J. Am. Chem. Soc. **1998,** *120,* 4167−4175

Cage and Entropy Effects in the Dynamics of Dissociative Electron Transfer

Claude P. Andrieux, Jean-Michel Savéant,* and Caroline Tardy

Contribution from the Laboratoire d'Electrochimie Moléculaire de l'Université Denis Diderot, Unité Associée au CNRS No. 438, 2 place Jussieu, 75251 Paris Cedex 05, France

Received July 30, 1997. Revised Manuscript Received November 10, 1997

Abstract: Dissociative electron transfers in condensed phases occur in two steps. The fragments are first formed within a solvent cage from which they further diffuse. The formation of caged, rather than free-moving, fragments is taken into account in an improved version of the dissociative electron transfer theory where entropic aspects are emphasized. A more detailed treatment than previously available of the fragmentation and solvent reorganization factors is given in terms of both energies and free energies. The reason that the bond dissociation energy, rather than the bond dissociation free energy, represents the contribution of fragmentation to the intrinsic barrier ensues. The resulting equations that relate the activation free enthalpy and entropy, as well as the symmetry factor, to the standard free enthalpy and entropy of the reaction are given for electrochemical, bimolecular, and intramolecular reactions. Solvation radii change upon electron transfer triggered bond cleavage. An iterative procedure is proposed for adapting the estimation of the solvent reorganization factor to the ensuing coupling of the fragmentation and solvent reorganization coordinates. Experimental examples illustrating applications of the theory are discussed.

Electron transfer to or from a molecule is often accompanied by the cleavage of a bond. The coupling of these two events is one of the most common pathways along which electron transfer can generate highly reactive species. This is, for example, one way by which electron transfer chemistry can open a route to radical chemistry. Such reactions are common in molecular electrochemistry[1] but also concern thermal homogeneous electron transfer[2] and photoinduced electron transfer.[3]

Electron transfer and bond breaking may occur successively or in a concerted manner. In the former case, electron transfer is of the outersphere type. Its dynamics may be described by the Marcus−Hush model.[4] In the concerted situation, electron transfer has an innersphere character. The dissociation of the bond is then expected to contribute to the activation barrier besides other changes in the internal nuclear configuration and in the interaction of the reacting system with the solvent. A model describing the dynamics of such dissociative electron transfers

$$\mathrm{R{-}X} \mp \mathrm{e}^- \rightarrow {}^{\bullet}\mathrm{R} + \mathrm{X}^{\pm}$$

was proposed some time ago.[5] It is based on a Morse curve approximation of the energy of the cleaving bond in the reactant and on the assumption that the repulsive interaction of the two fragments formed upon electron transfer is the same as the repulsive part of the reactant Morse curve. By associating this description of bond breaking with a Marcus−Hush modeling of the attending solvent reorganization, one obtains the following equations which summarize the predictions of the model. As with the Marcus−Hush model of outersphere electron transfers, the activation free energy, $\Delta G^{\ddagger}$, is a quadratic function of the free energy of the reaction, ΔG°

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^{\circ}}{4\Delta G_0^{\ddagger}}\right)^2 \tag{1}$$

where the intrinsic barrier free energy

$$\Delta G_0^{\ddagger} = \frac{D + \lambda_0}{4} \tag{2}$$

is the sum of two contributions. One involves the solvent reorganization free energy, λ_0, as in the Marcus−Hush model of outersphere electron transfer. The other, which represents the contribution of bond breaking, is one-fourth of the bond dissociation *energy*. Tests of these predictions have involved the electrochemical reduction of alkyl and benzyl halides as well as their reduction by homogeneous electron donors.[5,6]

---

(1) (a) Organic Electrochemistry, Lund, H.; Baizer, M. M., Eds.; Dekker: New York, 1990. (b) Andrieux, C. P.; Savéant, J.-M. In *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305-390.

(2) (a) Savéant, J.-M. Single Electron Transfer and Nucleophilic Substitution. In *Advances in Physical Organic Chemistry;* Bethel, D., Ed.; Academic Press: New York, 1990; Vol. 26, pp 1−130. (b) Lund, H.; Daasberg, K.; Lund, T.; Pedersen, S. U. *Acc. Chem. Res.* **1995**, *28*, 313. (c) Savéant, J.-M. *Tetrahedron* **1994**, *50*, 10117.

(3) (a) Saeva, F. D. *Topics Curr. Chem.* **1990**, *156*, 61. (b) Saeva, F. D. Intramolecular Photochemical Electron Transfer (PET)−Induced Bond Cleavage Reactions in some Sulfonium Salts Derivatives. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1994; Vol. 4, pp. 1−25. (c) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978. (d) Chen, L.; Farahat, M. S.; Gan, H.; Farid, S.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 6399.

(4) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979. (c) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (d) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (e) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(5) (a) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. (b) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455. (c) Savéant, J.-M. Dissociative Electron Transfer. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1994; Vol. 4, pp. 53−116.

(6) (a) Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 10595. (b) Andrieux, C. P.; LeGorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892. (c) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363.

S0002-7863(97)02598-5 CCC: $15.00

Formulations of the final equations have been given for electrochemical and homogeneous bimolecular electron transfers[5] and, more recently, for intramolecular dissociative electron transfer.[2c,5c,7]

There are several reasons to examine in more detail the theory of dissociative electron transfer. One derives from recent experimental evidence of the role of diffusion of the two fragments out of the solvent cage where they are formed in the case of intramolecular dissociative electron transfer. These observations concern homolysis of cation and anion radicals, but also heterolysis of some of these species which can be viewed as intramolecular dissociative electron transfers.[8a] One particularly clear example is the cleavage of the C−O bond in a series of α-phenoxyacetophenone anion radicals, where both the activation and diffusion-controlled behaviors could be characterized.[8b] Kinetic control by diffusion of the two fragments out of the solvent cage would represent an extreme situation unlikely to be often met in electrochemical and homogeneous bimolecular reactions. However, even if the kinetics are under activation control, the fact that the product system consists of caged rather than free-moving fragments should be taken into account in the bookkeeping of energies and entropies. The fact that the fragments are formed within a solvent cage from which they may diffuse apart is also an important issue in dissociative photoelectron transfer. The possibility of a termolecular back electron transfer competing with the escape of the fragments from the cage should indeed be taken into consideration if the presently available modeling of back electron transfer in photoinduced electron transfer[9] is to be extended to the dissociative case.

How the activation entropies derive from the dissociative electron transfer theory is another question of interest.[10] A related problem regards the expression of the intrinsic barrier free energy. Does it involve the bond dissociation *energy* (BDE) as in eq 2[5a] or, as sometimes stated,[11] the bond dissociation *free energy* (BDFE)?

The first section gives a description of the theory with more details than done before, in an attempt to answer the questions raised above. The second section is devoted to electrochemical and homogeneous examples illustrating the application of theory.

Theory

Thermodynamics of the Caged Product System. The global standard free enthalpy of the reaction, ΔG°, for converting the starting molecule into the two fragments, is given by the following equations. The notation used below makes a formal charge appear on the leaving group, $X^\pm$, which only represents the charge lost or gained upon electron transfer. It should be combined with the charge already present on RX to obtain the actual charge. The same is true for the dot representing the change in electron parity in the "remaining" group, $^\bullet$R. The potentials will be expressed in volts and the energies in electronvolts.

