

Dissociative Electron Transfer

by Flavio Maran and Mark S. Workentin

Predicting the rate of chemical reactions on the basis of reorganization energies and driving force is a fundamental challenge in all areas of chemistry and biochemistry. Considerable achievements in this regard have been reached in the area of electron transfer (ET) processes, thanks to the Marcus theory of ET and related treatments.¹ On the other hand, there are several chemical systems that, upon ET, are susceptible to undergo the cleavage of a σ bond, leading to formation of reactive species. The dissociation of the bond may follow or be concerted to the ET itself, as shown in the following Scheme:



Both cases are described as a dissociative ET (DET) process. In the concerted DET, the reaction proceeds along a reaction coordinate that, for the most common case of reduction of a neutral compound, does not involve the transient formation of the radical anion that is on a more energetic potential energy surface. Examples of stepwise DET processes are rather common in electrochemistry. This is particularly true for reductive processes.

Generally speaking, DET are useful in that they provide an elegant and chemically clean way to electrogenerate reactive species such as bases or nucleophiles. From a practical point of view, both stepwise and concerted DETs yield the same reactive species, the main difference being that for the latter reaction these species are directly generated at contact distance from the donor (either a solution species or electrode). Concerted DETs occur less frequently and thus are less known. The first contributions in this area were provided in studies by Hush and Ebersohn that concerned the reduction of halides and the oxidation of carboxylates.^{2,3} These concepts were then developed extensively by Ebersohn,⁴ who used the Marcus theory for outer-sphere ET to describe the rate/free energy relationship (*i.e.*, $\log k$ versus ΔG°) of these processes. By this

analysis it was evident that some DET reactions are characterized by a much weaker driving force ($\equiv -\Delta G^\circ$) dependence than that of other ET processes.

Only more recently have the kinetics of a number of reactions that follow a DET mechanism been quantified systematically to allow for a significant development of our knowledge in the field. Instrumental in this regard was the desire to experimentally test a model proposed by Savéant to describe concerted DETs and that established ways to distinguish between the two mechanistic pathways.⁵ In its most used and practical form, the Savéant model leads to a quadratic rate/free energy relationship that is formally identical to the well-known Marcus equation.¹ The intrinsic barrier (ΔG_0^\ddagger , which is the activation free energy at $\Delta G^\circ = 0$) of concerted DETs, however, is much larger than that of outer-sphere ETs. This is because of the significant reorganization energy associated with the progressive stretching of the cleaving bond along the reaction coordinate. In particular, Savéant showed that $\Delta G_0^\ddagger = (\lambda + \text{BDE})/4$, where λ is the sum of the solvent and inner reorganization energies (except for the mode corresponding to the cleaving bond) and BDE is the bond dissociation energy.⁵ Concerted DETs are thus intrinsically very slow ET processes (the BDE term is usually much larger than λ). In principle they are easily distinguishable from the much faster outer-sphere ETs that constitute the first step of stepwise DETs and for which the preponderant term is the solvent reorganization energy.

After a relatively slow beginning in the eighties, research on DET mechanisms and their possible consequences and applications is now an active area of research carried out in laboratories spread all over the world, including several groups who are active within the O&BE Division. The goal of this report is to outline the most important features of these DET processes. For the sake of simplicity only a few representative examples have been chosen with the aim to provide sufficient insight into this area. For more comprehensive accounts on the matter, the reader should refer to very recent reviews.⁶⁻⁸

The Rate/Free Energy Relationship

Our ability to predict the rate of a given reaction relies primarily on an understanding of how the reaction rate changes as a function of driving force. This has been one of the main goals of studies carried out with various dissociative-type acceptor molecules. A typical example is provided by the reduction of *tert*-butyl bromide (*t*-BuBr) by aromatic radical anions in dipolar aprotic amide solvents. For this system, which served as a test of the DET theory,^{9,10} the driving force could be changed significantly (~ 1.9 eV) and thus an overall variation of the intermolecular rate constant by 13 orders of magnitude could be measured, thanks to the work of Lund,¹¹ Savéant,¹² Grimshaw,¹³ and their co-workers. The experimental data, however, seem to fit almost equally well to a parabola, as predicted by the quadratic DET theory, and to a straight line. Similar results were obtained with other alkyl halides.¹⁰ There are plausible and intriguing hypotheses on the reasons for observing these experimental trends. In particular, the relatively fast rates measured at low driving force can be attributed to the possible role of a rate-enhancing inner-sphere (S_N2 -like) component,¹⁰ a more pronounced S_N1 -like contribution to the transition-state structure,¹⁴ or a driving-force dependent donor/acceptor electronic coupling.¹⁵

