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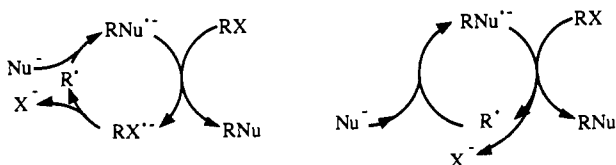
Electron Transfer, Bond Breaking, and Bond Formation

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For a long time, electron-pair transfer has provided a mechanistic basis for reactivity in most organic reactions. As an extreme example, the reductive hydrodimerization of activated olefins was thought originally to proceed by which one molecule of substrate extracting an electron pair from the electrode leading to a dianion then reacted with a second molecule of the substrate in a Michael-type fashion.¹ Since then, it has been established that electron transfers between electrodes and organic molecules are one-electron transfers, even if these primary steps are associated with homogeneous reactions that may be of the Lewis acid-base type.² In homogeneous chemistry and also in photochemistry, single-electron transfer has been shown to play an important role. As an illustration, consider the $S_{RN}1$ substitution reaction³⁻⁹ in which anion radicals are an essential part of the chain process,



and in which single-electron transfer plays an important role in both initiation and termination steps. Even classical electron-pair-transfer reactions such as S_N2 substitutions may be viewed in several cases as single-electron-transfer reactions, provided account is taken that electron transfer is concerted with bond breaking and bond formation.¹⁰

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As long as the electron-transfer step is of the outer-sphere type,¹¹ i.e., is not concerted with bond breaking or bond formation,¹² the Marcus-Hush model¹³⁻¹⁵ provides an efficient, though approximate, means of relating structure and reactivity. It indeed leads, for homogeneous as well as for electrochemical reactions, to a simple quadratic activation-driving force relationship and a simple expression of the intrinsic barrier. The reactivity of a given compound in a given solvent may thus be predicted from equilibrium characteristics of the initial and final states of the reactant system and from the optical and static dielectric constants of the solvent. It would be very useful to find similar relationships for reactions in which more chemistry is involved than in mere outer-sphere electron transfers, i.e., in which bonds are broken and/or formed. An important step in this direction is the recent extension of the Marcus-Hush model to dissociative electron transfers, i.e., reactions in which electron transfer is concerted with the breaking of one bond, showing that the main factor that controls the driving force and the intrinsic barrier is the dissociation energy of the bond being broken. The model may thus be used for estimating bond dissociation energies and, therefore, standard potentials and intrinsic barrier free energies, when these quantities are not available from other sources.

- (1) Baizer, M. M. *J. Electrochem. Soc.* **1964**, *111*, 215.
- (2) Andrieux, C. P.; Savéant, J.-M. *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.
- (3) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
- (4) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.
- (5) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323.
- (6) Rossi, R. A.; Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983.
- (7) Russell, G. A. *Adv. Phys. Org. Chem.* **1987**, *24*, 271.
- (8) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.
- (9) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1.

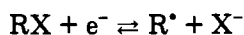
In reactions involving electron transfer and bond breaking, the two steps may be concerted or successive. How one can distinguish experimentally between the two mechanisms and what the factors are that control the occurrence of one or the other mechanism are questions that have important implications in all fields of electron-transfer chemistry. For example, the link between electron transfer and radical chemistry rests on the nature of the bond-breaking mechanism together with the redox properties of the radicals that may be thus generated. In photochemistry, strategies aimed at minimizing or suppressing the effects of back electron transfer are also dependent upon the mechanism of electron transfer–bond breaking reactions.¹⁶

In stepwise reactions, the anion radical, formed upon the initial electron transfer, cleaves in a second step, to the corresponding radical and the anion of the leaving group. The latter step may itself be viewed as a particular case of dissociative electron transfer where the unpaired electron located in one portion of the molecule dissociatively reduces a bond belonging to the same molecule. Adapting the intermolecular dissociative-electron-transfer model to these *intramolecular dissociative-electron-transfer* reactions will at the same time allow one to describe the dynamics of the reverse reaction, i.e., the reaction of a nucleophile with a radical as an *associative-single-electron-transfer reaction*. These two reactions are essential steps of the chain propagation loop in $S_{RN}1$ nucleophilic substitutions, and thus the modeling of their dynamics is an important step in the prediction of the dependency of $S_{RN}1$ reactivity upon the structures of the substrate and the nucleophile.

Dissociative electron transfer concepts may also be applied to entirely different fields of organic chemistry, for example, the deprotonation of cation radicals (H^+ transfer or concerted $H^+ - e^-$ transfer?).

Dynamics of Dissociative Electron Transfer

Modeling of the Dynamics of Dissociative Electron Transfer. As far as solvent reorganization and changes in lengths and angles of bonds that are not broken during the reaction are concerned, the Marcus–Hush approach may be followed. The main event occurring in the reaction



(R is not necessarily a carbon-centered radical, X^- is not necessarily a halogen ion, and e^- represents an electron from an electrode or from an outer-sphere electron donor), and the following equations summarize the description of dissociative-electron-transfer dynamics.^{9,17} These are based on the approximation of the potential energy of the reactant by a Morse curve and the potential energy of the products by a purely repulsive function equal to the repulsive portion of the reactant Morse curve (Figure 1).