In the electrochemical case

$$RX \mp e^- \rightarrow {}^\bullet R + X^\pm, \qquad \Delta G^\circ = E - E^\circ$$

where E is the electrode potential and $E^\circ = \mp \mu^\circ_{RX} \pm \mu^\circ_{R^\bullet} \pm \mu^\circ_{X^\pm}$ is the standard potential of the RX/$^\bullet$R + $X^\pm$ couple (the μ°'s are the chemical potentials of the subscript species).

For thermal homogeneous dissociative electron transfers,

$$A + RX \rightarrow B + {}^\bullet R + X^\pm, \qquad \Delta G^\circ = E^\circ - E^\circ_{A/B}$$

where, $E^\circ_{A/B} = \pm \mu^\circ_A \mp \mu^\circ_B$.

In the case of intramolecular dissociative electron transfer,

$$^{\pm\bullet}RX \rightarrow {}^\bullet R + X^\pm, \qquad \Delta G^\circ = \mu^\circ_{R^\bullet} + \mu^\circ_{X^\pm} - \mu^\circ_{RX^{\bullet\pm}}$$

The global entropy of the reaction, ΔS°, for converting the starting molecule into two free-moving fragments, may be decomposed into two contributions, one, ΔS°_F, corresponding to the fragmentation and the other, ΔS°_S, corresponding to the change in solvation attending the reaction: $\Delta S^\circ = \Delta S^\circ_F + \Delta S^\circ_S$. In fact, the two fragments are produced within a solvent cage from which they diffuse apart in a second step. Thus, the product system of the reaction involves two caged fragments rather than two free-moving fragments. The difference of the standard free enthalpies in these two situations essentially originates in the difference of entropies corresponding to the formation of the two fragments, $\Delta S^\circ_{F,C}$ and ΔS°_F, respectively:

$$\Delta G^\circ_C - \Delta G^\circ = -T(\Delta S^\circ_{F,C} - \Delta S^\circ_F)$$

The Q's and q's being the molar and molecular partition functions, respectively ($\ln Q = N_A \ln q - \ln(N_A!) \approx N_A \ln q - N_A \ln N_A + N_A$), the following equations apply in the electrochemical and intramolecular electron transfer cases:

$$\Delta S^\circ_{F,C} - \Delta S^\circ_F = S^\circ_{(R^\bullet,X^\pm)} - (S^\circ_{R^\bullet} + S^\circ_{X^\pm}) \quad \text{with}$$

$$S = k_B\left(\ln Q + \frac{\partial \ln Q}{\partial \ln T}\right) = R\left[\ln\left(\frac{q}{N_A}\right) + \frac{\partial \ln q}{\partial \ln T} + 1\right]$$

(R, k_B, and N_A are the gas, Boltzman, and Avogadro constants respectively). Thus

$$\Delta S^\circ_{F,C} - \Delta S^\circ_F = R\left\{\ln\left(\frac{N_A q_{(R^\bullet,X^\pm)}}{q_{R^\bullet} q_{X^\pm}}\right) + \frac{\partial[\ln(q_{(R^\bullet,X^\pm)}) - \ln(q_{R^\bullet} q_{X^\pm})]}{\partial \ln T} - 1\right\}$$

We may assume that the internal rotational and vibrational partition functions of each of the two fragments are the same inside and outside the cage. Outside the cage, the translation partition functions of the two fragments are

$$^{(3)}q^{\text{trans}}_{R^\bullet} = \frac{(2\pi m_{R^\bullet} k_B T)^{3/2}}{h^3} V^\circ \quad \text{and} \quad {}^{(3)}q^{\text{trans}}_{X^\pm} = \frac{(2\pi m_{X^\pm} k_B T)^{3/2}}{h^3} V^\circ, \quad \text{respectively}$$

V° is the volume occupied by the molecules in the standard state, 1 L, if the concentrations are expresses in molarities. The partition function of the caged product system may be expressed as

$$q_{(R^\bullet,X^\pm)} = \frac{[2\pi(m_{R^\bullet} + m_{X^\pm})k_B T]^{3/2}}{h^3} V^\circ q_{\text{cage}}$$

q_{cage} corresponds to the relative movements of the two fragments within the cage. As compared to the reactant system, they

---

[7] Savéant, J.-M. *J. Phys. Chem.* **1994**, *98*, 3716.

[8] (a) Anne, A.; Fraoua, S.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1996**, *118*, 3938. (b) Andersen, M. L.; Long, W.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1997**, *119*, 6590.

[9] Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

[10] (a) See the section devoted to this question and footnote 29 in ref 10b. (b) Marcus, R. A. *J. Phys. Chem. A* **1997**, *101*, 4072.

[11] Workentin, M. S.; Maran, F.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 2120.

involve the two rotations of the two fragments around their common center of mass (and also rotations of each of them around their own centers of mass if they are polyatomics). However, the vibration along the radial coordinate is now replaced, since the bond is broken, by the rotation of one fragment, say $R^\bullet$, around the other, $X^\pm$. The corresponding partition function may thus be regarded approximately as a three-dimensional translation within the cage. Thus,

$$q_{\text{cage}} = \frac{(2\pi m_{R^\bullet} k_B T)^{3/2}}{h^3} V^{\text{cage}}$$

(V^{cage} is the volume of the cage where $R^\bullet$ can move around $X^\pm$) and therefore,

$$\Delta S^\circ_{F,C} - \Delta S^\circ_F \approx R \ln\left(\frac{V^{\text{cage}}}{V^\circ/N_A}\right) \tag{3}$$

(neglecting the term $R\{(3/2)\ln[(m_{X^\pm} + m_{R^\bullet})/m_{X^\pm}] - 1\}$). This estimate of the fragmentation entropy within the solvent cage may not appear obvious if the reactants are thought as featureless hard spheres. It becomes clearer if one starts from the reactant system and goes to the transition state and to the caged product system. The partition function of the R−X molecule in its initial state contains a rotational contribution. In most practical cases, the bending vibrations of the R−X bond contribute negligibly to the partition function. At the transition state the rotational partition function is about the same as in the reactant, with a slightly larger moment of inertia. Since the bond is partially broken, the bending vibrations of the R−X bond have become more floppy and may therefore contribute appreciably. Going on to the caged product systems, where the bond is broken, these bending vibrations may be regarded as being converted into the cage translation of one fragment around the other. Turning back to eq 3, the difference in entropy between the caged and free products is expected to vanish when V^{cage} reaches V°/N_A, corresponding to the volume of $a \approx 7$ Å radius sphere. We may thus conclude that, depending of the shape and size of the fragments and of the cage, there may be a significant contribution of cleavage to standard entropy of the reaction even though the two fragments are formed within a solvent cage.

In the case of homogeneous bimolecular dissociative electron transfers, the bookkeeping of partition functions is more cumbersome since the cage contains three particles that ultimately diffuse away one from the other:

$$\Delta S^\circ_{F,C} - \Delta S^\circ_F = R\left\{\ln\left(\frac{N_A{}^2 q_{(B,R^\bullet,X^\pm)}}{q_B q_{R^\bullet} q_{X^\pm}}\right) + \frac{\partial[\ln(q_{(B,R^\bullet,X^\pm)}) - \ln(q_B q_{R^\bullet} q_{X^\pm})]}{\partial \ln T} - 2\right\}$$

From the possibility of confined translation within the cage of particles around one another, resulting from the breaking of the bond, we come again to the conclusion that there may be a significant contribution of cleavage to the standard entropy of the reaction. It is not necessarily the same as in the electrochemical and intramolecular cases. One would expect that it is smaller in view of the occupation of the solvent cage by the outersphere electron transfer reagent.