For halides and other acceptors characterized by relatively large bond dissociation energies (BDEs) the expected quadratic rate/free energy relationship may be difficult to detect. This is because the curvature of the parabola is inversely proportional to ΔG_0^\ddagger , which in turn is proportional to BDE, and concerted DETs are typically characterized by large intrinsic barriers. However, when ΔG_0^\ddagger is not too large, the parabolic pattern can be detected and differentiated from a linear correlation beyond experimental error. This is the typical situation that was encountered with the homogeneous or heterogeneous reduction of peroxides,¹⁵⁻²¹ compounds having low BDEs (in the range 25-40 kcal/mol) and thus lower ΔG_0^\ddagger . As representative examples, the rate/free ener-

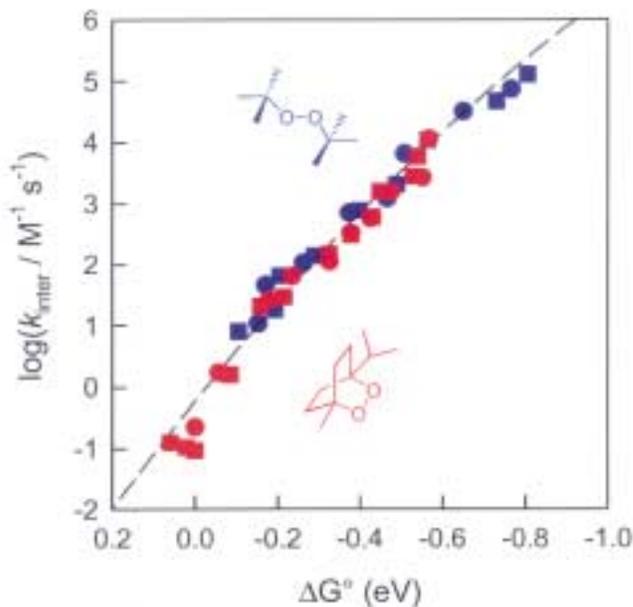


FIG. 1. Plot showing the free-energy dependence of the logarithm of the intermolecular DET rate constant for the reaction between aromatic radical anion donors and di-*tert*-butyl peroxide (■, DMF, ● MeCN) or dihydroascaridole (DASC) (■ DMF, ● MeCN) at 25°C. The curve has been drawn by using the DET quadratic equation. The data are from Refs. 16 and 21.

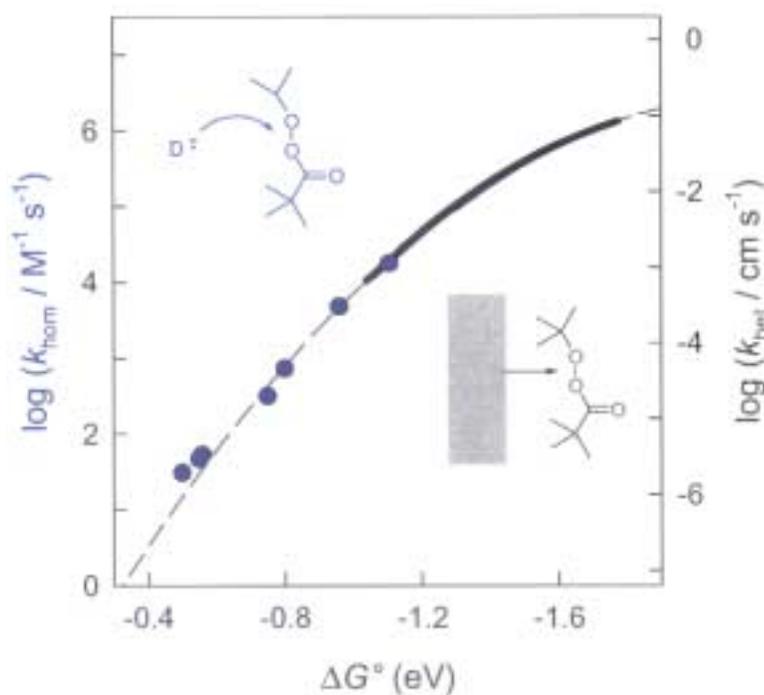


FIG. 2. Comparison between homogeneous (●) and heterogeneous (○) rate constants for the reduction of pivaloyl peroxide in DMF at 25°C. The dashed line is the second order fit to the data. The data are from Ref. 15.