(10) See the discussion in pp 96–98 of ref 9 and references cited therein.
(11) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970.

(12) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.

(13) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966.

(14) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962.

(15) Marcus, R. A. *Theory and Applications of Electron Transfers at Electrodes and in Solution*. In *Special Topics in Electrochemistry*; Rock, P. A., Ed.; Elsevier: New York, 1977; pp 161–179.

(16) Saeva, F. *Top. Curr. Chem.* **1990**, *156*, 61.

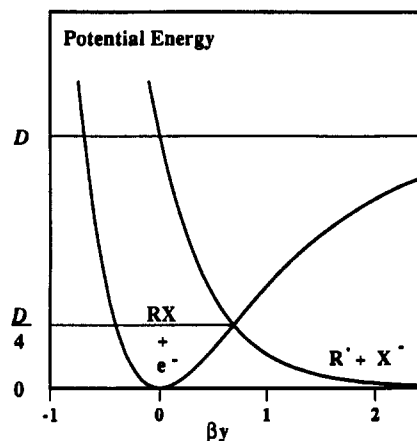


Figure 1. Morse curve approximation of the reactant and product systems: y , elongation of the breaking bond from the ground state; $\beta = \nu_0(2\pi^2m/D)^{1/2}$ (ν_0 , vibration frequency of the breaking bond; m , reduced mass).

$$G_R = G_R^\circ + w_R + \frac{\lambda_0}{2}(x - x_R)^2 + D[1 - \exp(-\beta y)]^2$$

$$G_P = G_P^\circ + w_P + \frac{\lambda_0}{2}(x - x_P)^2 + D[\exp(-\beta y)]^2$$

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

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

$$\alpha = \frac{\partial \Delta G^\ddagger}{\partial \Delta G^\circ} = 0.5 \left(1 + \frac{\Delta G^\circ - w_R + w_P}{4\Delta G_0^\ddagger} \right)$$

where ΔG^\ddagger is the activation free energy of dissociative electron transfer, $\Delta G^\circ = G_P^\circ - G_R^\circ$ is the standard free energy, ΔG_0^\ddagger is the intrinsic barrier free energy, D is the bond dissociation energy, λ_0 is the Hush–Marcus solvent reorganization factor, x is the fictitious charge on the reactants (x_R and x_P are its values for the reactant and product systems, respectively), w_R and w_P are work terms, and α is the symmetry factor. Ab initio calculations, taking methyl halides as examples, have confirmed that these approximations are quite reasonable.¹⁸

Experimental Testing of the Model. *The electrochemical reduction of butyl^{17,19} and benzyl²⁰ halides* provides a typical example where the model can be tested using cyclic voltammetric data as summarized below. The intrinsic barriers and the symmetric factors may be derived from the experimental cyclic voltammograms as summarized in Figure 2 and the following equations. The standard potential of the $RX/R^{\cdot} + X^-$ couple then used, E° , is derived from thermochemical data.^{17,19,20} The preexponential factor, A^{e1} , as well as the solvent reorganization factor, λ_0 , are obtained from comparison with typical outer-sphere electron-transfer reactions (reduction of aromatic hydrocarbons) in the same solvent.¹⁹

(17) Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

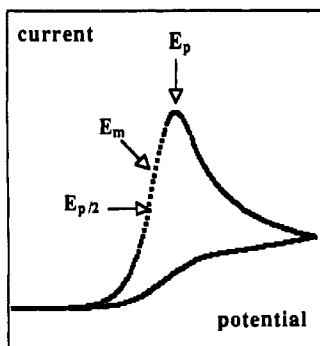


Figure 2. Cyclic voltammogram characteristic potentials in dissociative electrochemical reductions such as those of butyl and benzyl halides.

activation free energy:

$$\Delta G_{p(m)}^{\ddagger} = \frac{RT}{F} \ln \left[A^{e1} \left(\frac{RT}{\alpha F v D} \right)^{1/2} \right] - 0.780(+0.145) \frac{RT}{F}$$

A^{e1} : preexponential factor; v : scan rate;
 D : diffusion coefficient

driving force: $\Delta G^{\circ} = E_{p(m)} - E^{\circ} - \phi_r$

ϕ_r : potential at the reaction site

intrinsic barrier: $\Delta G_0^{\ddagger, \text{theor}} = \frac{D + \lambda_0}{4}$

$$\Delta G_0^{\ddagger, \text{exp}} = \frac{[(\Delta G^{\circ} - 2\Delta G_{p(m)}^{\ddagger})^2 - (\Delta G^{\circ})^2]^{1/2} - \Delta G^{\circ}}{4}$$

symmetry factor (transfer coefficient):

$$\alpha^{\text{exp}} = \frac{RT}{F} \frac{1.85}{E_{p/2} - E_p}, \quad \alpha^{\text{theor}} = 0.5 \left(1 + \frac{\Delta G^{\circ}}{4\Delta G_0^{\ddagger}} \right)$$

Comparison between the experimental data and the predictions of the model (see Tables I and II in ref 19) shows that there is a quite satisfactory agreement between the experimental and theoretical values of the intrinsic barrier free energy. The theory also accounts for the small value (distinctly below 0.5) of the symmetry factor which thus appears as a consequence of the fact that the effective reduction potential is far negative to the standard potential.

