is slightly sharper than that of the TCNB in toluene solution immediately after the intracomplex geometrical rearrangement (at 4-ps delay time in Figure 1a). This might be ascribed to the fact that, in addition to the geometrical rearrangement within the 1:1 complex, the polar groups of PMMA contribute slightly to the increase of the charge separation. Since an accurate measurement of the transient absorption band shape was difficult in the case of the previous nanosecond laser photolysis studies,[4,8] the somewhat sharp band shape at 465 nm in PMMA matrix leads to the above conclusion of almost complete charge separation within the 1:1 complex caused by the intracomplex geometrical rearrangement.

We have also examined TCNB-benzene, -mesitylene, -durene, and -hexamethylbenzene complexes in PMMA matrix. In all cases, we have observed a broad transient absorption band with peak at 465 nm and with shoulders and tails. The contribution of the broad tail to the observed transient absorption spectrum decreases with decrease of the ionization potential of the donor. This result suggests that the absorption band shapes with broad tails originate from the incomplete charge separation in the S_1 state of the 1:1 complex in the polymer matrix and that the extent of the charge separation within the 1:1 complex increases with decrease of the donor ionization potential.

E. Concluding Remarks. It is well-known that the photoinduced CS is greatly enhanced by the interaction of the donor-acceptor system with polar solvent molecules.[1] In the above sections, we have demonstrated by means of femtosecond and picosecond laser photolysis and time-resolved transient spectral measurements on the TCNB in benzene and methyl-substituted benzene solutions that the configurational rearrangements including the geometrical change within the 1:1 complex as well as the 1:2 complex formation are necessary for the IP state formation in the course of the relaxation from the excited FC state. Whether such configurational changes necessary for the CS of these strongly interacting D-A systems in the nonpolar or only slightly polar environment are still necessary for the CS in considerably or strongly polar solvent, is an important and interesting problem and will be examined in subsequent papers.

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Theory of Electron-Transfer Rates across Liquid-Liquid Interfaces

R. A. Marcus

Noyes Laboratory of Chemical Physics,[†] California Institute of Technology, Pasadena, California 91125

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The theory developed in a previous paper for the geometry of the encounter complex, the reorganization energy, and the electron-transfer rate constant at a liquid-liquid interface is applied to existing data on the rate constant. To treat cyclic voltammetric (CV) studies of electron transfer across the interface, the nature of the encounters is examined and a bimolecular-type rate treatment is used. When one redox pair is in large excess, it has been pointed out that a single-phase CV analysis for diffusion/reaction can be utilized. In the present paper we avoid in this analysis the assumption that the second ("concentrated") phase is metallike. The experimental result deduced in this way for the true exchange current electron-transfer rate constant at the interface is compared with that estimated from the present theory of the rate constant, using metal-liquid electrochemical exchange rate constants. The type of agreement found is encouraging, considering the various approximations involved, and further experimental studies and tests would be of interest.

1. Introduction

Recently, we described a theory of electron transfer from one reactant to another, across an interface between two immiscible liquids.[1] The treatment focused on two aspects: the reorganization of the two solvent media prior to and after the electron transfer, and the geometrical aspects of a "precursor state" formed by the two reactants, each confined to its own liquid phase. To obtain some idea of the effect of partial reactant penetration of the other phase on the geometrical probability of forming a precursor state, an estimate of the latter was made also for the case where such penetration occurs. The results of ref 1 are extended and applied here to recent data on an electron-transfer reaction rate constant.[2]

2. Theory

We consider first the expression obtained[1] for the reorganization energy λ_0 for electron transfer across a liquid-liquid interface. From dielectric continuum theory λ_0 was found to be given by