gy relationships experimentally determined for di-*tert*-butyl peroxide¹⁶ and an endoperoxide,¹⁹ using series of aromatic radical anions as the donors, are shown in Fig. 1. For these compounds the curvature is indeed verified beyond experimental error, in full agreement with the nuclear factor of the rate constant expression proposed for concerted

DET.⁵ Interestingly, the result of careful analyses carried out on these and similar results by using both the adiabatic⁷ and nonadiabatic²² DET theories, led to the discovery that the dissociative reduction of peroxides is intrinsically nonadiabatic.^{15,18} ET to peroxides is thus much slower than predicted, which leads to a consequence that per-

oxides are, in practice, kinetically slow oxidants.

DET Mechanisms and Mechanistic Transition

In recent years several groups have collected data and provided insights into the dynamics of DETs. In some studies, the use of various electrochemical and nonelectrochemical (such as pulse radiolysis) kinetic methods has allowed the exploration of a large driving-force range, as shown very nicely for the concerted DET to *t*-BuBr.¹⁰ It has even been shown that the heterogeneous DET rate/driving force relationship, obtained by using the convolution analysis approach,¹⁷ is approximately complementary to the homogeneous DET results.^{15,20} Using the convolution methodology, the explored driving-force range can be extended quite significantly (Fig. 2). By combining these methodologies, it is possible to evaluate the average slope of the log *k* versus ΔG° in any explored ΔG° range. Common stepwise DET processes, such as those encountered with aryl halides (which form usually short-living radical anions), are also well characterized in terms of log *k* versus ΔG° (or donor E° plots).²³ What is particularly important is that the average slope of the activation region of these ETs, *i.e.*, the region where the rate-determining step is the actual ET, is much steeper than that of the concerted processes. Because of this characteristic, the two processes can be often quite easily distinguished.

Extrapolation of the kinetic results to other free-energy ranges, however, may be sometimes hazardous. This is because competitive or borderline mechanisms may be triggered. For example, the S_N2 mechanism is intrinsically slower (*i.e.*, has a larger ΔG_0^\ddagger) than the concerted DET because of the need of forming a new bond between nucleophile and the electrophilic carbon. This aspect and related issues have been elegantly tackled by Marcus.²⁴ However, because of the thermodynamic advantage associated with the formation of this bond, the S_N2 may be the main mechanism at low driving forces. At large driving forces (*i.e.*, with particularly strong reductants), the initial outer-sphere ET step of stepwise DETs may overwhelm the intrinsically slower concerted DET.²⁵ Because of the intrinsic-barrier difference, the two ETs respond to changes in the driving force in a quite different way. For the stepwise mecha-

nism, $\log k$ is quite dependent on ΔG° with the consequence that $\log k$ (function, through the Marcus or the DET equation, of both ΔG° and ΔG_0^\ddagger) may become larger than that for the concerted DET, in spite of a less favorable driving force. In fact, the concerted reaction is thermodynamically favored over the corresponding stepwise process when the E° for the formation of the radical anion is sufficiently negative, the cleaving bond is weak and B $^-$ is a good leaving group (the E° of a concerted DET can be expressed as a function of the bond dissociation free energy, BDFE, of the cleaving bond and the E° of the leaving group: $E_{AB/A\cdot, B^-}^\circ = E_{B\cdot/B^-}^\circ - \text{BDFE}/F$).

Some evidence for a concerted-to-stepwise mechanistic transition was first obtained by Vianello and co-workers who studied the C-S bond cleavage induced by homogeneous ET (aromatic electron donors) to triphenylmethyl phenyl sulfide.²⁶ More convincing data can be obtained by using the heterogeneous approach, which is intrinsically more sensitive than the corresponding homogeneous one. The heterogeneous intrinsic barrier depends essentially on the acceptor molecule, while the homogeneous ΔG_0^\ddagger depends also on the electron donor. In addition, in the homogeneous case the number of donors is often limited, but in the heterogeneous reaction the free energy can be varied continuously by simply changing the applied potential E . This important feature is conveniently exploited when the convolution approach is employed.^{6,17} In fact, unlike conventional electrochemical methods, all of the experimental i - E data are used in the kinetic analysis and, in addition, the kinetic data can be analyzed without the need of defining *a priori* the ET rate law.²⁷