Contribution of Cleavage to the Free Enthalpy and Entropy of Activation. We consider, in a first stage, the limiting case where solvent reorganization would contribute negligibly to the dynamics of the reaction. The energy of transition state is obtained from the intersection of the reactant (in the encounter complex) and product (in the cage) potential energy curves.[12a] The former is represented by a Morse curve:[5a]

$$U_R = U^\circ_R + D(1 - Y)^2 \quad \text{with} \quad Y = \exp(-\beta y)$$

D is the BDE of the breaking bond, U°_R the standard energy of the reactant system, and y the elongation of the breaking bond. $\beta = \nu(2\pi^2\mu/D)^{1/2}$ (ν, stretching frequency; μ, reduced mass). In cases where the homolytic dissociation is accompanied by changes in the hydridization of the bonded atoms, as is the case for a carbon atom in, e.g. an alkyl halide, the BDE is assumed to include this change of the nuclear configuration.

The purely repulsive product curve is assumed to be the same as the repulsive part of the reactant curve: $U_P = U^\circ_P + DY^2$. Thus, at the transition state

$$1 - Y^{\neq} = \frac{1}{2}\left(1 + \frac{\Delta U^\circ}{D}\right)$$

and the activation energy is given by

$$\Delta U^{\neq} = D(1 - Y^{\neq})^2 = \frac{D}{4}\left(1 + \frac{\Delta U^\circ}{D}\right)^2$$

The entropies of the reactant and product systems should be equal at the transition state. We assume that

$$S^{\neq} = S^\circ_R + (1 - Y^{\neq})\Delta S^\circ_{F,C} = S^\circ_{P,C} - Y^{\neq}\Delta S^\circ_{F,C}$$

meaning that there is a smooth variation of the entropy from the initial (S°_R) to the final ($S^\circ_{P,C}$) state owing to the increasing interference of floppy bending vibrations as already sketched in the preceding section. Thus, for the forward reaction, the activation entropy is given by

$$\Delta S^{\neq} = (1 - Y^{\neq})\Delta S^\circ_{F,C}$$

The free enthalpy of activation may thus be expressed as follows:[12b]

$$\Delta G^{\neq} = D(1 - Y^{\neq})^2 - T(1 - Y^{\neq})\Delta S^\circ_{F,C} = \frac{D}{4}\left(1 + \frac{\Delta U^\circ}{D}\right)^2 - \frac{T\Delta S^\circ_{F,C}}{2}\left(1 + \frac{\Delta U^\circ}{D}\right) \tag{4}$$

This expression is not identical to the application of eq 1 to the present situation, *viz.*

$$\Delta G^{\neq} = \frac{D}{4}\left(1 + \frac{\Delta G^\circ_{F,C}}{D}\right)^2 \tag{5}$$

But how far is it in practice? Rearrangement of eq 4 leads to

$$\Delta G^{\neq} = \frac{D}{4}\left(1 + \frac{\Delta G^\circ_{F,C}}{D}\right)^2 - \frac{(T\Delta S^\circ_{F,C})^2}{4D} \tag{4'}$$

The second term in the right-hand side of eq 5 is very small in all practical situations as illustrated by the examples represented in Figure 1 for typical values of D and $\Delta S^\circ_{F,C}$.

If the BDFE were to be used instead of the BDE in eq 5, leading to eq 6, the computed values of $\Delta G^{\neq}$ would be more seriously in error, as can be seen in Figure 1.

---

(12) (a) The reaction is assumed to be adiabatic, and at the same time, the avoided crossing energy is assumed to be small enough for the intersection of the two diabatic curves to give the activation energy with a reasonable accuracy. (b) Since the reactions we discuss occur in solution, the small difference between free energy and free enthalpy may be neglected.

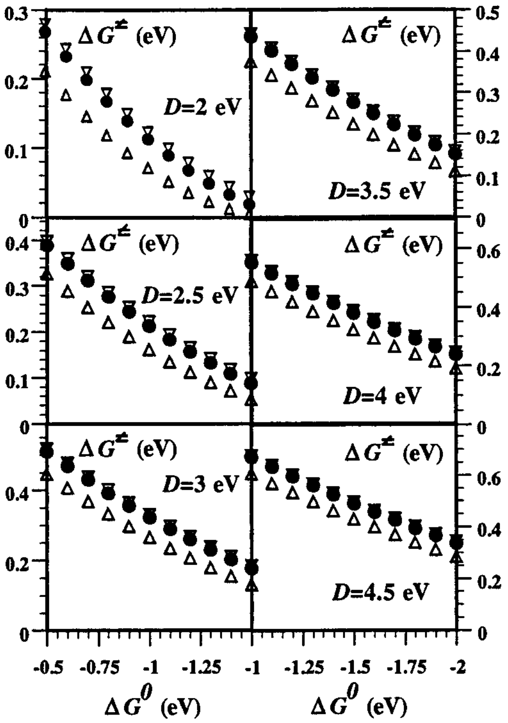

Figure 1. Activation free enthalpy vs standard free enthalpy in the absence of significant solvent reorganization according to eq 4 (●), 5 (▽), and 6 (△). $\Delta S^\circ_{F,C} = 1$ meV/K.

$$\Delta G^{\neq} = \frac{(D - T\Delta S^\circ_{F,C})}{4}\left(1 + \frac{\Delta G^\circ_{F,C}}{D - T\Delta S^\circ_{F,C}}\right)^2 \qquad (6)$$

Contribution of Solvent Reorganization to the Free Enthalpy and Entropy of Activation. In the classical theory of outersphere electron transfer,[4] leading to the following activation/driving force relationship

$$\Delta G^{\neq} = \frac{\lambda_0}{4}\left(1 + \frac{\Delta G^\circ}{\lambda_0}\right)^2$$

the activation entropy is simply derived from differentiation of the above equation toward temperature, assuming that λ_0 varies negligibly with temperature:

$$\Delta S^{\neq} = \frac{\Delta S^\circ_S}{2}\left(1 + \frac{\Delta G^\circ}{\lambda_0}\right) = \alpha \Delta S^\circ_S \qquad (7)$$

where ΔS°_S is the change of the solvation entropy during the reaction and α is the symmetry factor.

It is interesting to examine the implication of this derivation in terms of potential energy curves as a preliminary for the combination of the dynamics of cleavage and solvent reorganization to be discussed in the next section. At the transition state, the energies and entropies of the reactants are equal. The free enthalpy of the transition state may thus be expressed by the following equations:

$$G^{\neq} = G^\circ_R + \lambda_0 X^2 = G^\circ_P \lambda_0 + (1 - X)^2$$

(X is the solvent reorganization variable which varies from 0 to 1 from reactants to products[4]). Thus

$$S^{\neq} = S^\circ_R - 2\lambda_0 X\frac{\partial X}{\partial T} = S^\circ_P + 2\lambda_0(1 - X)\frac{\partial X}{\partial T}$$

$$\text{leading to} \quad \frac{\partial X}{\partial T} = \frac{-\Delta S^\circ_S}{2\lambda_0}$$

and to the above expression of the activation entropy. The transition state energy may be derived from the above expressions of the activation free enthalpy and entropy or, alternatively, from the intersection of the following two energy curves (the U's are the energies).

$$U_R = U^\circ_R + \lambda_0 X^2 + XT\Delta S^\circ_S U_P = U^\circ_P + \lambda_0(1 - X)^2 - (1 - X)T\Delta S^\circ_S$$

leading to the classical expressions given at the beginning of this section.