Homogeneous Reduction of Butyl²¹ and Benzyl²² Halides by Electrochemically Generated Aromatic Anion Radicals. Comparison between theoretical predictions based on the above model and experiment (Figure 3)^{17,19} reveals excellent agreement for the tertiary halides. Passing to secondary and primary halides, the reactions become faster than predicted by the theory. This result combined with previous stereochemical results²³ and entropy measurements^{12,24} points to the conclusion that the S_N2 mechanism prevails over the

simple dissociative-electron-transfer mechanism as shown in the reaction scheme in Figure 3. Low-valent metalloporphyrins (Co(I), Fe(I), Fe("0")) generated electrochemically provide other examples where the predictions of the dissociative-electron-transfer model are satisfactorily followed when steric hindrance at the reacting carbon and/or in the porphyrin impedes the bonding interactions in the transition state, whereas an S_N2 mechanism is followed in the absence of steric hindrance as revealed by a reactivity that is higher than predicted by the dissociative-electron-transfer model.^{12,25}

Application to the Estimation of Bond Dissociation Energies. Since the above described model satisfactorily reproduces the experimental rate data for reactions where the standard potential of the $RX/R^{\bullet} + X^{-}$ couple is available from external sources, it may be used to estimate such thermodynamic parameters in cases where they are not known. The main quantity of interest in this connection is the bond dissociation energy, and the most convenient source of experimental data is the peak potential of the cyclic voltammogram reduction of the substrate. Both the $RX/R^{\bullet} + X^{-}$ standard potential and the intrinsic barrier are simple functions of the bond dissociation energy:

$$E^{\circ}_{RX/R^{\bullet}+X^{-}} = D + C, \quad \Delta G_0^{\ddagger} = (D + \lambda_0)/4$$

where

$$C = -T(\bar{S}_{RX} - \bar{S}_{R^{\bullet}} - \bar{S}_{X^{-}}) + E^{\circ}_{X^{\bullet}/X^{-}}$$

The same equations, given before, that relate the peak potential to the standard potential and the intrinsic barrier may thus be used in reverse to estimate D . For the same halogen and for molecules of similar sizes, C and λ_0 may be regarded as approximately constant. The determination of several previously unknown bond dissociation energies from the peak potentials is illustrated in Figure 4.^{20,26} It is seen that the linear relationship,

$$\Delta D \text{ (eV)} = \frac{2}{3} \Delta(F^{\circ}_{X^{\bullet}/X^{-}} - E_p) \text{ (V)}$$

which is obtained from the neglect of the quadratic character of the activation-driving force relationship, is a good approximation for a quick and straightforward estimate of the bond dissociation energy. Another outcome of the method is the determination of the standard potential and the intrinsic barrier of the reaction.

Single Electron Transfer and Bond Breaking. Stepwise versus Concerted Mechanisms

For electrochemical reactions, a convenient way for distinguishing between the two mechanisms derives from the analysis of the potential location of the cyclic voltammogram wave, its variation with the scan rate, and its shape.² A particularly illustrative example is the reduction of differently substituted benzyl halides where the transition between one mechanism and the other is observed upon changing the substituent.²⁰ The nitro derivatives undergo a stepwise reductive cleavage

(25) Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* 1981, 103, 6806.

(26) Andrieux, C. P.; Differding, E.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.*, in press.

(18) Bertran, J.; Gallardo, I.; Moreno, M.; Savéant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 9576.

(19) Savéant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 10595.

(20) Andrieux, C. P.; Le Gorand, A.; Savéant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 6892.

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

(22) Lund, T.; Lund, H. *Acta Chem. Scand. B* 1987, 41, 93.

(23) Hebert, E.; Mazaleyrat, J. P.; Nadjo, L.; Savéant, J.-M.; Welvert, Z. *Nouv. J. Chem.* 1985, 9, 75.

(24) Daasbjerg, K.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* 1991, 24, 470.