In practice, the heterogeneous rate constant k_{het} is obtained as a function of E . By this method, the quadratic rate/free energy relationship of peroxides was established very nicely.^{15,17,20,21,28,29} The final step of the convolution analysis is the determination of the transfer coefficient α , which describes how variations of ΔG° affect the activation free energy ($\alpha = \partial \Delta G^\ddagger / \partial \Delta G^\circ$). If the double-layer effect is neglected, α can be easily obtained from the experimental data as $\alpha = -2.303(RT/F) \partial \log k_{\text{het}} / \partial E$, being $\Delta G^\circ = F(E - E^\circ)$. Provided only one DET mechanism takes place, α depends linearly on E , being $\alpha = 0.5 + F(E - E^\circ) / 8\Delta G_0^\ddagger$. Because of the large activation overpotential suffered by the concerted DET,

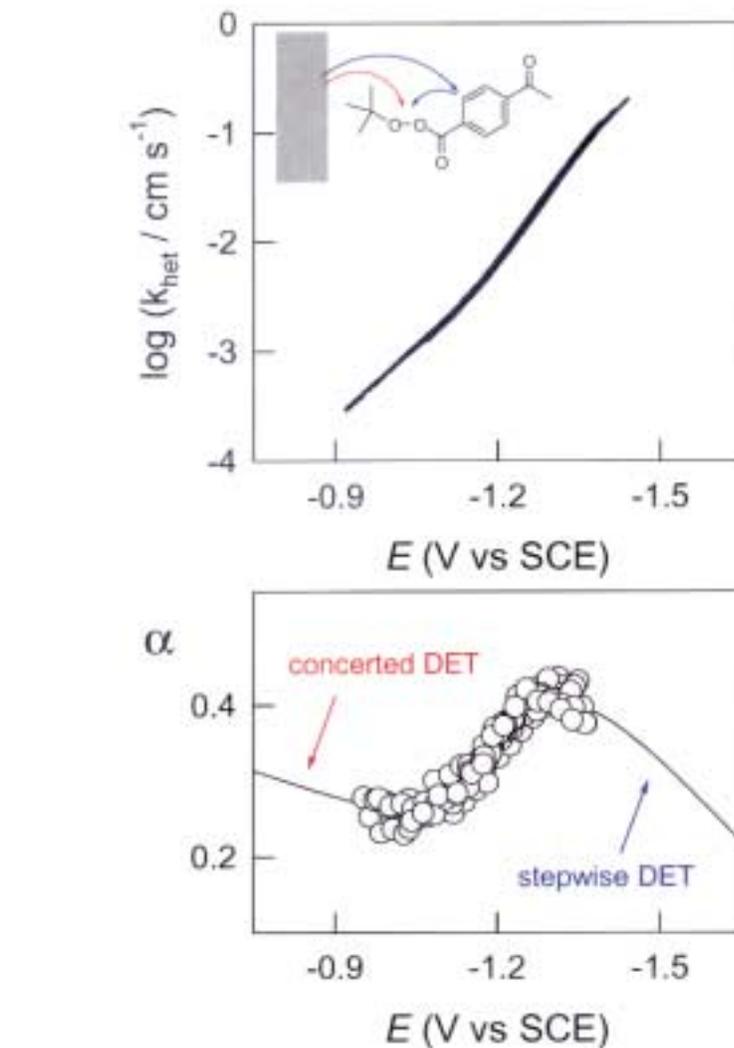


FIG. 3. Potential dependence of the logarithm of the heterogeneous rate constant (upper curve) and transfer coefficient α (lower curve) for the reduction of tert-butyl para-acetylperbenzoate in DMF. The solid line has been calculated from estimated quantities by assuming a stepwise/concerted competition mechanism. The data are from Ref. 29.

the potentials where the actual reduction occurs are much more negative than the E° . Therefore, values of α significantly lower than 0.5 are found. On the other hand, if the initial ET leads to the formation of an intermediate radical anion $AB^{\cdot-}$, the usual effect of the cleavage reaction is to cause the voltammetric peak to appear close or even before $E_{AB/A\cdot, B^-}^\circ$; thus, apparent α values close or larger than 0.5 are expected. An analogous description can be applied to the homogeneous DET counterpart. When the standard potential for the formation of the electron donor (homogeneous ET) or the electrode potential E is made less negative, it may be possible to observe a progressive transition from a stepwise to a concerted mechanism. In the borderline situation, the reduction may occur through both mechanisms, although with different rates.