Combined Contributions of Cleavage and Solvent Reorganization to the Free Enthalpy and Entropy of Activation. The variable representing the stretching of the cleaving bond, Y, is the same as already defined. It varies from 1 in the reactant system, R, to 0 in the product system, P. Solvent reorganization is represented by the same variable, X, as in the preceding section. It varies from 0 to 1 from reactants to products. The entropy of the reaction may be split in two parts, one corresponding to cleavage and the other to solvation:

$$S^\circ_{P,C} - S^\circ_R = \Delta S^\circ_C = \Delta S^\circ_{F,C} + \Delta S^\circ_S$$

For any given values of Y and X, the free enthalpies of the reactant and product systems are given by the following equations:

$$G_R = G^\circ_R + D(1 - Y)^2 - (1 - Y)T\Delta S^\circ_{F,C} + \lambda_0 X^2 G_{P,C} = G^\circ_{P,C} + DY^2 + YT\Delta S^\circ_{F,C} + \lambda_0(1 - X)^2$$

In these expressions, the contribution of cleavage to entropy is described by the same linear approximation between reactants in the encounter complex and caged products as above. One of the best ways to test the validity of this approximation is to resort to experimental data. This is what is done in the section devoted to experimental examples below.

It follows from the above equations that

$$S_R = S^\circ_R + (1 - Y)\Delta S^\circ_{F,C} - 2\lambda_0 X\frac{\partial X}{\partial T}$$

$$S_{P,C} = S^\circ_{P,C} - Y\Delta S^\circ_{F,C} + 2\lambda_0(1 - X)\frac{\partial X}{\partial T}$$

The transition state belongs to a set of $X-Y$ points for which $S_R = S_{P,C}$. Therefore, as in the preceding section, $\partial X/\partial T = -\Delta S^\circ_S/2\lambda_0$. The energies of the reactant and product systems for any values of Y and X are thus given by the following equations:

$$U_R = U^\circ_R + D(1 - Y)^2 + \lambda_0 X^2 + XT\Delta S^\circ_S$$

$$U_{P,C} = U^\circ_P + DY^2 + \lambda_0(1 - X)^2 - (1 - X)T\Delta S^\circ_S$$

Locating the lowest point on the intersection of the two free energy surfaces through

$$\frac{\partial G_R/\partial Y}{\partial G_{P,C}/\partial Y} = \frac{\partial G_R/\partial X}{\partial G_{P,C}/\partial X}$$

leads to the following relationship between the transition state values of the coordinates X and Y.

$$X^{\neq} = 1 - Y^{\neq} - \frac{T\Delta S^{\circ}_{\mathrm{F,C}}}{2D}$$

Combining this equation with the intersection of the two potential energy surfaces, one obtains the transition state values of each coordinate

$$1 - Y^{\neq} = \frac{1}{2}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0} + \frac{T\Delta S^{\circ}_{\mathrm{F,C}}}{D}\right)$$

$$X^{\neq} = \frac{1}{2}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0}\right) \quad (8)$$

($\Delta G^{\circ}_{\mathrm{C}} = G^{\circ}_{\mathrm{P,C}} - G^{\circ}_{\mathrm{R}}$) and the expression of the activation free enthalpy and entropy:

$$\Delta G^{\neq} = D(1 - Y^{\neq})^2 - (1 - Y\neq)T\Delta S^{\circ}_{\mathrm{F,C}} + \lambda_0 X^{\neq 2} - \rho \quad (9)$$

$$\Delta S^{\neq} = (1 - Y^{\neq})\Delta S^{\circ}_{\mathrm{F,C}} + X^{\neq}\Delta S^{\circ}_{\mathrm{S}} \quad (10)$$

ρ is the avoided crossing (resonance) energy at the transition state for an adiabatic reaction.

It is also interesting to derive the expression of the transfer coefficient (symmetry factor) defined as $\alpha = \partial\Delta G^{\neq}/\partial\Delta G^{\circ}_{\mathrm{C}}$. Thus from eqs 7 and 8

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0}\right) \quad (11)$$

Combination of eqs 8 and 9 provides an expression of the relationship between the activation free enthalpy and the standard free enthalpy of the reaction:

$$\Delta G^{\neq} = \frac{D + \lambda_0}{4}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0}\right)^2 - \frac{(T\Delta S^{\circ}_{\mathrm{F,C}})^2}{4D} - \rho \quad (12)$$

It also follows that

$$\Delta S^{\neq} = \alpha\Delta S^{\circ}_{\mathrm{C}} + \frac{T(\Delta S^{\circ}_{\mathrm{F,C}})}{2D} \quad (13)$$

In most practical circumstances, the second-order entropic terms in eqs 12 and 13 may be neglected, leading to the following simpler expressions of the activation free enthalpies and entropies (this will be illustrated by the experimental examples given in the next section).

$$\Delta G^{\neq} = \frac{D + \lambda_0}{4}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0}\right)^2 - \rho$$

$$\Delta S^{\neq} = \alpha\Delta S^{\circ}_{\mathrm{C}} = \frac{1}{2}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{C}}}{D + \lambda_0}\right)\Delta S^{\circ}_{\mathrm{C}} \quad (14)$$

For simplicity, we did not introduced explicitly in the above expressions work terms that may be required to bring the reactant and/or product systems into a reacting position. We considered that the product system consists in the products inside the solvent cage before they diffuse apart and assumed that the free enthalpies and entropies of the cage products differs from those of the separated products by a different cleavage entropy term ($\Delta S^{\circ}_{\mathrm{F,C}} \leq \Delta S^{\circ}_{\mathrm{C}}$). Additional work terms may be required, as for example those taking account of the effect of the double layer in electrochemical experiments. When necessary, the corresponding free enthalpies and entropies should be introduced in eqs 12−14.

So far, bond cleavage and solvent reorganization have been assumed to contribute independently from one another to the activation process, the pertinent energies thus being the sum of two terms representing each phenomenon. In this framework, the solvent reorganization free energy, λ_0, may be derived from the following classical expressions:[4]

electrochemical reactions:

$$\lambda_0 = \frac{N_{\mathrm{A}}{e_0}^2}{4\pi}\left(\frac{1}{\epsilon_{\mathrm{op}}} - \frac{1}{\epsilon_{\mathrm{S}}}\right)\frac{1}{2}\left(\frac{1}{a_{\mathrm{RX}}} - \frac{1}{d'}\right) \quad (15)$$

homogeneous bimolecular reactions:

$$\lambda_0 = \frac{N_{\mathrm{A}}{e_0}^2}{4\pi}\left(\frac{1}{\epsilon_{\mathrm{op}}} - \frac{1}{\epsilon_{\mathrm{S}}}\right)\left(\frac{1}{2a_{\mathrm{RX}}} + \frac{1}{2a_{\mathrm{A}}} - \frac{1}{a_{\mathrm{RX}} + a_{\mathrm{A}}}\right) \quad (16)$$

intramolecular reactions:

$$\lambda_0 = \frac{N_{\mathrm{A}}{e_0}^2}{4\pi}\left(\frac{1}{\epsilon_{\mathrm{op}}} - \frac{1}{\epsilon_{\mathrm{S}}}\right)\left(\frac{1}{2a_{\mathrm{R}}} + \frac{1}{2a_{\mathrm{X}}} - \frac{1}{a_{\mathrm{R}} + a_{\mathrm{X}}}\right)$$

ϵ_{op} and ϵ_{S} are the optical and static dielectric constants, respectively. The a's are the radii of hard spheres representing the reactants, and d' is the distance between the reactant and its mirror image in the electrode.