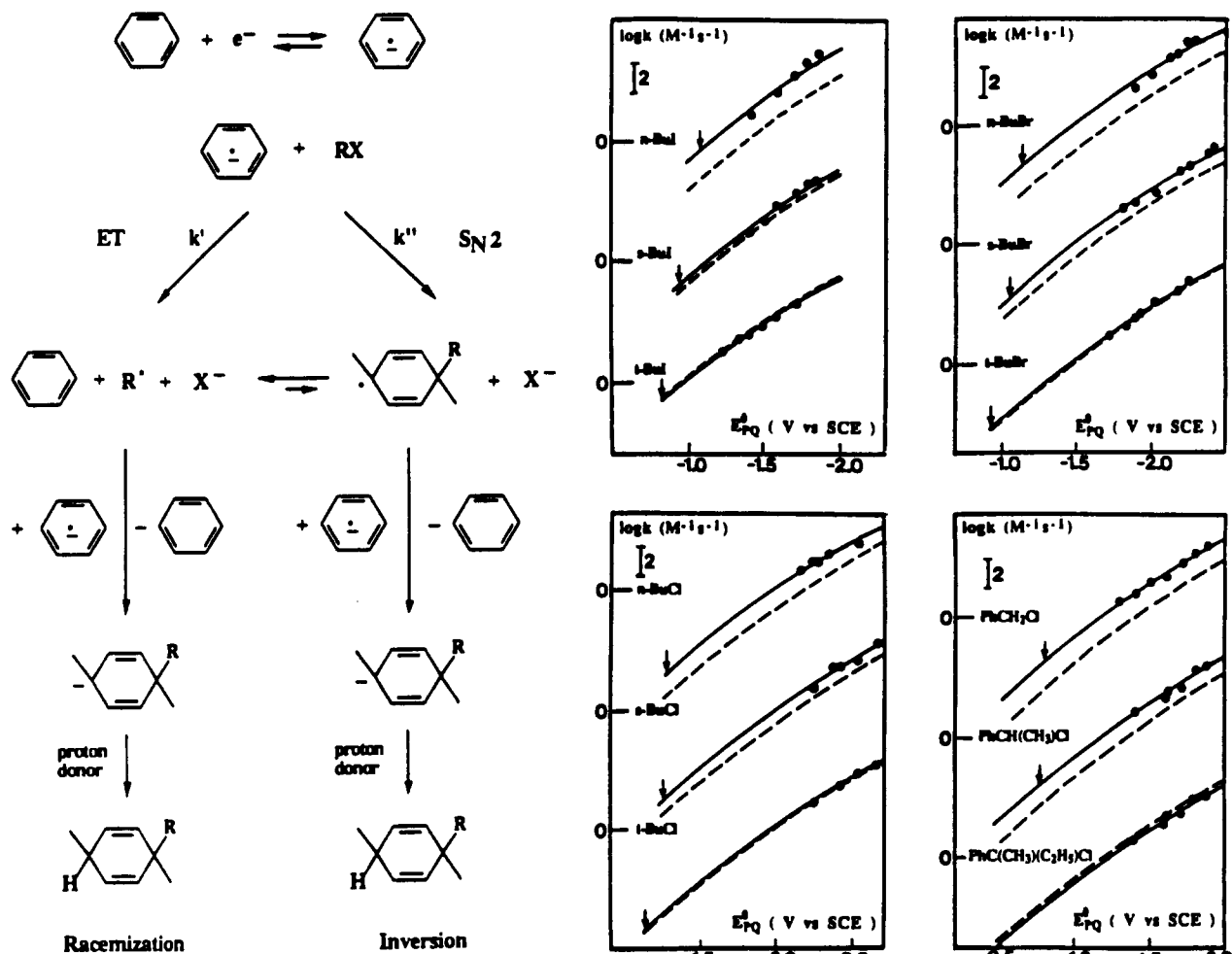


Figure 3. Experimental testing of the dissociative-electron-transfer model with homogeneous reactions. Reaction of tertiary, secondary, and primary butyl and benzyl halides with electrochemically generated aromatic anion radicals in DMF. The points and solid lines represent the experimental data, and the dashed lines represent the predictions of the model.

as indicated by the characteristics of the peak where the reductive cleavage takes place (see Figure 2 in ref 20). The thickness of the peak and the variations of the peak potential with the scan rate are indicative of mixed kinetic control of the reaction by an electron-transfer step followed by an irreversible chemical reaction. $RX^{\cdot-}$ is observed through its reoxidation wave at high scan rates, and the peak potential at low scan rate is not very distant from the standard potential of the $RX^{\cdot-}/RX$ couple, which is a measure of the energy of the π^* orbital of the substituted phenyl ring.

All the other benzyl or aryl methyl halides (Figure 2 in ref 20) undergo dissociative electron transfer as indicated by the fact that the reduction potentials are very positive with respect to the energy of the π^* orbital and by the small value (~ 0.3) of the symmetry factor.

With simple aliphatic halides, dissociative electron transfer is always observed,^{9,21} whereas the reduction of aromatic halides has always been found to go through the intermediacy of the anion radical.²⁷⁻²⁹

The same conclusion has been reached for homogeneous reactions of aromatic halides (and also for vinylic halides) in which the electron donors were electro-

chemically generated aromatic anion radicals, using as a diagnostic tool the assignment of the rate-determining steps and the values of the symmetry factor.²⁷⁻³⁰ Under the same conditions, aliphatic and unsubstituted benzylic halides have been shown to follow the dissociative mechanism as in the electrochemical case, provided steric hindrance is strong enough for impeding the S_N2 reaction.¹⁹ The reaction is then followed by coupling of the alkyl radical thus generated with the aromatic anion radical.

