Theory of Electron-Transfer Rates across Liquid–Liquid Interfaces. 2. Relationships and Application

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In part 1 an expression was obtained for the exchange current rate constant k_{12}^{II} for an electron transfer between a reactant in one liquid and a second reactant in a second immiscible liquid, across an (assumed) sharp interfacial boundary. This expression is used to obtain a relation between k_{12}^{II} and the self-exchange rate constants k_{11} and k_{22} for electron transfer in homogeneous solutions, each redox species being in its respective liquid phase. The relation provides an extension of the "cross-relation" for one-phase electron transfer to this two-phase case. An expression is also given relating k_{12}^{II} to the usual metal–liquid electrochemical exchange current rate constants k_1^{el} and k_2^{el}, these k^{el}'s referring to each reactant in its respective solvent phase. An alternative limiting model for the interfacial region is also considered, in which that region is now broad, instead of sharp. The results of both models are compared with the limited available kinetic data, and the desirability of further experimental studies is noted.

1. Introduction

Recently, Geblewicz and Schiffrin[1] described the measurement of electron-transfer rates across an interface of two immiscible liquids, from a reactant in one liquid to a second reactant in the second liquid. The kinetic measurements, the first of their kind, are interesting in their own right and for the information they can provide on electron transfers across boundaries and on the interfacial region itself. In an article, denoted hereinafter as part 1,[2] it was shown how the results obtained by Geblewicz and Schiffrin could be used to determine "exchange current" rate constants k_{12}^{II} for the electron transfer per unit area across the interface (units of M^{-1} cm s^{-1} for the rate constants). Geblewicz and Schiffrin[1] assumed a "degenerate" metal model for one of the phases, an approximation replaced in part 1 by a bimolecular treatment for the interfacial electron transfer.

In the present paper the cross-relation, derived many years ago for homogeneous solutions,[3,4] which relates the rate constant k_{12} of a "cross-reaction" to the self-exchange rate constants k_{11} and k_{22}, all measured in the same solvent, is extended to this two-phase system (section 2). We also relate k_{12}^{II} to the electron-transfer exchange current rate constants k_1^{el} and k_2^{el} for these two systems, each for its respective liquid–metal electrode system (section 2).[2b]

In the model used in part 1 for the two-phase system a sharp boundary interface is assumed. An alternative limiting model is one where the boundary region is, instead, perhaps several molecular layers thick and has an electron-transfer reorganization energy λ which is approximately the mean of those of the pure phases. Rate constant expressions based on such a model are given for comparison in section 2. The results for these two limiting models are compared in section 3 and applied to the available kinetic data, namely, that of Geblewicz and Schiffrin.[1] The need for further data to test theory adequately is noted: several theoretically predicted relationships of concentration dependences and of other effects, for example, derived in part 1 could be tested with appropriate variation of experimental conditions.[2] Further, the measurement of both k_1^{el} and k_2^{el} is needed in one of the tests, but only k_1^{el} for the system studied in ref 1 is presently known, and even it may be complicated by the high charges of the reactants and the resulting ion pairing and other salt effects. Further extension of these interesting and pioneering experiments to other conditions and to other systems would be especially instructive.

Various results are discussed in section 4, including an additivity approximation, shown there to be valid to second order in the difference in the radii of the two reactants. As noted there, the deviation is of the same form as that[4] for the usual one-phase cross-relation. Electrostatic dielectric image effects occur in sharp boundary two-phase systems and so play an important role in the various theoretical relations deduced here and elsewhere.[2,4,5] They are discussed in section 4, using a new result[6] on fast electrochemical rates obtained with nanometer-sized electrodes. A possible implication for image effects, which are occasionally omitted in the literature in treating reorganization energies at metal–liquid interfaces, is discussed in section 4.