$$\begin{aligned}\lambda_0 = {}& \frac{(\Delta e)^2}{2a_1}\left(\frac{1}{D_1^{\mathrm{op}}} - \frac{1}{D_1^{\mathrm{s}}}\right) + \frac{(\Delta e)^2}{2a_2}\left(\frac{1}{D_2^{\mathrm{op}}} - \frac{1}{D_2^{\mathrm{s}}}\right) - \\ & \frac{(\Delta e)^2}{4d_1}\left(\frac{D_2^{\mathrm{op}} - D_1^{\mathrm{op}}}{D_1^{\mathrm{op}}(D_2^{\mathrm{op}} + D_1^{\mathrm{op}})} - \frac{D_2^{\mathrm{s}} - D_1^{\mathrm{s}}}{D_1^{\mathrm{s}}(D_2^{\mathrm{s}} + D_1^{\mathrm{s}})}\right) - \\ & \frac{(\Delta e)^2}{4d_2}\left(\frac{D_1^{\mathrm{op}} - D_2^{\mathrm{op}}}{D_2^{\mathrm{op}}(D_1^{\mathrm{op}} + D_2^{\mathrm{op}})} - \frac{D_1^{\mathrm{s}} - D_2^{\mathrm{s}}}{D_2^{\mathrm{s}}(D_1^{\mathrm{s}} + D_2^{\mathrm{s}})}\right) - \\ & \frac{2(\Delta e)^2}{R}\left(\frac{1}{D_1^{\mathrm{op}} + D_2^{\mathrm{op}}} - \frac{1}{D_1^{\mathrm{s}} + D_2^{\mathrm{s}}}\right) \end{aligned} \tag{2.1}$$

In eq 2.1 D_i^{s} and D_i^{op} refer to the static and optical dielectric constants of phase i ($i = 1, 2$), Δe is the charge transferred, d_i is the perpendicular distance from the center of reactant i to the interfacial boundary, R is the center-to-center separation distance between the two reactants, and the a_i are the radii of the two reactants. Equation 2.1 differs in some respects from the one

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[†] Contribution No. 8037.

(1) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050.

(2) Geblewicz, G.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 27.

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appearing earlier in the literature.[3]

Apart from work terms the rate constant k_0 per unit concentration of each reactant and per unit area of interface was found to be[1]

$$k_0 = 2\pi(a_1 + a_2)\kappa\nu(\Delta R)^3 e^{-\Delta G^*/kT} \tag{2.2}$$

where ΔR appears in an exponent for the dependence of the rate of electron transfer on separation distance R ($\propto \exp(-R/\Delta R)$). Typically,[4,5] ΔR is about 1 Å, varying from this value for various systems investigated by less than a factor of 2; ν is a typical frequency for the nuclear motion along the reaction coordinate. If we omit work terms for simplicity (we return to them later), the free energy barrier to reaction ΔG^* is given by[4,6]

$$\Delta G^* = {}^1\!/_4\lambda(1 + \Delta G^\circ/\lambda)^2 \tag{2.3}$$

where λ equals $\lambda_0 + \lambda_i$, λ_i being the usual vibrational reorganization term. The κ in eq 2.2 is the usual adiabaticity/nonadiabaticity Landau-Zener factor.[4,6] Paralleling the arguments in ref 6 eq 2.3 can be obtained with statistical mechanics instead of dielectric continuum theory, but now λ_0 would be given by a statistical mechanical expression instead of by eq 2.1.

Equations 2.1 and 2.2 were derived for the case that each reactant did not penetrate the boundary between the two immiscible liquids. When each reactant can penetrate the other phase, such that the center of the reactant could even lie on the phase boundary, a larger preexponential factor was obtained, larger by a factor f:[1]

$$f = {}^1\!/_2(a_1 + a_2)^2/(\Delta R)^2 \tag{2.4}$$

The value of λ_0 for this case would be more complicated and was not estimated.

We next consider the relationship between the λ_0 in eq 2.1 and the reorganization energies, λ_0^{el}, for each reactant at the metal–liquid interface. Treating the metal as a classical electrical conductor and the solvent as a dielectric continuum, the λ_0^{el} are given by[4,6,7]

$$\lambda_{0,i}^{\mathrm{el}} = \frac{1}{2}\left(\frac{1}{a_i} - \frac{1}{2d_i}\right)\left(\frac{1}{D_i^{\mathrm{op}}} - \frac{1}{D_i^{\mathrm{s}}}\right) \tag{2.5}$$

where reactant i is in liquid phase i having dielectric properties D_i^{op} and D_i^{s}. We noted in ref 1 that for the particular case that $d_1 = d_2 = {}^1\!/_2R$ we have

$$\lambda_0 = \lambda_{0,1}^{\mathrm{el}} + \lambda_{0,2}^{\mathrm{el}} \tag{2.6}$$