One important controlling factor of the passage from the stepwise to the concerted mechanism is the energy of the π^* orbital as exemplified by the behavior of the arylmethyl halides. The π^* orbital energy, as measured by the standard potential of the $RX^{\cdot-}/RX$ couple, increases from the nitro derivative to the other compounds in the series. It is low enough in the former case to trap the unpaired electron in the π^* orbital before it dissociatively reduces the carbon-halogen bond in a successive step. In the other cases, the direct dissociative reduction of the carbon-halogen bond is energetically more favorable than the injection of the electron in the π^* orbital. The electrochemical reduc-

(27) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Savéant, J.-M.; *J. Am. Chem. Soc.* 1979, 101, 3431.

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

(29) Andrieux, C. P.; Savéant, J.-M.; Zann, D. *Nouv. J. Chim.* 1984, 8, 107.

(30) Gatti, N.; Jugelt, W.; Lund, H. *Acta Chem. Scand. B* 1987, 41, 646.

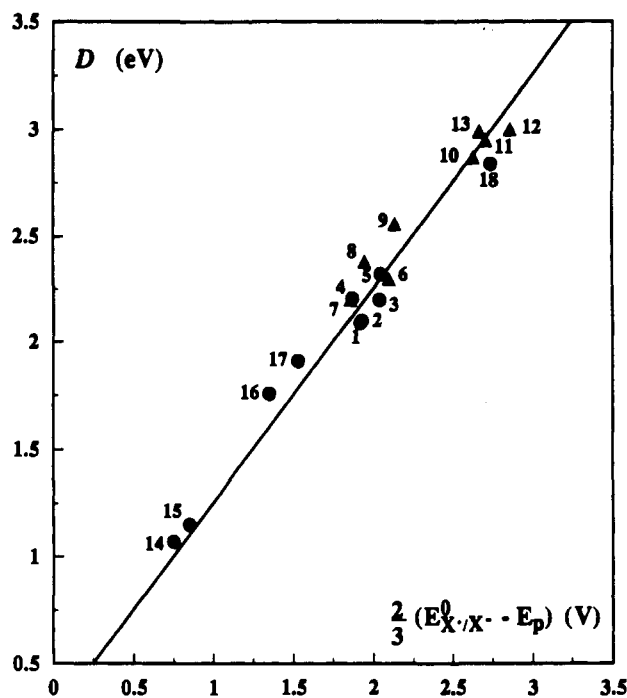
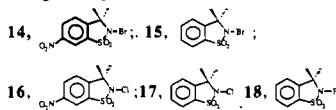


Figure 4. Correlation between bond dissociation energies and reduction peak potentials (at 0.1 V/s): ▲, D derived from thermochemical data; ●, D derived from peak potentials.

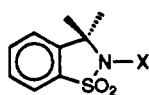
Carbon-halogen bonds:

1, 2-cyanobenzyl bromide; 2, 4-cyanobenzyl bromide; 3, 3-cyanobenzyl bromide; 4, 4-acetyloxybenzyl bromide; 5, 9-anthracenylmethyl chloride; 6, benzyl bromide; 7, *t*-butyl iodide; 8, *s*-butyl iodide; 9, *n*-butyl iodide; 10, *t*-butyl bromide; 11, *s*-butyl bromide; 12, *n*-butyl bromide; 13, benzyl chloride.

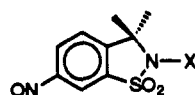
Nitrogen-halogen bonds:



tion of aromatic *N*-halosultams²⁶ exhibits the same trends and, at the same time, reveals the role of the



X = Br, Cl, F: concerted mechanism



X = Br, Cl: concerted mechanism
X = F: stepwise mechanism

bond dissociation energy. The smaller the bond dissociation energy, the larger the tendency for the concerted mechanism to prevail over the stepwise mechanism. The fact that nitro *N*-bromosultams and nitro *N*-chlorosultams undergo dissociative electron transfer whereas benzyl bromides and chlorides of similar π^* orbital energy follow the stepwise mechanism is a consequence of N-X bonds being much weaker than C-X bonds.

In most cases, the conclusions of direct or indirect electrochemical studies agree with the conclusions derived from gas-phase studies or of γ -ray irradiation in apolar or weakly polar solid matrices at low temperature, although in the latter case it is sometimes difficult to distinguish between a weakly bound R^{\cdot} , X-adduct and a true $RX^{\cdot-}$ anion radical. With these techniques, anion radicals are found with aryl halides

and not with aliphatic halides.³¹⁻³⁴ Pulse radiolysis studies also point to the formation of the anion radical with the aryl halides in water.³⁵⁻³⁷

An interesting borderline case is that of perfluoroalkyl halides where the gas-phase and low-temperature matrix studies indicate the intermediacy of the anion radical,³⁸⁻⁴⁰ whereas the electrochemical reduction appears to follow the concerted mechanism.⁴¹ As revealed by recent theoretical calculations,¹⁸ this difference of behavior is related to the polar character of the solvent used in the electrochemical studies.