As we have seen, α is obtained in an unbiased form from the experimental rate/free energy plots and thus, being a derivative, is particularly sensitive to changes in the slope of these plots. This feature is very important in detecting the transition between concerted and stepwise DETs and has been verified by studying the reduction of a family of perbenzoates.^{28,29} Figure 3 illustrates the experimental detection of the DET transition in terms of both k_{het} , in which the overlapping of two different rate/driving force curves is evident, and α , which has a wavelike potential dependence connecting the two linear variations describing the pure mechanisms. These results point to a mechanistic transition that can be described as a simple competition problem where two different reaction coordinates and transition states are provided to the DET reaction. Therefore, the actual for-

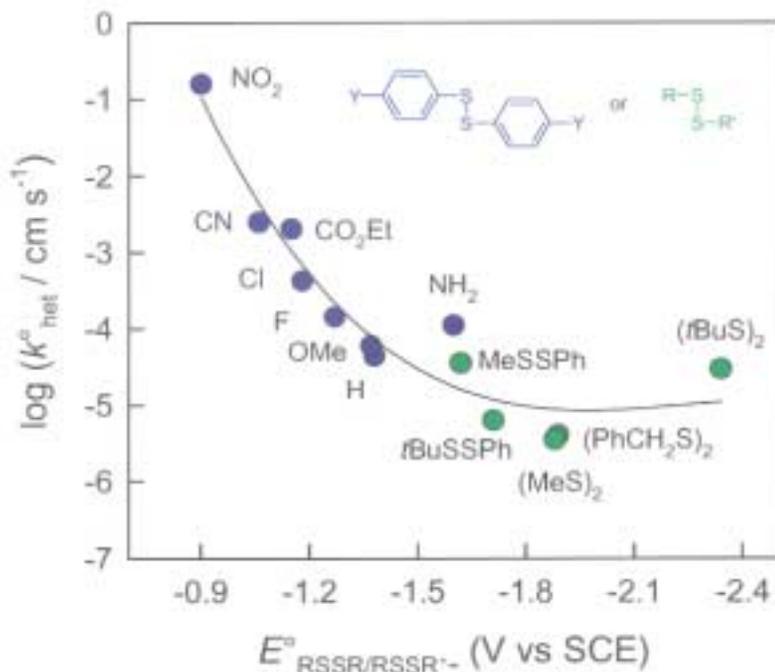


FIG. 4. Comparison between the heterogeneous standard rate constants of the reduction of disulfides. The data are plotted as a function of E° and were obtained in DMF at 25°C. The data are taken from Refs. 32 (●) and 33 (●). The solid line is meant to underline the experimental trend.

mation (or lack of formation) of AB^{\bullet} from AB must be considered a function of the competition between the rates of the stepwise and concerted pathways.

Besides the already discussed “classical” DET mechanisms, there are two borderline mechanisms that are worth mentioning. Let us consider first the case of a stepwise mechanism. If the ET product is a quite delocalized radical anion, such as with aromatic compounds, a small inner reorganization is required and thus the most important contribution to the intrinsic barrier comes from the solvent reorganization. Consequently, the ET is fast and the DET reaction occurs in the endergonic region ($\alpha > 0.5$). However, there are chemical systems for which it is reasonable to expect that in the formation of the radical anion the breaking bond will weaken and stretch to some extent. This would cause an increase of the inner reorganization and thus the ET becomes slow. The voltammetric peak becomes electrochemically irreversible and is pushed to more negative potentials than E° . Thus, α can be lower than 0.5, almost as low as with concerted DETs, even though the mechanism is still stepwise. Studies on the reductive cleavage of the C-S³⁰ and, particularly, S-S bond³¹⁻³³ have provided com-

pellent evidence for this borderline mechanism, in which the ET step is almost as slow as that of a concerted DET. Typically, this situation is verified when the ET yields a σ^* radical anion, which then undergoes an endergonic cleavage. The formation of these loose radical anions is accompanied by a significant increase of the bond length, which amounts to 0.8 Å for the S-S bond.³³ This large inner reorganization is responsible for the low values of k°_{net} observed for these compounds. Of course, this depends on the nature of the substituents. Figure 4 shows that for the least easily reducible compounds (which form σ^* radical anions) there is little difference. Only for diaryl disulfides containing good electron-withdrawing groups (*e.g.*, NO_2) the π^* character of the SOMO is such to reduce the inner reorganization term quite significantly.