More generally, it can be estimated that the two sides of eq 2.6 differ only by a quantity which is second order in $d_1 - d_2$: From eqs 2.1 and 2.5 we have

$$\lambda_0 - \lambda_{0,1}^{\mathrm{el}} - \lambda_{0,2}^{\mathrm{el}} = \frac{(\Delta e)^2}{2}\left(\frac{1}{D_1^{\mathrm{op}} + D_2^{\mathrm{op}}} - \frac{1}{D_1^{\mathrm{s}} + D_2^{\mathrm{s}}}\right)\left(\frac{1}{d_1} + \frac{1}{d_2} - \frac{4}{R}\right) \tag{2.7}$$

In the transition state one would expect that roughly $R \simeq d_1 + d_2$. The last factor in eq 2.7 then equals $(d_1 - d_2)^2/d_1d_2(d_1 + d_2)$, and so is of second order in $d_1 - d_2$. When $d_1 > d_2$ and the D^{op}'s are comparable, and the D^{s}'s also, and when $d_i \sim a_i$, the ratio of the right-hand side of eq 2.7 to the larger of the two λ_0^{el}'s, $\lambda_{0,2}^{\mathrm{el}}$, is $(d_1 - d_2)^2/d_1(d_1 + d_2)$, a factor of 1/6 when d_1 is as large as $2d_2$.

We next calculate the rate constant k_0 for the electron transfer across the interface of the two immiscible liquids. In addition to eq 2.6 there is also an additivity of the intramolecular terms λ_i for each reactant, since they can be assumed to be largely unaffected by the presence of the interface

$$\lambda_i = \lambda_{i,1} + \lambda_{i,2} \tag{2.8}$$

where $\lambda_{i,j}$ ($j = 1, 2$) is the intramolecular λ for reactant j.

Apart from work terms, the k_0 for the "exchange current" is obtained from (2.2) and (2.3)

$$k_0 = 2\pi(a_1 + a_2)(\Delta R)^3\kappa\nu \exp(-\lambda/4k_\mathrm{B}T) \tag{2.9}$$

when each reactant is confined to its own solvent phase. Here, $\lambda = \lambda_0 + \lambda_i$. The d_1, d_2, and R appearing in eqs 2.1 are the most probable values for the transition state of the two-immiscible-phase reaction.

The electrochemical rate constant (exchange current rate constant) for the metal–liquid system k_1^{el} is, omitting any work terms at the moment for brevity,[4,6,8]

$$k_1^{\mathrm{el}} = \Delta R\kappa\nu \exp[-(\lambda_{0,1}^{\mathrm{el}} + \lambda_{i,1})/4k_\mathrm{B}T] \tag{2.10}$$

A similar equation, with subscripts 2 instead of 1, applies to k_2^{el}. From eqs 2.6 and 2.8–2.10 we obtain

$$k_0 \cong 2\pi(a_1 + a_2)(\Delta R)^2(k_1^{\mathrm{el}}k_2^{\mathrm{el}})^{1/2} \tag{2.11}$$

when the d_i in the transition state for the two-immiscible-liquid system equals the d_i in the transition state for the ith metal–liquid system ($i = 1, 2$).

If, instead, the half-penetration expression were used for k_0, the right side of (2.11) would be multiplied by the factor f given in eq 2.4,[1] and the λ in eq 2.9 would also change, in a potentially complicated way.

When, instead of there being a fairly sharp boundary, the interfacial region is fairly thick (thickness L) and the reaction occurs homogeneously in that region, (2.9) is obtained but with the right-hand side multiplied by $2(a_1 + a_2)L/(\Delta R)^2$, a result to be derived elsewhere. When the additivity relation (2.6) still prevails for λ in this mixed-solvent region, (2.11) is again obtained but with the right-hand side larger by the above factor. For an $L \sim a_1 + a_2 \sim 10$ Å and $\Delta R \sim 1$ Å, this factor is $\sim$200.