2. Theoretical Relations

i. Sharp Boundary Model. In a derivation for the rate constant k_{12}^{II} for an electron-transfer reaction, eq 1, between a reactant 1

$$Ox_1(\text{liq } 1) + Red_2(\text{liq } 2) \rightarrow Red_1(\text{liq } 1) + Ox_2(\text{liq } 2) \quad (1)$$

in one liquid and reactant 2 in a second, immiscible liquid, it was shown that for a sharp boundary model of the interface k_{12}^{II} is given by[5,7]

$$k_{12}^{II} = 2\pi(a_1 + a_2)(\Delta R)^3 \kappa\nu \exp(-\Delta G^*/k_B T) \quad (2)$$

where in eq 1 Ox_i and Red_i are the oxidized and reduced forms of reactant i. In eq 2, ν is a typical frequency of molecular motion, the a's are the reactants' radii, the reactants being treated as spherical, κ is a nonadiabatic factor at the distance of closest approach of the reactants ($\kappa = 1$ for an adiabatic electron transfer at that distance), and ΔR is the parameter appearing in the expression $\exp(-R/\Delta R)$ for the dependence of electron transfer rate on separation distance R between the reactants. ΔR is usually denoted by β^{-1} in the literature and is typically[8] about 1 Å. For the case of "work term corrected rate constants", ΔG^* is given by[2,4,9]

$$\Delta G^* = (\lambda/4)(1 + \Delta G^{\circ\prime}/\lambda)^2 \quad (3)$$

$\Delta G^{\circ\prime}$ being the "standard" free energy of reaction 1 for the prevailing media. More precisely, for the present case where the reaction occurs across a liquid–liquid interface, the driving force $\Delta G^{\circ\prime}$ is replaced by[2,4,9] $(E - E^{\circ\prime})ne$, where n is the number of electrons transferred in the reaction, e is the electronic charge, E is the potential drop across the interface, and $E^{\circ\prime}$ is the

† Contribution No. 8182.

(1) Geblewicz, G.; Schiffrin, D. J. *J. Electroanal. Chem.* **1988**, *244*, 27.
(2) (a) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 4152 (part 1). (b) Addendum. *Ibid.* **1990**, *94*, 7742.
(3) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *No. 29*, 21.
(4) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.
(5) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050.
(6) Penner, R. M.; Heben, M. J.; Longin, T. L.; Lewis, N. S. *Science* **1990**, *250*, 1118.
(7) Equation 2 is given by eqs 26 and 27 of ref 5.
(8) E.g.: Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
(9) Reference 4, eqs 85 and 86.

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equilibrium potential drop that occurs when the forward and reverse rates are equal, at unit concentrations of all four species in reaction 1:

$$\Delta G^{\ddagger} = (\lambda/4)[1 + ne(E - E^{\circ\prime})/\lambda]^2 \quad (4)$$

In eqs 3 and 4, λ is the reorganization energy, being approximately equal to[2]

$$\lambda = \lambda_1^{el} + \lambda_2^{el} \quad (5a)$$

where λ_i^{el} is the λ for reactant i in liquid i at a metal–liquid interface. Similarly, as seen below

$$\lambda = \tfrac{1}{2}(\lambda_{11} + \lambda_{22}) \quad (5b)$$

where λ_{11} is the λ for a self-exchange reaction between the oxidized and reduced forms of reactant 1 in liquid 1, and λ_{22} is similarly defined. The additivity relations, eqs 5a and 5b, are discussed later in section 4.

In obtaining eq 5a it is assumed in ref 2 and in the present section 4 that the distance from reactant 1 to the liquid–liquid interface in the transition state of the reaction 1 is about the same as that in the liquid–metal electrode case and that typically the two reactants are not "off-center" in the transition state. (In the liquid–metal case the distance referred to one-half the distance from the center of the reactant to its electrostatic image in the metal.[10])

The rate constant for an electron transfer at a metal–liquid interface k^{el} is given by[2]

$$k^{el} = \kappa\nu(\Delta R) \exp(-\Delta G^{el,\ddagger}/k_B T) \quad (6)$$

where[4,9]

$$\Delta G^{el,\ddagger} = (\lambda^{el}/4)[1 + n(E - E^{\circ\prime})e/\lambda^{el}]^2 \quad (7)$$

E being the metal–solution potential difference, $E^{\circ\prime}$ the "standard" value in the prevailing electrolyte medium, and λ^{el} the reorganization energy, a subscript i (i = 1 or 2) being added to the various quantities to obtain k_1^{el} or k_2^{el}.