There are two difficulties with the estimation of the solvent reorganization free energy. One is that the above expressions, being based on a Born model of solvation, tend to overestimate its value.[13] A more realistic approach consists in the determination of the factor that multiplies the inverse radii term by means of previous experimental data pertaining to outersphere electron transfer reactions.

The second is that, for electrochemical and homogeneous bimolecular reactions, the solvation radius of the moiety, X, to be charged or discharged during the reaction, varies as the oxidative or reductive cleavage proceeds. One starts from a situation where X is partly hindered from solvation by the presence of the neighboring R group and ultimately goes to a situation where full solvation can develop. Thus, solvent reorganization is not, strictly speaking, independent of the progress of cleavage. Various manners of estimating an in-between value of λ_0 have been described that may apply satisfactorily to certain classes of compounds but not to others.[5a,6a] A better strategy should be to allow for a variation of the effective λ_0 as a function of the progress of cleavage as defined by the value of the Y coordinate. Two limiting values of λ_0 are thus defined, one involving an equivalent radius for X in RX appropriate for the initial state, noted a_{R}, and the other a radius, a_{P}, appropriate for the final state. The solvent reorganization free energy is then obtained as a weighted linear combination of these two limiting values:

$$\lambda_0 = Y^{\neq}\lambda_0^{\mathrm{R}} + (1 - Y^{\neq})\lambda_0^{\mathrm{P}} \quad (17)$$

Application of eqs 12−14 may then be performed in an iterative manner. One starts the calculation with a value of λ_0 obtained from a guessed value of $Y^{\neq}$, say 0.5, then uses the newly calculated value of $Y^{\neq}$ in the next step and so on until convergence is reached with the desired precision. Illustrating examples are given in the next section.

---

(13) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 2120.

Comparison with experiments may be performed using activation free enthalpies or rate constants. In both cases, an expression of the pre-exponential factor, A, is needed. The following approximate expressions may be used.

$$Z_{\text{electrochemical}} = \left(\frac{k_B T}{2\pi m_{RX}}\right)^{1/2} \tag{18}$$

$$Z_{\text{bimolecular}} = d^2\left(\frac{8\pi k_B T}{m_A m_{RX}/(m_A + m_{RX})}\right)^{1/2} \tag{19}$$

$$Z_{\text{intramolecular}} = \nu$$

The m's are the molecular masses of the subscript species, d is the distance between the centers of the two reactants in the encounter complex, and ν is the stretching frequency of the breaking bond. These expressions apply for adiabatic electron transfers. The modification of the pre-exponential factor arising from nonadiabatic effects may be obtained by adapting previous treatments of outersphere electron transfer[14] to the dissociative case.[15]

Experimental Examples

In their reaction with tertiary alkyl halides, aromatic anion radicals are likely to behave as outersphere electron donors because steric hindrance should prevent the occurrence of a S_N2 pathway.[6a] These reactions are thus good candidates for examining the application of the theory. In this category, the reduction of *tert*-butyl bromide by the aromatic anion radical of anthracene in *N*,*N'*-dimethylformamide (DMF) is the only example where activation entropy data are available.[16−18] It appeared interesting to examine also the application of the theory to the electrochemical reduction of *tert*-butyl bromide in the same solvent. Before reporting and discussing the corresponding data, we will discuss the electrochemical reduction of acetophenone in DMF. This compound is expected to undergo an outsphere electron transfer where solvent reorganization is the main factor controlling the reaction dynamics. The aim of these experiments was to examine whether the entropy of activation follows the predictions of Marcus−Hush theory for solvent reorganization as a preliminary to the case of a dissociative electron transfer reaction where solvent reorganization is also involved besides bond breaking.

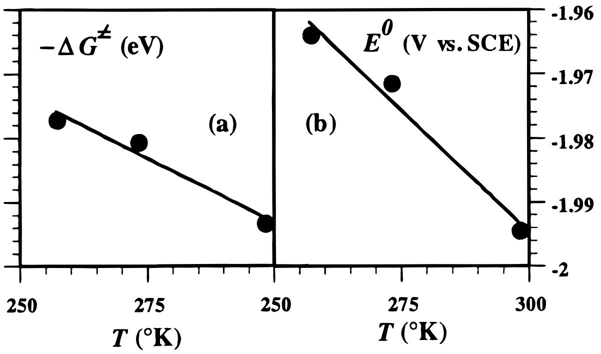

Figure 2. Electrochemical reduction of acetophenone (1 mM) in DMF + 0.1 M *n*-Bu_4BF_4. Variation of the activation free energy (a) and of the standard potential (b) with temperature.

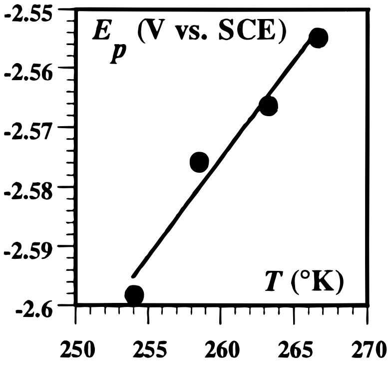

Figure 3. Electrochemical reduction of *t*-BuBr in DMF + 0.1 M *n*-Bu_4-BF_4. Variation of the cyclic voltammetric peak potential with temperature. Scan rate: 0.2 V/s.

Electrochemical Reduction of Acetophenone in DMF. The cyclic voltammetry of acetophenone in DMF exhibits a wave that is chemically reversible at a scan rate of 30 V/s. The wave tends to become irreversible upon decreasing the scan rate as a result of the dimerization of the anion radical.[18] The standard electrochemical rate constant, k_S, was derived from the cathodic-to-anodic peak separation.[1b] The value of the transfer coefficient was found to be close to 0.5 within the investigated range of temperature. The standard potential was determined as the midpoint between the cathodic and the anodic peaks. Its variation with temperature was measured using a reference electrode maintained at constant temperature and connected to the electrochemical cell by a non-isothermal salt bridge (see the Experimental Section). The activation free energy, $\Delta G^{\neq}$, is obtained from the following equation

$$\Delta G^{\neq} = -\frac{RT}{F}\ln\left(\frac{k_S}{Z}\right)$$

where k_S is the standard electrochemical rate constant, noncorrected from double-layer effects, and Z is given by eq 18, i.e. in the present case, Z (cm/s) = 3638 $[T(K)/M\,(g)]^{1/2}$ (M = molar mass). The results are displayed in Figure 2.

$\Delta S° = \partial E°/\partial T$ and, neglecting the variation of the double-layer effect with temperature, $\Delta S^{\neq} = -\partial \Delta G^{\neq}/\partial T$. It follows from Figure 2 that $\Delta S^{\neq} = -0.40$ meV/(mol K) with $\Delta S° = -0.76$ meV/(mol K). Since α is close to 0.5, we may conclude that eq 7 provides a correct prediction of the relationship between the activation entropy and the entropy of the reaction in the case of an outersphere electron transfer where solvent reorganization is the main factor governing the reaction dynamics.