Intramolecular Dissociative Electron Transfer and Associative Electron Transfer

In reductive cleavage reactions, electron transfer and bond breaking are two distinct successive steps as in



The first step is a simple outer-sphere electron-transfer reaction, and its dynamics may therefore be described in a general and approximate manner by the Marcus-Hush model.¹³⁻¹⁵ It is interesting to consider also a model describing the dynamics of the second step in which an anion radical cleaves to form a radical and an anion. It also allows the description the dynamics of the reverse reaction in which a bond is created upon reaction of a nucleophile with a radical. These reactions are two essential steps of the propagation chain of the $S_{RN}1$ substitution reactions evoked in the introduction,³⁻⁹ and therefore such models may help to relate structure and reactivity in $S_{RN}1$ reactions. The dissociation of anion radicals may be viewed as an intramolecular dissociative single-electron transfer, and correlatively the reverse reaction may be viewed as an associative single-electron transfer. A Morse curve model of the same type as that described earlier for intramolecular or electrochemical dissociative electron transfers has recently been proposed for describing the kinetics of these two reactions.⁴² Representing the potential energy curve of the $RX^{\cdot-}$ dissociation by a Morse curve,

$$G_{RX^{\cdot-}} = G^{\circ}_{RX^{\cdot-}} + D_{RX^{\cdot-}} \{1 - \exp[-\beta(y - y_{RX^{\cdot-}})]\}^2$$

in which the shape factor β is the same as for the substrate, RX , and the activation-driving force relationship for the $RX^{\cdot-} \rightarrow R^{\cdot} + X^-$ reaction is the same quadratic expression as for the $RX + e^- \rightarrow R^{\cdot} + X^-$ reaction, the intrinsic barrier being expressed as

(31) Wentworth, W. E.; Becker, R. S.; Tung, R. *J. Phys. Chem.* **1967**, *71*, 1652.

(32) Steelhammer, J. C.; Wentworth, W. E. *J. Chem. Phys.* **1969**, *51*, 1802.

(33) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223.

(34) Compton, R. N.; Reinhart, P. W.; Cooper, C. C. *J. Chem. Phys.* **1978**, *68*, 4360.

(35) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103.

(36) Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 2280.

(37) Bays, J. P.; Blumer, S. T.; Baral-Tosh, S.; Behar, D.; Neta, P. *J. Am. Chem. Soc.* **1983**, *105*, 320.

(38) Hasegawa, A.; Williams, F. *Chem. Phys. Lett.* **1977**, *46*, 66.

(39) Hasegawa, A.; Shiatani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, *157*. (c) Kuhn, A.; Illenberger, E. *J. Phys. Chem.* **1989**, *93*, 7060.

(40) Kuhn, A.; Illenberger, E. *J. Chem. Phys.* **1990**, *93*, 357.

(41) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509.

(42) Savéant, J.-M. Submitted.

$$\Delta G_{0, \text{RX}^{\cdot-} \rightarrow \text{R}^{\cdot} + \text{X}^-}^{\ddagger} = \frac{D_{\text{RX}^{\cdot-}} + \lambda'_0}{4}$$

The standard free energy of the dissociation reaction may be related to the various characteristic standard potentials and to the dissociation energy of the R-X bond by

$$\Delta G_{\text{RX}^{\cdot-} \rightarrow \text{R}^{\cdot} + \text{X}^-}^{\circ} = E_{\text{RX/RX}^{\cdot-}}^{\circ} - E_{\text{RX/R}^{\cdot} + \text{X}^-}^{\circ} = D_{\text{RX}} + E_{\text{RX/RX}^{\cdot-}}^{\circ} - E_{\text{X}^{\cdot-}/\text{X}^-}^{\circ} + T(\bar{S}_{\text{RX}} - \bar{S}_{\text{R}^{\cdot}} - \bar{S}_{\text{X}^{\cdot-}})$$

(the standard free energy of the dissociation reaction is the opposite) and the bond dissociation energy of the anion radical. The key factor in the intrinsic barrier of the dissociation and association reactions is given by the following two expressions according to whether the unpaired electron is located on the R or the X moiety of the $\text{RX}^{\cdot-}$ molecule, respectively:

$$D_{\text{RX}^{\cdot-}} = D_{\text{RX}} + E_{\text{RX/RX}^{\cdot-}}^{\circ} - E_{\text{R}^{\cdot}/(\text{R}^{\cdot})^-}^{\circ} + T(\bar{S}_{\text{RX}} - \bar{S}_{\text{RX}^{\cdot-}} + \bar{S}_{(\text{R}^{\cdot})^-} - \bar{S}_{\text{R}^{\cdot}})$$

$$D_{\text{RX}^{\cdot-}} = D_{\text{RX}} + E_{\text{RX/RX}^{\cdot-}}^{\circ} - E_{\text{X}^{\cdot-}/(\text{X}^{\cdot-})^-}^{\circ} + T(\bar{S}_{\text{RX}} - \bar{S}_{\text{RX}^{\cdot-}} + \bar{S}_{(\text{X}^{\cdot-})^-} - \bar{S}_{\text{X}^{\cdot-}})$$

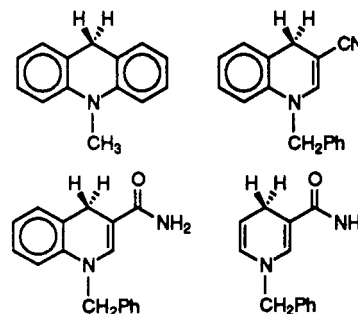
The solvent reorganization energy, λ'_0 , for the dissociation and association reactions may be expressed from the reactant radii in the Marcus way.⁴² It is expected to be smaller than for the $\text{RX} + e^- \rightarrow \text{R}^{\cdot} + \text{X}^-$ and $\text{RX} + e^- \rightarrow \text{RX}^{\cdot-}$ reactions.