The corresponding expression for the rate constant k_{12} of a homogeneous electron-transfer reaction is[2,8,9,11]

$$k_{12} = 4\pi(a_1 + a_2)^2 \Delta R \kappa\nu \exp(-\Delta G^{\ddagger}/k_B T) \quad (8)$$

where $\Delta G^{\ddagger}$ is again given by eq 3 for a work term corrected rate constant, but now λ and $\Delta G^{\circ\prime}$ refer to reaction 1 in a homogeneous system. For a self-exchange reaction between the oxidized and reduced forms of reactant 1, k_{12} becomes k_{11}, $a_2 = a_1$, $\Delta G^{\circ\prime} = 0$, and $\lambda = \lambda_{11}$.

From eqs 2 to 8 various relations can be derived, such as that between k_1^{el} and the self-exchange constant k_{11}.[4] Another relation is that between k_{12}^{II}, k_1^{el}, and k_2^{el}. We consider first the case where $E = E^{\circ\prime}$ in eq 4. Thereby, k_{12}^{II} now refers to the "exchange current" rate constant for electron transfer across the interface. From eqs 2, 4, 5a, 6, and 7 we have (cf. also ref 2b)

$$k_{12}^{II} = [2\pi(a_1 + a_2)\Delta R/\kappa\nu]k_1^{el}k_2^{el} \quad (E = E^{\circ\prime}) \quad (9)$$

Alternatively, if eqs 5b and 8 are used instead of eqs 5a and 7, we have

$$k_{12}^{II} = [(\Delta R)^2/2(a_1 + a_2)](k_{11}k_{22})^{1/2} \quad (E = E^{\circ\prime}) \quad (10)$$

ii. Several Layer Deep Interfacial Region Model. As noted in part 1, one alternative limiting simple model for the interface of a pair of immiscible liquids is one in which the change of composition occurs over a distance L, perhaps of the order of a few solvent molecules thick. In this case $\Delta G^{\circ\prime}$ becomes a varying function of the position in this interfacial layer, and there is also a concentration variation of each reactant in the region. We consider for the comparison the case where the conditions are such that $\Delta G^{\circ\prime} = 0$ (i.e., $E = E^{\circ\prime}$) and that the interfacial layer, of thickness L, is more or less uniform in solvent composition. We shall assume λ in this layer to be the sum of λ_1^{el} and λ_2^{el} so that eqs 5a and 5b remain applicable and ignore any preferential solubility or concentration gradient of a reactant in the interfacial region. There are various elaborations of this model which are possible, e.g., using a dielectric continuum treatment for the three phases with the middle phase varying in composition in some more or less linear manner between the two outer phases and then calculating the reorganization energy and work terms. Computer simulations treating the solvents at the molecular level should provide a useful guide for this and other elaborations of the various models.

In this case of an interfacial layer rather than an interfacial boundary, the rate constant k_{12}^{II} is given by the bimolecular rate constant in eq 8, multiplied by the volume of the interfacial region per unit cross-sectional area, namely, multiplied by the layer thickness L. Thus, for this model we have, at $E = E^{\circ\prime}$

$$k_{12}^{II} = 4\pi(a_1 + a_2)^2 \Delta R L \kappa\nu \exp(-\lambda/4k_B T) \quad (E = E^{\circ\prime}) \quad (11)$$

Comparing eqs 2 and 3 with eq 11, we see that the latter is larger by a factor of $2(a_1 + a_2)L/(\Delta R)^2$, the factor cited, though not derived, in part 1. We now have, instead of eqs 9 and 10

$$k_{12}^{II} = [4\pi(a_1 + a_2)^2 L/\Delta R\, \kappa\nu]k_1^{el}k_2^{el} \quad (E = E^{\circ\prime}) \quad (12)$$

and

$$k_{12}^{II} = L(k_{11}k_{22})^{1/2} \quad (E = E^{\circ\prime}) \quad (13)$$

The k_{12}^{II} given by eqs 9, 10, 12, and 13 refers to an exchange current k, as noted above. For other values of E, the potential drop across the interface differs from $E^{\circ\prime}$ and the right-hand sides of these equations should be multiplied by a factor f_E deduced from eq 4:

$$f_E = \exp\{[(E - E^{\circ\prime})ne/2k_B T] + [(E - E^{\circ\prime})ne]^2/4\lambda k_B T\} \quad (14)$$