3. Adaptation of a Single-Phase Cyclic Voltammetry Treatment to a Two-Immiscible-Liquid Electron Transfer

Geblewicz and Schiffrin[2] have applied a one-phase treatment[9] of cyclic voltammetry to the two-immiscible-liquid electron-transfer reaction. Nicholson solved the diffusion-reaction equation numerically for electron transfer at a metal–liquid interface.[9] They adapted that result to the electron transfer at a two-immiscible-liquid interface, by using a large excess of the redox pair in the second phase.[2] In this way only the diffusion-reaction problem in the first phase needed to be solved. They regarded the phase containing the concentrated redox pair as being metallike, and a one-phase treatment became immediately applicable. The authors took care to select reagents and a solvent pair to favor each reactant being confined to its own liquid phase, rather than using reactants which had some solubility in both phases.

To avoid this assumption of a metallike second phase we can proceed as follows. The liquid phase containing the concentrated redox pair is denoted by 2; $c_{0,i}$ denotes the concentration of the oxidized form of species i in liquid i ($i = 1, 2$) and $c_{\mathrm{r},i}$ the concentration of the corresponding reduced form. The flux of $c_{0,1}$ at the interface $x = 0$ is $-D\,\partial c_{0,1}/\partial x$ and the boundary condition at $x = 0$ in phase 1, namely that the diffusive flux there equals the reactive flux, can be written as

$$\left.\frac{D\,\partial c_{0,1}}{\partial x}\right|_{x=0} = k_0\left[c_{0,1}(0)c_{\mathrm{r},2} - c_{\mathrm{r},1}(0)c_{0,2}\exp\left[\frac{(E - E^\circ)ne}{k_\mathrm{B}T}\right]\right]f(E-E^\circ) \tag{3.1}$$

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(5) Siddarth, P.; Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 2985, and references to experimental data cited therein.

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(8) Cf., Marcus, R. A. *Int. J. Chem. Kinet.* **1981**, *13*, 865.

(9) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

where the $c(0)$'s denote the concentrations of the first redox pair at $x = 0$, D is a diffusion constant, phase 1 occupies the region $x \geq 0$, ne is the charge Δe transferred, and[4,6,7]

$$f(E-E^\circ) = \exp\left[\frac{(E-E^\circ)ne}{2k_BT} + \frac{(E-E^\circ)^2(ne)^2}{4k_BT\lambda}\right] \quad (3.2)$$

Here, E is the potential drop across the interface. E° is the potential drop which occurs when the forward and reverse rates at unit c's in (3.1) are equal: At equilibrium, it is seen from (3.1) that $E = E^\circ + (k_BT/ne)\ln[c_{0,1}(0)c_{r,2}/c_{r,1}(0)c_{0,2}]$.

The k_0 in eq 3.1 is given by eq 2.9 and the $(E-E^\circ)ne$ in eqs 3.2 and 3.3 is ΔG°, the "standard" free energy of reaction at the prevailing E for reaction 3.3:

$$\text{ox}_1(\text{phase 1}) + \text{red}_2(\text{phase 2}) \rightleftharpoons \text{red}_1(\text{phase 1}) + \text{ox}_2(\text{phase2}) \quad (3.3)$$

(The argument is similar to that in ref 6.)

To adapt a one-phase formalism to the present expression 3.1 we can approximate the function $f(x)$ via the Tafel formula (used, for example, in eq 7 of ref 9)

$$f(x) \cong e^{\alpha x ne/k_BT} \quad (3.4)$$

where α is the Tafel coefficient. Alternatively the numerical integration, e.g., that in ref 9, could be repeated by using eq 3.2 instead of 3.4, with λ instead of α being a parameter.