Electrochemical Reduction of *tert*-Butyl Bromide. The entropy of activation was derived from the variation of the irreversible cyclic voltammetric peak potential, E_p, of *tert*-butyl bromide in DMF with temperature (Figure 3). We thus find that $\partial E_p/\partial T = 3.3$ mV/K. The transfer coefficient at the peak, α_p, does not depend significantly upon temperature and is equal

---

(14) (a) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275. (b) Sutin, N. Theory of Electron Transfer Reactions: Insights and Hindsights. *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1983; Vol. 30, pp 441−497. (c) Newton M. D.; Sutin, N. *Ann. Rev. Phys. Chem.* **1984**, *35*, 437.

(15) German, E. D.; Kuznetsov, A. M. *J. Phys. Chem.* **1994**, *98*, 6120.

(16) (a) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617. (b) Daasbjerg, K.; Pedersen, S. U.; Lund, H. *Acta Chem Scand.* **1991**, *45*, 424.

(17) (a) Activation entropies and free enthalpies have also been determined for an intramolecular dissociative electron transfer, namely the cleavage of chloride ion in the anion radicals of 1-, 2-, and 9-chloroanthracenes.[17b] However, the thermochemical data required for a quantitative analysis are lacking. The negative values found for the activation entropy (−1, −0.35, and −0.6 meV/K, respectively) indicates that, in eq 7 or 14, the fragmentation entropy term is overcompensated by the solvation entropy term. (b) Andrieux, C. P.; Delgado, G.; Savéant, J.-M. *J. Electroanal. Chem.* **1993**, *348*, 123.

(18) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1971**, *33*, 419.

to 0.27. The variation of the peak potential with the temperature may be related to the activation entropy as follows.

According to the electrochemical version of the theoretical eq 12, the activation free energy at the cyclic voltammetric peak, $\Delta G_{\mathrm{p}}^{\neq}$, is expressed as

$$\Delta G_{\mathrm{p}}^{\neq} = \frac{D+\lambda_0}{4}\left(1+\frac{E_{\mathrm{p}}-E_{\mathrm{C}}^{\circ}}{D+\lambda_0}\right)^2 - \frac{(T\Delta S_{\mathrm{F,C}}^{\circ})^2}{4D} - \rho \quad (20)$$

where $E_{\mathrm{C}}^{\circ} = E^{\circ} - T(\Delta S_{\mathrm{F}}^{\circ} - \Delta S_{\mathrm{F,C}}^{\circ})$ is the standard potential for the formation of the caged products. The variation of the peak potential, E_{p}, with temperature, which is the quantity we measure, as well as the variation of $\Delta G_{\mathrm{p}}^{\neq}$ with temperature arises from two sources. One comes from the variation of the standard potential, E_{C}°, which gives rise to the entropy of activation, $\Delta S_{\mathrm{p}}^{\neq}$, as expressed by eq 13. The other results from the variation of the pre-exponential factor, Z, with temperature (eq 18) and from the balance between the reduction rate and the diffusion rate at the electrode surface. The second set of factors can be obtained from the differentiation of eq 21 with respect to temperature. Equation 21 is based on the approximation that the transfer coefficient does not vary significantly along the cyclic voltammetric wave and is equal to its value at the peak potential, α_{p}.

$$\Delta G_{\mathrm{p}}^{\neq} = \frac{RT}{F}\ln\left[0.458Z\left(\frac{RT}{\alpha_{\mathrm{p}}F\nu D_{\mathrm{i}}}\right)^{1/2}\right] \quad (21)$$

(see ref 6a and particularly eq 15 therein; D_{i} is the diffusion coefficient). Thus

$$\frac{D+\lambda_0}{4}\left(1+\frac{E_{\mathrm{p}}-E_{\mathrm{C}}^{\circ}}{D+\lambda_0}\right)^2 - \frac{(T\Delta S_{\mathrm{F,C}}^{\circ})^2}{4D} - \rho = \frac{RT}{F}\ln\left[0.458Z\left(\frac{RT}{\alpha_{\mathrm{p}}F\nu D_{\mathrm{i}}}\right)^{1/2}\right]$$

Differentiation with respect to temperature leads to

$$\frac{\partial E_{\mathrm{p}}}{\partial T} = \frac{\Delta S^{\neq}{}_{\mathrm{p}} + \sigma}{\alpha_{\mathrm{p}}} \quad \text{with}$$

$$\sigma = \left\{\frac{R}{F}\ln\left[0.458Z\left(\frac{RT}{\alpha_{\mathrm{p}}F\nu D_{\mathrm{i}}}\right)^{1/2}\right] + 1 - \frac{T}{2D_{\mathrm{i}}}\frac{\partial D_{\mathrm{i}}}{\partial T}\right\} \quad (22)$$

With the following numercial values, $T = 263.05$ K (mean value of the temperature range investigated), $\nu = 0.2$ V/s, $D_{\mathrm{i}} = 10^{-5}$ cm^2 s^{-1}, and $(1/D_{\mathrm{i}})\ (\partial D_{\mathrm{i}}/\partial T) = 0.02$ (from the variation of the peak current with temperature). Thus $Z = 5 \times 10^3$ cm s^{-1} and $\sigma = 0.985$ mV/K. Thus, from eq 22, $\Delta Sp^{\neq}/\alpha_{\mathrm{p}} = -0.35$ meV/(mol K). For pursuing the analysis of the data the following thermochemical parameters were used:

$$D = 2.87\ \mathrm{eV},^{19}$$

$$\Delta S_{\mathrm{F}}^{\circ} = S_{t\text{-Bu}\bullet}^{\circ} + S_{\mathrm{Br}\bullet}^{\circ} - S_{t\text{-BuBr}}^{\circ} = 1.27\ \mathrm{meV/(mol\ K)}^{19}$$

In using these parameters, we assume that they do not change significantly from the gas phase to the DMF solution.[19,20] The estimation of the standard potential, E°, for the formation of the separated products, at a given temperature, say 298 K, does not require the knowledge of the absolute S° of Br$^-$ in DMF. Knowing the value of the conventional S° (with the convention that $S_{\mathrm{H+}}^{\circ} = 0$) suffices since E° is defined toward a reference electrode (here the aqueous saturated calomel electrode). The value of E°, obtained as described in ref 21,[21] is -0.92 V vs SCE. The absolute value of $S_{\mathrm{Br-}}^{\circ}$ is however needed to estimate $\Delta S_{\mathrm{S}}^{\circ} \approx S_{\mathrm{Br-}}^{\circ} - S_{\mathrm{Br}\bullet}^{\circ} = -1.307$ meV/(mol K).[22] On total, the standard entropy for the formation of the separated products is very close to zero, $\Delta S^{\circ} = -0.037$ meV/(mol K), as a result of the compensation of the (positive) entropy created by the formation of two particles out of one and of the (negative) entropy for the solvation of Br$^-$. As a consequence, the variation of the standard potential referred to a constant-temperature (298 K) reference electrode, as corresponds to our experimental conditions, is very small. At 263.05 K, $E^{\circ} = -0.918$ V vs SCE.