As in the usual cross-relation[4] the λ in eq 14 can be expressed in terms of the self-exchange k's and also, in the present case, of the k^{el}'s. For example, from eqs 5a, 6 (at $E = E^{\circ\prime}$), and 7, it is seen that

$$\exp(-\lambda/4k_B T) = k_1^{el}k_2^{el}/Z_{el}^2 \quad (15a)$$

where Z_{el} denotes

$$Z_{el} = \kappa\nu\Delta R \quad (15b)$$

Alternatively, λ can be expressed in terms of the self-exchange homogeneous rate constants, using eqs 5b, 8, and 10

$$\exp(-\lambda/4k_B T) = (k_{11}k_{22}/Z_{soln}^2)^{1/2} \quad (16a)$$

where Z_{soln} denotes

$$Z_{soln} = 4\pi(2a)^2 \Delta R \kappa\nu \quad (16b)$$

a subscript 1 or 2 being added to Z's in eqs 15 and 16 if they differ substantially for the two reactants.

3. Application

At present only one rate constant for electron transfer from a reactant 1 in one liquid to a reactant 2 in a second immiscible liquid has been reported experimentally.[1] The reaction studied was that between the lutetium biphthalocyanine couple $LuPc_2^{+/2+}$ in 1,2-dichloroethane and the hexacyanoferrate couple $Fe(CN)_6^{4-/3-}$ in aqueous solution. The value measured for k_{12}^{II} at $E = E^{\circ\prime}$, when reinterpreted as in part 1, is about 0.03 M^{-1} cm s^{-1}.

The value of k^{el} for the hexacyanoferrate electron transfer at a metal/aqueous solution interface, measured by Geblewicz and

(10) When a dielectric continuum treatment is used for the metal and one for the liquid, there is a sharp boundary between the two phases, and the cited distance equals that from the charge center of the ionic (or future ionic) reactant to this boundary. In a molecular treatment for an ion in solution in the presence of the metal, the interaction energy is calculated as a function of distance and at longer distances the result can be fitted to an image contribution. An effective distance from the charge to this image can be deduced from this plot. The half-distance typically differs by a few tenths of an angstrom from the distance from the charge center to a plane displaced outward one-half a lattice spacing from the surface layer of metal atoms. Cf. ref 24 in ref 5.

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

Schiffrin,[1] is 0.035 cm s^{-1}. The value for the $Lu(Pc)_2^{+/2+}$ couple in 1,2-dichloroethane is unknown. Until recently, electron-transfer rate constants of organic redox couples at metal electrodes appeared to be no higher than, say ~1 cm s^{-1}.[12-14] Recently, increasingly large values have been measured.[6,14,15] Bond et al.[15] obtained a lower bound of 5 cm s^{-1} for the ferrocene–ferrocenium couple, while Lewis and his collaborators, using nanometer-sized electrodes to avoid some of the extra ac impedance, reported a value of about 220 cm s^{-1} for this system.[6] This latter study, if sustained by future studies of other "fast" systems, can have another major implication on image effects, to which we return later. In the absence of any data on $Lu(Pc)_2^{+/2+}$ we shall for the moment use a value ~200 cm s^{-1} and examine for illustrative purposes only its implication for eqs 9 and 11. It should be stressed, however, that at present there are insufficient data to test these equations: the $Lu(Pc)_2^{+/2+}$ value is unknown, the $Fe(CN)_6^{3-/4-}$ couple has, because of the high charges, substantial ion pairing and other salt effects, and it is not clear how much of this will cancel in eqs 9 and 12. Data on other liquid–liquid systems would be desirable for such tests, accompanied by tests of the various concentration and other effects given in part 1. Further, because of some of the problems involving fast systems, it would be useful to have k_{12}^{ll}'s for slower ones as well as fast ones.