Equation 3.1 can be rewritten as

$$\left.\frac{D\,\partial c_{0,1}}{\partial x}\right|_{x=0} = k_s\left[c_{0,1}(0)c_{r,2} - c_{r,1}(0)c_{0,2}\exp\left[\frac{(E-E^\circ_N)ne}{k_BT}\right]\right]f(E-E^\circ_N) \quad (3.5)$$

where E°_N and k_s are, in the case of ref 9, Nicholson's E° and exchange rate constant. They are related to E° and k_0, upon comparing (3.1) with (3.5), by the relations

$$k_s = k_0c_{r,2}f(E-E^\circ_N)/f(E-E^\circ)$$
$$= k_0c_{r,2}[f(E-E^\circ_N)/f(E-E^\circ)]\exp[(E^\circ-E^\circ_N)ne/k_BT] \quad (3.6)$$

From eqs 3.4 and 3.6 we find that E°_N and k_s are the solutions of

$$c_{r,2}/c_{0,2} = \exp[(E^\circ - E^\circ_N)ne/k_BT] \quad (3.7)$$

and

$$k_s = k_0c_{0,2}{}^{\alpha}c_{r,2}{}^{(1-\alpha)} \quad (3.8)$$

It follows that the true rate constant k_0 can be obtained from the data by using eq 3.8 and the k_s, which in turn is obtained by fitting a solution based on 3.5 to the experimental CV data. The consistency of this interpretation of the experiment can be tested by seeing if, using different values of $c_{0,2}$ and $c_{r,2}$, the k_0 obtained from eq 3.8 is constant. (α could be inferred from the data on the CV curves.) As a further check of the interpretation, the E°_N can be obtained from the CV data as a function of the ratio $c_{r,2}/c_{0,2}$ and then eq 3.7 can then be tested for this system. (E° is independent of this ratio.)

4. Application of Theory

We turn next to an application of the present results to the data of Geblewicz and Schiffrin.[2] They studied the rate of electron transfer between the $\text{Fe(CN)}_6{}^{4-/3-}$ redox couple in aqueous solution and the lutetium biphthalocyanine couple $\text{Lu(PC)}_2{}^{+/2+}$ in 1,2-dichloroethane. Since the data were reported for only one pair of values of $c_{0,2}$ and $c_{r,2}$, eqs 3.7 and 3.8 cannot be tested with the existing data. In the absence of this additional information it will be supposed for the present purpose that $\alpha = 1/2$, the value expected from eq 3.2 when $(E-E^\circ)ne/2\lambda \ll 1$ (and when the work terms can be neglected). This value of $\alpha \simeq 1/2$ is common in metal–liquid systems.

The experimental values of k_s, $c_{r,2}$, and $c_{0,2}$ were 0.9×10^{-3} cm s^{-1}, 0.01 M, and 0.1 M, respectively. Thereby, from eq 3.8 we have

$$k_0 \cong 0.03\ \text{M}^{-1}\ \text{cm s}^{-1} \quad (4.1)$$

We next compare this result with the theoretical value estimated from eq 2.11. The value of k_2^{el} (aqueous ferro–ferricyanide pair) was determined by Geblewicz and Schiffrin[2] to be 0.035 cm s^{-1}. The value of k_1^{el} does not appear to have been measured as yet for the $\text{Lu(Pc)}_2{}^{+/2+}$ pair in 1,2-dichloroethane. Values for various metallocenes are in the neighborhood of 1 cm s^{-1}.[10] The k^{el} for the phthalocyanine compound may be somewhat larger because of its larger ionic size, unless it also has a higher λ_i. For concreteness we shall use $k_1^{\text{el}} \sim 1$ cm s^{-1} as one choice. If the sum of the radii, $a_1 + a_2$, of the two reactants is about 10 Å, then from eq 2.11 and[4,5] $\Delta R \sim 1$ Å, one finds

$$k_0 \simeq 0.01\ \text{M}^{-1}\ \text{cm s}^{-1} \quad (4.2)$$

Considering the various uncertainties stated above, particularly the unknown value of k_1^{el}, the values for k_0 in eqs 4.1 and 4.2 can be considered to be in reasonable agreement. Use of eq 2.4 for comparison, *assuming the same* λ, would yield a value larger than the k_0 given by eq 4.2 by a factor f of $\sim{}^1/_2(10)^2/1^2$, i.e., 50. While, at present, there is no need to assume such partial penetration, one cannot really eliminate it on this basis, since we have not calculated λ_0 for that case. Also, k_1^{el} should be measured, and there could be corrections to the k's for work terms, as noted in the next section.

We have considered in section 2 an alternative, thick interfacial region model, which for the particular parameters used there yields $\sim$2 M^{-1} cm s^{-1} instead of (4.2).