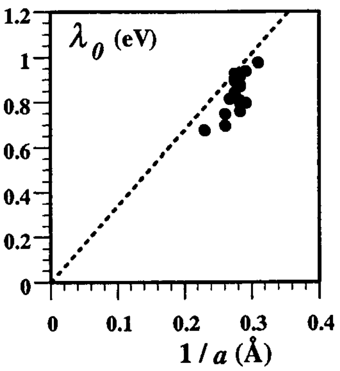

Figure 4. Solvent reorganization energies derived from the standard rate constants of the electrochemical reduction of aromatic hydrocarbons in DMF uncorrected from double-layer effects.[13] Variation with the equivalent hard sphere radii. Dotted line: Hush's preduction.

Defining ϕ as the ratio between the entropy for the formation of the products in the cage and the entropy for the formation of the free products, $\phi = \Delta S_{\mathrm{F,C}}^{\circ}/\Delta S_{\mathrm{F}}^{\circ}$, eq 13 leads to

$$\frac{\Delta S^{\neq}{}_{\mathrm{p}}}{\alpha_{\mathrm{p}}} = \Delta S_{\mathrm{S}}^{\circ} + \phi\Delta S_{\mathrm{F}}^{\circ} + \phi^2\frac{T(\Delta S_{\mathrm{F}}^{\circ})^2}{2D}$$

From this equation we may thus estimate which value of ϕ fits the entropy data derived from the variation of the peak potential with temperature. We may also estimate which value of ϕ fits with the location of the peak potential in the middle of the temperature range. Agreement between these two values provides a test of the theory.

As pointed our earlier[23] and can be seen in Figure 4 for the case of electrochemical reduction of aromatic hydrocarbons in DMF,[13] Hush's estimation of the solvent reorganization energy[4c,d] provides a satisfactory prediction when applied to standard activation energies uncorrected from double-layer effects. In the following estimates of the solvent reorganization energies we thus apply the relationship λ_0 (eV) = 3/a (Å). Taking the

---

(19) (a) Benson, S. N. *Thermochemical Kinetics*; Wiley: New York, 1976. (b) Cox, B. G.; Hedvig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477.

(20) $\Delta S_{\mathrm{F}}^{\circ}$ is calculated from the gas phase S°'s[19] with correction for the change in the standard state from the gas phase to the liquid phase (1 atm and 1 mol/L, respectively) which amounts to decreasing each of the S°'s by $R/F\ \ln(22.4) = 0.268$ meV/(mol K).

(21) Andrieux, C. P.; Gallardo, I.; Savéant, J.-M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638.

(22) (a) $S_{\mathrm{Br-,DMF}}^{\circ} = S_{\mathrm{Br-,H_2O}}^{\circ}(104.6) - \Delta S_{\mathrm{Br-,transfer\ H_2O\rightarrow DMF}}^{\circ}(107.4) = -2.78$ J/(mol K). (b) $S_{\mathrm{Br\bullet(1L)}}^{\circ} = 175.022 - 25.85 = 123.37$ J/(mol K).[19b,20] $\Delta S_{\mathrm{S}}^{\circ} \approx S_{\mathrm{Br-}}^{\circ} - S_{\mathrm{Br}\bullet}^{\circ} = -128.1$ J/(mol K). (b) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.

(23) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

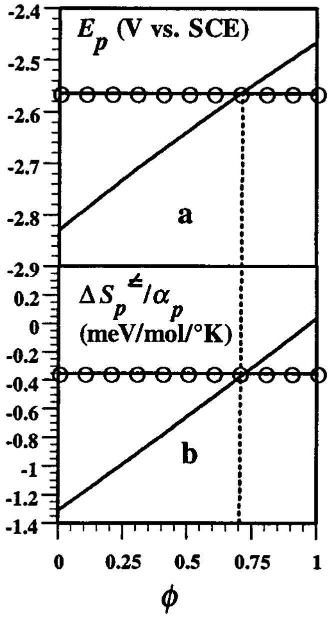

Figure 5. Electrochemical reduction of *tert*-butyl bromide in DMF. Comparison of the experimental (○) and predicted (solid lines) peak potentials (a) and entropies of activation (b).

radius of Br^- as equal to 1.96 Å,[24] one obtains $\lambda_0^P = 1.53$ eV. CPK models indicate that, in *t*-BuBr, *ca*. 60% of the surface of the bromide atom is exposed to the solvent. Thus, $\lambda_0^R = 0.92$ eV. We may now start the iterative procedure for determining λ_0 by application of eq 17 for each value of ϕ. At the cyclic voltammetric peak, combination of eqs 9 and 17 leads to

$$\Delta G_p^{\neq} + \rho = D\,(1 - Y^{\neq})^2 - (1 - Y^{\neq})T\phi\Delta S_F^\circ + [Y^{\neq}\lambda_0^R + (1 - Y^{\neq})\lambda_0^P]\left(1 - Y^{\neq} - \frac{T\phi\Delta S_F^\circ}{2D}\right)^2$$

From eqs 18 and 22 it is found that $\Delta G_p^{\neq} = 0.296$ eV. A reasonable estimate of ρ, to insure that the reaction is adiabatic, is 1−2 kcal/mol, say 1.5 kcal/mol (0.065 eV).[6a,14a] Iterative resolution of the above equation thus leads to the value of $Y^{\neq}$ for each value of ϕ. From $Y^{\neq}$ we then derive

$$X^{\neq} = 1 - Y^{\neq} - T\phi\Delta S_F^\circ/2D = \alpha_p$$

$$E_p - E_C^\circ = \Delta G_C^\circ = (D + \lambda_0)(2X^{\neq} - 1)$$

Taking into account that $E_C^\circ = E^\circ - T\Delta S_F^\circ(1 - \phi)$, we finally obtain E_p as a function of ϕ. The variations of the predicted values of E_p and $\Delta S_p^{\neq}/\alpha_p$ are shown in Figure 5. The value of ϕ that fits the experimental data is practically the same in both cases ($\phi = 0.70$). $\lambda_0 = 1.13$ eV and $\alpha_p = 0.30$ (to be compared with the experimental value 0.27).

We may thus conclude that there is a satisfactory agreement between experiment and theory.

Reaction of *tert*-Butyl Bromide with Anthracene Anion Radical in DMF. Available data indicate a value of 0.550 eV for the activation free energy and −0.46 meV/(mol K) for the activation entropy at 298 K, taking k_BT/h (6.2×10^{12} M^{-1} s^{-1}) the pre-exponential factor.[16b] For testing the theory we take as pre-exponential factor Z as defined in eq 19, i.e. 3×10^{11} M^{-1} s^{-1}.[13] Thus, $\Delta G^{\neq} = 0.471$ eV and $\Delta S^{\neq} = -0.20$ meV/(mol K).

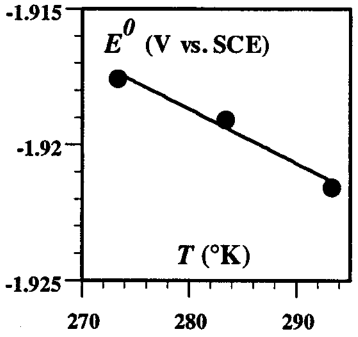

Figure 6. Variation of the standard potential of anthracene with temperature from the midpoint of the cathodic and anodic peak potentials in DMF + 0.1 M *n*-Bu_4BF_4.