We consider first eq 12. If $a_1 + a_2$ and L are both about 5 and 10 Å, respectively, $\kappa\nu$ is about 10^{12} cm s^{-1} (cf. section iii), and ΔR is its usual value, ~1 Å, and if the above values are used for k_1^{el} and k_2^{el}, eq 12 yields, in units of M^{-1} cm s^{-1}

$$k_{12}^{ll,calc} \sim 0.01 \text{ M}^{-1} \text{ cm s}^{-1} \quad \text{(based on eq 9)} \qquad (17)$$

and

$$k_{12}^{ll,calc} \sim 1 \text{ M}^{-1} \text{ cm s}^{-1} \quad \text{(based on eq 12)} \qquad (18)$$

A larger value of $\kappa\nu$ would correspondingly increase these $k_{12}^{ll,calc}$'s. Although the model based on the sharp boundary result, eq 17, yields a $k_{12}^{ll,calc}$ in better agreement with the experimental value of k_{12}^{ll} of 0.03 M^{-1} cm s^{-1}, the uncertainties in the k^{el}'s at present are sufficiently great that, as noted earlier, no definitive conclusions can be drawn.

4. Discussion

We consider here several features mentioned earlier, the deviation of additivity in eq 5b (the deviation in eq 5a is given in eq 2.7 in part 1[16]), the electrostatic image terms which occur in the various expressions, and the preexponential factors, i.e., the Z's in eqs 15b and 16b.

i. Deviation from Additivity. For eq 5a, we use eq 2.1 of part 1 for the value of the solvent reorganization contribution to λ, λ_0, for the two-phase system, and subtract from it the mean of the values $^1/_2(\lambda_{0,11} + \lambda_{0,22})$ for the two individual homogeneous reaction systems, each for its own solvent phase. For $\lambda_{0,ii}$ we shall suppose, as a first approximation, that the separation distance R_{ii} in the homogeneous reaction i equals $2d_i$, twice the distance of reactant i to the interface in the two-phase system. We then have from eq 2.1 of part 1 and eq 89 of ref 4

$$\lambda_0 - \frac{1}{2}(\lambda_{0,11} + \lambda_{0,22}) = \frac{(\Delta e)^2}{2}\left(\frac{1}{d_1} + \frac{1}{d_2} - \frac{4}{R}\right)\left(\frac{1}{D_1^{op} + D_2^{op}} - \frac{1}{D_1^s + D_2^s}\right) \qquad (19)$$

where R is the separation distance between the two reactants in the two-phase system, the D's refer to the optical and static dielectric constants of the two solvents, and ΔE is the charge transferred, ne.

The deviation in eq 19 from additivity is identical with that in eq 2.7 in part 1 for $\lambda_0 - (\lambda_{0,1}^{el} + \lambda_{0,2}^{el})$, a result which is expected, because of the relation[4] between the homogeneous and electrochemical λ_0's for the assumptions given.

In the transition state of reaction 1 one expects, as a first approximation, that $R \simeq d_1 + d_2$. In that case the deviation from additivity in eq 19 is seen to be proportional to $(d_1 - d_2)^2/d_1d_2(d_1 + d_2)$. Thus, the reorganization parameter λ_0 in the two-phase system is somewhat larger than the mean of the values for the two self-exchange reactions, though only by a second-order quantity. The effect on eq 5a of having R different from $d_1 + d_2$ can also be calculated by using the various expressions for $\lambda_0, \lambda_{0,1}^{el}$, and $\lambda_{0,2}^{el}$ given in part 1, but we omit doing so here.