As discussed in detail in ref 42, all available quantitative rate data and semiquantitative structure-reactivity trends concerning the dissociation of anion radicals and the coupling between radicals and nucleophiles may be rationalized in the framework of the model. This is the case for the approximate linear correlation that has been observed between the cleavage rate constant of $\text{RX}^{\cdot-}$ and the standard potential of the $\text{RX/RX}^{\cdot-}$ couple for aryl chlorides and bromides (see Figure 1 in ref 42), which points to a near constancy of the RX dissociation energy in the series and to a mutual compensation between the $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ and $E_{\text{R}^{\cdot}/(\text{R}^{\cdot})^-}^{\circ}$ terms in the expression of the intrinsic barrier (as the energy of the π^* orbital in the R group decreases, the stabilities of both $\text{RX}^{\cdot-}$ and $(\text{R}^{\cdot})^-$ increase to about the same extent). The lesser reactivity of the phenyl radical vis-à-vis phenyl radicals substituted by electron-withdrawing groups and polyaromatic radicals results essentially from the fact that the driving force of coupling is less because $E_{\text{RX/RX}^{\cdot-}}^{\circ}$ is more negative. The poor reactivity of cyanide ions as compared to other nucleophiles is a striking example of a high intrinsic barrier due to the strength of the bond being formed which counteracts a favorable driving force. The fact that benzyl radicals need to be substituted by strong electron-withdrawing groups to react with nucleophiles, whereas phenyl radicals do not, is the result of the fact that the bond being formed is much weaker (20 kcal/mol) in the first case than in the second, which then requires compensation by a positive shift of $E_{\text{RX/RX}^{\cdot-}}^{\circ}$.

Other Applications

The dissociative-electron-transfer model may find applications in areas of chemical reactivity that would at first sight seem remote from electron-transfer chemistry. One example is the deprotonation of cation

radicals. The activation-driving-force relationships were investigated in detail for the deprotonation of the cation radicals of the following NADH synthetic analogues by an extended series of bases in acetonitrile using cyclic voltammetry at ultramicroelectrodes, redox catalysis, and laser flash photolysis as experimental techniques.⁴³⁻⁴⁵



The activation-driving-force plots are remarkably monophasic independently of the nature of the bases. The intrinsic barriers that are extracted from these plots correlate with the bond dissociation energy $\text{AH}^{\cdot+} \rightarrow \text{A}^+ + \text{H}^{\cdot}$ but not with the pK_a of $\text{AH}^{\cdot+}$. The same appears upon analysis of previous rate data concerning the deprotonation of cation radicals of polymethylbenzenes.^{46,47}

In contrast with the behavior of "normal acids" in which the ionic resonant form predominates in the ground state and where intrinsic barriers are low, cation radicals appear to undergo concerted H-atom-electron transfer, with higher intrinsic barriers, as a consequence of the dominance of the covalent resonant form in the ground state. The potential energy vs C-H bond length to be expected is schematically represented in Figure 5 for each case.⁴⁵

There are in fact additional reaction coordinates such as those representing solvent reorganization and those corresponding to the other half-reaction, i.e., the protonation of the opposing base. The latter being part of a "normal" acid-base couple has a small self-exchange intrinsic barrier that probably does not vary considerably in the series. This is presumably the reason that monophasic activation-driving-force plots are obtained in spite of the use of bases belonging to largely different families and also that the intrinsic barriers appear to follow approximately the predictions of the dissociative-electron-transfer theory.⁴⁶

Concluding Remarks

Criteria for distinguishing concerted from stepwise mechanisms in electrochemical and homogeneous reductive cleavage reactions in polar solvents have been successfully applied in a number of cases. The main factors that govern the occurrence of one or the other mechanism appear to be the bond dissociation energy,

(43) Hapiot, P.; Moiroux, J.; Savéant, J.-M. *J. Am. Chem. Soc.* 1990, 112, 1337.

(44) Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Savéant, J.-M. *J. Phys. Chem.* 1991, 95, 2370.

(45) Anne, A.; Hapiot, P.; Moiroux, J.; Neta, P.; Savéant, J.-M. *J. Am. Chem. Soc.* 1992, 114, 4694.

(46) Schlessener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* 1984, 106, 7472.

(47) Schlessener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* 1986, 90, 3747.