The various pertinent thermochemical parameters are as follows:

$$D = 2.87 \text{ eV}, \qquad \Delta S_F^\circ = 1.27 \text{ meV/(mol K)}$$

For estimating ΔG° and ΔS_S° we need the standard potential of the anthracene/anthracene anion radical couple at 298 K and its variation with temperature. From the data in Figure 6:

$$E_{\text{anth}}^\circ \text{ (298 K)} = -192 \text{ V vs SCE},$$

$$\Delta S_{\text{anth}\to\text{anth}^{\bullet -}}^\circ = \partial E_{\text{anth}}^\circ/\partial T = -0.20 \text{ meV/(mol K)}$$

Thus

$$\Delta G^\circ = E_{\text{anth}}^\circ - E_{\text{RX}}^\circ = -1 \text{ eV}, \qquad \Delta S_S^\circ = -1.107 \text{ meV/(mol K)}$$

In estimating the solvent reorganization energies we use the formal dependency with the equivalent hard sphere radii depicted by eq 16 and an experimental proportionality factor derived from previous data obtained in the case of aromatic hydrocarbon self-exchange,[13] i.e. λ_0 in electronvolts and angstroms.

$$\lambda_0^R = 4\left(\frac{1}{2a_{\text{RX}}} + \frac{1}{2a_{\text{anthracene}}} - \frac{1}{a_{\text{RX}} + a_{\text{anthracene}}}\right)$$

$$\lambda_0^P = 4\left(\frac{1}{2a_{\text{X}^-}} + \frac{1}{2a_{\text{anthracene}}} - \frac{1}{a_{\text{X}^-} + a_{\text{anthracene}}}\right)$$

Thus, $\lambda_0^R = 0.572$ eV and $\lambda_0^P = 0.852$ eV ($a_{\text{anthracene}} = 3.8$ Å[13]). The strategy we use for testing the theory consists of considering the ratio between the entropy for the formation of the products in the cage and the entropy for the formation of the free products, $\phi = \Delta S_{F,C}^\circ/\Delta S_F^\circ$, as an adjustable parameter varying from 0 to 1 and examining whether the value of ϕ obtained from the comparison between the experimental and predicted free energies of activation is the same as the value obtained from the comparison of the experimental and predicted entropies of activation.

For each value of ϕ, $Y^{\neq}$ is derived by iteration from eq 8, i.e.

$$Y^{\neq} = 1 - \frac{1}{2}\left(1 + \frac{\Delta G^\circ + T\Delta S_F^\circ(1 - \phi)}{D + \lambda_0} + \frac{T\Delta S_F^\circ\phi}{D}\right)$$

and eq 17. $X^{\neq}$ is then obtained from the second eq 8. The variations of $X^{\neq}$ and $Y^{\neq}$ with ϕ are shown in Figure 7a. The predicted values of $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are then computed from eqs 9 and 10 as functions of ϕ, taking the same value of the avoided crossing energy as in the electrochemical case. As seen from

---

(24) *Handbook of Chemistry and Physics*, 72nd Ed.; CRC: Cleveland, OH, 1991−1992; p 12-8.

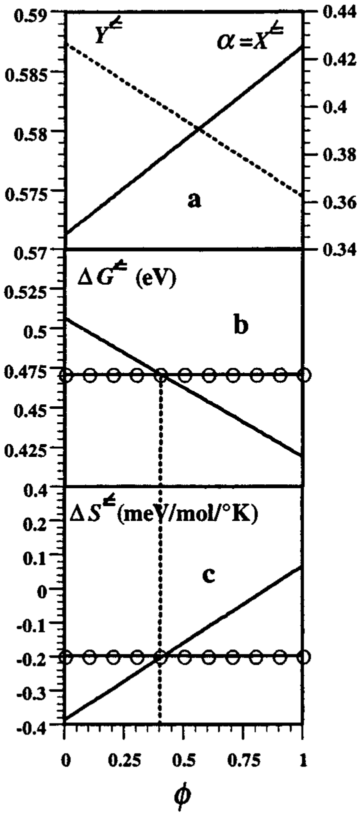

Figure 7. Reaction of *tert*-butyl bromide with anthracene anion radical in DMF. Comparison of the experimental (○) and predicted (solid lines) free energies (b) and entropies (c) of activation. (a) Theoretical variations of $\alpha = X^{\neq}$ and $Y^{\neq}$ with ϕ.

Figures 7b,c, the values of ϕ corresponding to the experimental values are practically the same for the activation free energy and the activation entropy. This common value of $\phi = 0.41$ is smaller than in the electrochemical case (0.70) as predicted from the theory. The symmetry factor as a value of 0.38, clearly below 0.5, as expected for a dissociative electron transfer reaction.

In total, we may conclude that there is a satisfactory agreement between the theoretical predictions and the experimental data.

Conclusions

In summary,

1. Application of the dissociative electron transfer theory to the prediction of the activation free enthalpy and entropy and of the symmetry factor involves eqs 8−11. Determining a value of the solvent reorganization free energy that reflects the variation of the solvation radius with the length of the breaking bond requires a rapidly converging iteration defined by eq 17.

2. In most practical cases, simplification of the rigorous equations into the approximate eq 14 produces satisfactory predictions. The contribution of cleavage to the intrinsic barrier involves the bond dissociation energy rather than the bond dissociation free energy.

3. When the cleaving molecule bears no charge in the initial state, the activation entropy is a compensating combination of a negative contribution induced by the change in solvation and of a positive contribution resulting from floppy bending vibrations of the breaking bond.

4. In relating the activation free enthalpy to the driving force, the formation of caged rather than free moving fragments should be taken into account through the corresponding standard entropy of cleavage. This factor is not generally available from independent sources. A way of circumventing this difficulty is to analyze simultaneously the activation free enthalpy and entropy data. Regarding the activation entropy as close to zero should lead to satisfactory results for more approximate applications.

5. Application of the theory to the electrochemical reduction of *tert*-butyl bromide and to its homogeneous reduction by the anthracene anion radical in DMF lead to a satisfactory agreement between the theoretical predictions and the experimental data.

Experimental Section

Chemicals. The solvent (DMF), the supporting electrolyte (n-Bu_4BF_4), and t-BuBr were Fluka products and were used as received.

Cyclic Voltammetry. The instrument consisted of a three-electrode arrangement equipped with a potentiostat and a positive feedback correction of the ohmic drop.[25] The working electrode was a 3-mm-diameter glassy carbon (Tokai) disk carefully polished and rinsed before each run. The cell was thermostated by means of a cryostat with a 2-propanol circulation. The reference electrode was maintained at 20 °C by means of another thermostat. The non-isothermal salt bridge arrangement was the same as previously described[26] except that the Cd−Hg amalgam reference electrode was replaced by an aqueous SCE.

Acknowledgment. We are indebted to J. Moiroux (Laboratoire d'Electrochimie Moléculaire de l'Université Denis Diderot), J.-P. Morel (Université de Clermont-Ferrand), and D. D. M. Wayner (NRC, Ottawa) for their criticisms and/or suggestions on various parts of the manuscript. Discussions with R. A. Marcus (Caltech) about the manuscript in ref 10b and during the preparation of the present paper were extremely helpful.

JA972598P

---

(25) Garreau, D.; Savéant, J.-M. *J. Electroanal. Chem.* **1972**, *35*, 309.

(26) Anxolabéhère, E.; Lexa, D.; Momenteau, M.; Savéant, J.-M. *J. Phys. Chem.* **1992**, *96*, 9348.