Equation 10 serves to extend the usual cross-relation,[4,8,16] but now it relates the rate constant of a cross-reaction in a two-phase system to those of the individual self-exchange reactions in their respective single-phase systems. The deviation from additivity in eq 19 is similar to that in the theoretical expression[4] leading to the usual cross-relation. For that deviation from additivity, if we denote the separation distance R_{ii} in the transition state for self-exchange reaction of species i by $2d_i$ to stress the similarity to eq 19, one finds (e.g., using the expression for λ_0 in ref 14)

$$\lambda_{0,12} - \frac{1}{2}(\lambda_{0,11} + \lambda_{0,22}) = \frac{(\Delta e)^2}{4}\left(\frac{1}{d_1} + \frac{1}{d_2} - \frac{4}{R}\right)\left(\frac{1}{D^{op}} - \frac{1}{D^s}\right) \qquad (20)$$

For eq 20 there is only one solvent, and so no subscripts are added to the D's. The deviation from additivity in eq 19 is seen to be comparable to that in eq 20, and the latter appears to be comparatively small, judging from the many experimental tests[8] of the cross-relation over the years. Equation 19 reduces to eq 20 when $D_1^{op} = D_2^{op}$ and $D_1^s = D_2^s$, as indeed it should. Clearly, other things being equal, the closer the reactants are in their radii, the smaller will be $(d_1 - d_2)^2$ and hence the smaller will be the deviation from additivity.

ii. Electrostatic Image Effects. A second point concerns the presence of dielectric image terms, which abound in the expressions used here and in part 1 for two-phase systems, in particular derived[4,5,17] for the liquid–liquid and metal–liquid systems. Sometimes the image terms are omitted.[18] We consider the implications for such terms of some recent data on k_s^{el}.[6]

In the interpretation of the relation between self-exchange rate constants k_{ii} in homogeneous solution and the corresponding electrochemical exchange current rate constants k_i^{el}, it was predicted[4] that if the center-to-center separation distance R_{ii} in the transition state of the former was approximately twice the distance d_i from the center of the reactant to the metal–liquid interface, one would have $\lambda_{0,ii} = 2\lambda_0^{el}$ for a reaction. (However, $\lambda_{0,ii}$ will be less than $2\lambda_0^{el}$ if $R_{ii} < 2d_i$.) In addition, there is a vibrational contribution λ_i to λ (i here denoting "inner," not reaction i), and for the λ_i for a self-exchange reaction is twice that (λ_i^{el}) for the electrochemical exchange current rate constant.[4,8] Thus, the total λ, which is the sum $\lambda_0 + \lambda_i$, now equals $2\lambda^{el}$. In this case, it was predicted[4] that a plot of ln k_i^{el} vs ln k_{ii} would have a slope of $^1/_2$. Making the corrections of the k's for the work terms, so as to better test the relation, is discussed by Hupp and Weaver.[19]

For k's that were not large, it appeared that this prediction was more or less obeyed,[12] but it also appeared that the fastest k_{el}'s were substantially less than those expected from the k_{ii}'s in the above ln–ln plots.[12] One explanation was that perhaps the dielectric image term for the metal-liquid system is unimportant: λ_0^{el} is proportional to[4,17] $1/a - 1/2d$, where a is the reactant's radius and $2d$ is the distance from the center of the reactant to the

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(18) The cases of image and no image contributions are considered in: Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.
(19) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2795.

electrostatic image (i.e., twice the distance to the interface). In the absence of the image term the $1/2d$ disappears and λ_0^{el} is then about twice as large as when $d \simeq a$ (reactant touching the electrode). A large λ^{el} would lead to a small k^{el}. This effect on λ_0^{el}, it has been suggested, could have been obscured in the case of the slow reactions, since for those the λ would be dominated by the vibrational contribution λ_i for which the relationship[4] $\lambda_{i,II} = 2\lambda_i^{el}$ should indeed be a good approximation.

The recent work of Lewis et al.,[6] referred to earlier, on the ferrocene–ferrocenium couple using nanometer-sized metal electrodes now requires that the earlier findings be reexamined: the new k_{el} for a fast reaction is much higher than that found previously, by a factor of about 200. The new data of Lewis and co-workers would now yield a slope of $^1/_2$ for the ln k_i^{el} vs ln k_{il} plot, even when the fast k_{el} is included.[6] The interest in the fast systems arises since only they tend to have reorganization energies λ dominated by solvation rather than vibrational effects. Thus, it is of particular interest that some of the very fast systems be reinvestigated to see whether they are indeed substantially faster than was originally reported. For the fast processes a theoretical slope of $^1/_2$ rests on a dielectric image expression and on $d \simeq 2a$ in that expression. It has been suggested that one reason why the previous "fast" reaction k^{el}'s may be too small is the residual ac impedance, which can dominate that due to the electron transfer when k^{el} is large and which may have been attributed to the electron transfer itself.[20]