It will be useful to explore some questions further when more systems have been studied, both for the liquid–liquid and the corresponding metal–liquid systems. In an earlier experimental study[11] the rate of electron transfer between aqueous $\text{Fe(CN)}_6{}^{4-/3-}$ and ferrocene $\text{FeCp}_2{}^{0/+}$ in nitrobenzene had been investigated, but the $\text{FeCp}_2{}^+$ ion is somewhat soluble in water. No rate constants k_s were determined in that study from the cyclic voltammetry data, although it might be interesting to again apply some single-phase analysis, as in ref 2, making use also of the present eqs 3.7 and 3.8.

5. Remark on Work Terms

The relevant work terms are w^r, the work to bring the two reactants from the body of each phase to their mean separation distance in the transition state, and $-w^p$, the corresponding work to separate the products. Paralleling the arguments in ref 6, eqs 85 and 86 there, eq 2.3 for ΔG^* would be replaced by

$$\Delta G^* = w^r + {}^1\!/_4\lambda(1 + [\Delta G^\circ + w^p - w^r]/\lambda)^2 \quad (5.1)$$

Consequently, the right-hand side of eq 2.9 would contain an additional factor $\exp[(w^r + w^p)/2k_BT]$. Equation 2.11 would now refer to k_0, k_1^{el}, and k_2^{el}, where each had been corrected for the work terms. Instead of the $(E-E^\circ)ne$ in eq 3.2 we would have (ref 5, eq 86) $(E-E^\circ)ne + w^p - w^r$. Reference 6 also contains approximate expressions for the reorganizational contribution of the supporting electrolyte to λ (eqs 91 and 92), when specific ionic effects are absent. An analogous expression could be derived for the present (liquid/liquid) system.

In the case of the dependence of the rate of the forward step on $E-E^\circ_N$ in eqs 3.1 and 3.4, the α can differ in principle from $^1/_2$, even when $(E-E^\circ)ne/2\lambda$ is small, because of the work terms. Each of them, w^r and w^p, contains essentially three contributions, one due to double-layer effects in phase 1, another due to such effects in phase 2, and a third due to the interaction of reactants 1 and 2. The first two of these contributions can vary when E

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[10] Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787.

[11] Samec, Z.; Mareček, V.; Weber, J.; Homolka, D. *J. Electroanal. Chem.* **1981**, *126*, 105.

is varied and so contribute to α. The role of α via eqs 3.1 and 3.4 is to correct the rate constant to the value k_s it would have at $E = E°_N$ (eq 3.5). The value of k_0, obtained via eq 3.8, is then to be compared with the theoretical k_0 obtained from eqs 2.2 and 5.1. Alternatively, should one wish to test eq 2.11, the experimental k_0 can be corrected for the work terms by using eq 5.1, and then compared with k_1^{el} and k_2^{el}, as in eq 2.11, each having also been corrected for the work terms.

In the case of the work terms mentioned there may be an advantage to minimizing the electrostatic contribution to them, by (1) *using large supporting electrolyte concentrations and* (2) using reactants and products with small or zero charge. The increased supporting electrolyte reorganizational contribution to λ will be larger, at larger electrolyte concentrations, but may approximately cancel in a ratio such as $k_0/[k_1^{el}k_2^{el}]^{1/2}$ in eq 2.11. Should it be necessary in other cases to calculate the work terms there is an option of doing so with numerical, e.g., Monte Carlo, or continuum-like (e.g., modified Gouy–Chapman), or still other methods.[12] Which method would be employed, or whether one would be employed at all, would depend both on the experimental conditions and on experimental results on the effect of supporting electrolytes on the rate constants. Some discussion of electrolyte effects on equilibrium properties of interfaces is given in ref 12. The use of a large supporting electrolyte concentration also serves to uncouple the electron transfer across the interface from any ion transfer, which might otherwise have been required to maintain local electrical neutrality.