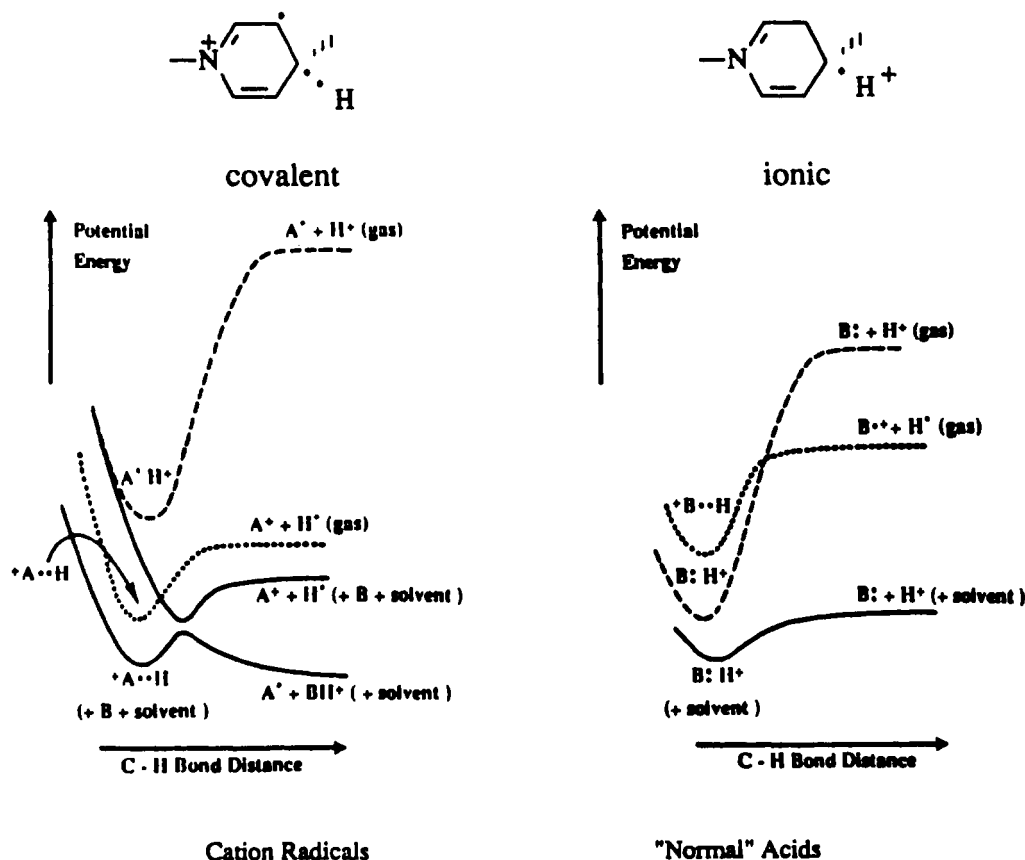


Figure 5. Schematic representation of the potential energy curves for the deprotonation of cation radicals and of "normal acids".

the standard potential of the $RX/RX^{\cdot-}$ couple, i.e., the energy of the orbital in which the unpaired electron may reside transiently, and the free energy of the electron in the electron donor. More experimental examples showing the effect of the latter parameter on the transition between the two mechanisms in the reductive cleavage of a given molecule would certainly be welcomed. Besides the structure of the starting compound, the nature of the reaction medium (solvent, ion pairing with counterions) most probably plays an important role in the determination of the mechanism mostly through the ensuing variations of the $RX/RX^{\cdot-}$ standard potential and thus warrants further investigation.

When the concerted mechanism prevails, the Morse curve model has been shown to describe with good accuracy the dynamics of the reaction for several organic molecules. It may thus be used to estimate bond dissociation energies, standard potentials, and intrinsic barriers for reactions involving heterogeneous and homogeneous outersphere electron donors and cleaving acceptors for which the necessary thermochemical data are lacking.

Extension of the model to the cleavage of anion radicals, viewed as an intramolecular dissociative electron transfer, and to the reverse reaction, i.e., the coupling of radicals with nucleophiles that thus appears as an associative electron transfer, provides a useful tool for rationalizing and predicting structure-reactivity relationships in the area of $S_{RN}1$ nucleophilic substitution.

The deprotonation of cation radicals, which appears to follow a concerted H-atom-electron exchange mechanism rather than a strict proton transfer, is an example

illustrating the applicability of the dissociative-electron-transfer concepts to areas of chemistry that would *a priori* seem far from single-electron-transfer chemistry.

The experimental examples investigated so far have mostly involved the reduction of carbon-halogen and nitrogen-halogen bonds. Extension to other molecules, including inorganic small molecules, and also to oxidative cleavage reactions is certainly warranted. Among the improvements of the theory that the multiplication of experimental examples will most probably call for, some may already be envisioned. For example, the assumption that the contributions of bond breaking and of solvent reorganization may be treated separately and additively is rather crude and may appear as a significant shortcoming in cases where the latter factor plays a relatively more important role than in the cases investigated so far where the contribution of solvent reorganization is not more than *ca.* 20% of the total. Refinement of the theory, including the modeling of the dependency of the solvent reorganization on the bond length, may then appear necessary. Another problem, which may at first sight appear to concern solely electrochemical cleavages, is the influence that the intense electric field that exists at the reaction site may have on the dynamics of the dissociative electron transfer. Similar questions may arise in homogeneous reactions in the form of salt effects.

I am indebted to many co-workers and collaborators whose names appear in the reference list below and whose contributions have been essential to the development of our research in the field.