One mechanism for electron transfer across the interface that could occur when a reactant is soluble in both phases is for the transfer to be preceded by a transfer of the reactant across the interface, followed by a homogeneous electron transfer. This mechanism is quite different from that treated in this paper and is not explored here.

iii. The Z's in Eqs 15b and 16b. Finally, we should like to comment on the Z's in eqs 15b and 16b. If $\kappa\nu \sim 10^{13}$ s^{-1} and with $\Delta R \sim 1$ Å and $2a \sim 5$ Å, Z_{el} and Z_{soln} are about 10^5 cm s^{-1} and 2×10^{12} M^{-1} s^{-1}, values which are higher than the collision frequencies often used for Z's, $\sim 10^4$ cm s^{-1} and 10^{11} M^{-1} s^{-1}. We have discussed this point elsewhere.[11] Electron transfers differ from the conventional reactions in that transfer can occur readily over a distance, for example $\sim$1 Å (the ΔR), with only a minor reduction in probability, whereas in other reactions, such as atom transfers, a "contact is required", say a $\Delta R \sim 0.1$ Å in the present notation. Thus, the usual Z's are a factor of the order of 10 less than in eqs 15b and 16b. However, the reaction may not be adiabatic at contact, though the recent work of Schultze and co-workers[21] supports adiabaticity for $Ru(NH_3)_6^{2+/3+}$ at metal electrodes. (The rate constant was independent of the electronic density of states of the metal.[21]) When $\kappa \sim 0.1$ the Z's in eqs 15b and 16b become comparable to the usual 10^4 and 10^{11} values.

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Intramolecular Charge Transfer and Thermal Exciplex Dissociation with *p*-Aminobenzonitriles in Toluene

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The rate constants of the reversible intramolecular excited-state charge-transfer (CT) reaction of 4-(dimethylamino)benzonitrile (DMABN; I) in toluene were determined as a function of temperature, from double-exponential fluorescence decays measured by time-correlated single-photon counting. The same decay times were found for the locally excited (LE) and the CT state, as shown by global analysis. For the CT state, the stabilization enthalpy ΔH (−6 kJ mol^{-1}) and the change in entropy ΔS (−24 J K^{-1} M^{-1}) were determined. A correlation of the charge-transfer time of DMABN with the longitudinal dielectric relaxation time was not observed. The presence of dimers or solute/solvent complexes in the ground state was excluded by ^{1}H NMR experiments. A reversible excited-state reaction was shown to occur in toluene for the planar molecules 1-methyl-5-cyanoindoline (NMCI; II) and 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (NMCQ; III) as well as for 3,5-dimethyl-4-(dimethylamino)benzonitrile (DMADBN; IV), based on the wavelength dependence of the double-exponential fluorescence decays. Such a dependence was not found for *N*-methyl-4-aminobenzonitrile (MABN; IH), 4-aminobenzonitrile (ABN; IHH), and 3,5-dimethyl-4-aminobenzonitrile (ADBN; IVHH), which is attributed to an increase in energy of the CT state relative to the LE state in these secondary and primary aromatic amines. The implications of these results with respect to the importance of bond rotation in twisted internal charge transfer (TICT) are discussed.

Introduction

Intramolecular charge transfer in donor/acceptor-substituted benzenes in the excited state has been studied extensively since Lippert discovered the dual luminescence of 4-(dimethylamino)benzonitrile (DMABN; I) in 1959.[1] Dual fluorescence of DMABN has been found in several solvent classes of medium and high polarity, such as alcohols, ethers, nitriles, and chloroalkanes.[1-3] No red-shifted new emission was observed in alkanes,[1] whereas in the aromatic solvents benzene[1a] and toluene[3] only a shoulder was detected in the fluorescence spectrum of DMABN at room

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