor photoelectrochemical point of view as well as simple electron transfer kinetics.

Registry No. ZnO, 1314-13-2; TH⁺, 34507-27-2; THd₈⁺, 87803-11-0; DPA⁺, 34480-04-1; deuterium, 7782-39-0.

(10) Fujikawa, H.; Kawamura, A.; Takagi, T.; Sakaki, Y. *J. Am. Chem. Soc.* 1983, 105, 125.