The various approximations made in obtaining the principal equations, eq 2.11, have been mentioned. It is possible, as has happened in earlier work,[6] that ratios of rate constants such as 2.11 involve somewhat milder assumptions than those used to derive individual expressions for each rate constant. Nevertheless, some of the assumptions made in deriving, say, 2.2 may be summarized: They include an "ideal" (sharp boundary) interface, a local and linear dielectric continuum theory, spherical reactants, and no specific reactant–solvent or reactant–reactant effects. Use of more refined treatments of these aspects can be expected to lead to more accurate though also to more complicated expressions with more detailed information or parametrization being needed for interpretation of experiments. Such detailed approaches can be considered as complementary to the present first-order type theory, as recent statistical mechanical results for an electron transfer in homogeneous solution have already shown.[13]

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[12] Samec, Z.; Maraček, V. In *The Interface Structure and Electrochemical Processes at the Boundary Between Two Immiscible Liquids*; Kazarinov, V. E., Ed.; Springer-Verlag: New York, 1987. This article mentions shortcomings of a Gouy–Chapman-type analyses. Other references which provide information on the work terms include: Girault, H. H. J.; Schiffrin, D. J. *Electroanal. Chem.* **1989**, *15*, 1 and references cited therein. Among the latter are various Gouy–Chapman-type calculations (e.g., Samec, Z.; Mareček, V.; Holub, K.; Račinský, S.; Hájková, P. *J. Electroanal. Chem.* **1987**, *225*, 65) and a Monte Carlo calculation (Torrie, G. M.; Valleau, J. P. *J. Electroanal. Chem.* **1986**, *206*, 69).

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Laser Induced Fluorescence Studies of the Reactions of $NH(a^1\Delta)$ with NO and HCN

W. Hack* and K. Rathmann

Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, West Germany

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The reactions of electronically excited imidogen $NH(a^1\Delta)$ with NO and HCN have been studied at room temperature and low total pressures (20 mbar): NH(a) + NO → products (1); NH(a) + HCN → products (2). NH(a), produced by laser photolysis of HN_3 at $\lambda_L = 308$ nm, was detected directly by laser-induced fluorescence (LIF). Measurements of the rate constants were performed under pseudo-first-order conditions, i.e., $[R] \gg [NH(a)]$, whereby the time resolution resulted from the delay between the photolysis and the probe lasers. The following rate constants were measured at $T = 298$ K: $k_1 = 1.7 \times 10^{13}$ cm³/(mol s); $k_2 = 2.1 \times 10^{13}$ cm³/(mol s). Direct detection of the primary products NH(X), OH(X), $NH_2(\tilde{X})$, $CH_2(\tilde{a}^1A_1)$, and CN(X) was performed by LIF. The contribution of physical quenching of NH(a) to form NH(X) for reactants NO and HCN was found to be 40% and 4%, respectively. In reaction 1 OH and in reaction 2 CN were detected as chemical products.

Introduction

The electronic structure determines the reactivity of any chemical species. An intriguing radical with which to study experimentally the influence of electronic structure on reactivity is the imidogen radical in its five lowest electronic states [$NH(X^3\Sigma^-, a^1\Delta, b^1\Sigma^+, c^1\Pi$, and $A^3\Pi)$]. The reactions of NH(a) have attracted the experimental and theoretical interest, mainly since it is isoelectronic to $CH_2(\tilde{a})$ and $O(^1D)$. The excitation energy of NH(a), $\Delta E_{el} = 151$ kJ/mol, lies between the excitation energies of $O(^1D)$ (190 kJ/mol) and $CH_2(\tilde{a}^1A_1)$ (39 kJ/mol).

HN_3 or HNCO laser photolysis provides a suitable NH(a) source.[1] Three different methods to detect NH(a) directly are described in the literature, namely, absorption,[2] laser-induced fluorescence (LIF),[3] and phosphorescence from the forbidden transition NH(a–X),[4] besides the somewhat more indirect method using the chemiluminescence of $NH_2(\tilde{A}^2A_1)$ formed in the reaction $NH(a) + HN_3 \rightarrow NH_2(\tilde{A}) + N_3$. In this work LIF, by means of the (c–a) transition, was used to detect NH(a) since it is a very sensitive method and simultaneously enables direct detection of NH(X) by the A–X transition formed by physical quenching.

Several reactions of NH(a) have been studied. The quenching by inert gases[4,5] was found to be significantly slower than quenching of $CH_2(\tilde{a})$[6] due to the small energy gaps between

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