The other borderline DET mechanism originates when a concerted DET yields fragments that may interact electrostatically in the solvent cage.^{34,35} This mechanism has been recently identified, particularly, with ring-substituted benzyl chlorides.³⁴ In fact, although for these compounds the E° of the concerted DET is almost substituent independent, the rates of the homoge-

neous ET are substituent dependent. This trend is similar to that found also with the substituted benzyl bromides.³⁶ The substituent effect on the ET rate is not driven by thermodynamics but is ruled by the ET intrinsic barrier. For these processes the substituent effect is attributed to the existence of a stabilizing ion-dipole type interaction between the halide ion and the substituted benzyl radical within the solvent cage. By enhancing the electron-withdrawing character of the aryl substituent and thus the dipole moment of the benzyl radical, the interaction becomes stronger, the transition state becomes more reactant-like, and the activation energy decreases. A quadratic rate/free energy relationship has been developed to describe this particular mechanism.³⁵ In conclusion, it seems now reasonably well established that a reactivity difference of as much as a few orders of magnitude may be caused by specific interactions between the caged fragments. The intrinsic barrier of this type of fast concerted DET may turn out to be similar to that of the slow stepwise DET mechanism proceeding through formation of loose radical anions. Distinguishing between these two types of mechanism is the current challenge.

Intramolecular DET

In the electrochemical literature there are many examples of radical anions decaying by fragmentation of a σ bond.^{4,6-8} As a rule, the intramolecular reaction is an activated rearrangement of the electrogenerated radical anion to yield a transition state leading to the formation of the fragmentation products. The overall process may be accompanied by a significant solvent reorganization. Usually, the fragmentation of radical anions is described as heterolytic or homolytic, depending on whether the extra electron crosses the cleaving bond or not. For heterolytic cleavages, particularly but not exclusively, the process can sometimes be viewed as an intramolecular DET.³⁷ This happens when the antibonding orbital initially hosting the electron (most often a π^* orbital) is weakly coupled to the σ^* orbital of the cleaving bond and thus an intramolecular $\pi^* \rightarrow \sigma^*$ ET appears as a quite realistic description of the mechanism. Most often, however, the coupling is strong and thus an actual intramolecular DET cannot be easily invoked.³⁸ The fact that the fragmentation occurs by either mechanism depends on a

delicate balance between driving force, intrinsic barrier, and electronic coupling. The former issue has been discussed in some detail for example by Evans, Lessard and their co-workers for the substituent dependent heterolytic/homolytic transition observed upon reduction of α -nitrocumenes.³⁹ Other interesting discussion on these matters can be found in the literature.^{6,7,37,40}

In order to have an unequivocal intramolecular DET, either homolytic or heterolytic, the electron exchanging centers must be clearly identified and so must their thermodynamics (E° and BDE). This is accomplished by connecting two electroactive moieties, the donor D and the acceptor A, by means of a spacer, Sp. Most often the latter is an active molecular bridge mediating the intramolecular ET. This type of strategy has led to fascinating results in the area of intramolecular nondissociative ETs, leading to a deep knowledge on how electrons are transferred through bonds and space.⁴¹ Research in the area of DETs is still in its infancy, despite the relevance of such reactions in some chemical systems (for example, O-O and S-S bond cleavage in biologically relevant molecules).

This problem was tackled by focusing initially on the DET free-energy dependence in well-defined D-Sp-A molecular systems.^{42,43} With a first series of compound, in which a tertiary bromide was A, ring-substituted benzoates were the donors, and cyclohexyl was the spacer,⁴² it was found that the intramolecular DET rate was more sensitive to variation of ΔG° than found for the corresponding intermolecular reaction (free diffusing D/A couples). This experimental outcome was explained by considering the effect of the ring substituent. In fact, a more electron-withdrawing para substituent produces a shift of the centroid of the donor π^* orbital, in which the unpaired electron is initially located, away from the acceptor.

With a similar series of D-Sp-A compounds, in which a peroxide was A, substituted phthaloyl groups provided the D moieties, and cyclohexyl was the spacer,⁴³ the relative D/A distance could be controlled. As expected, the intramolecular slope was found to be slightly smaller than the intermolecular one, thanks to a larger solvent reorganization energy (and thus ΔG_0^\ddagger). Figure 5 illustrates the results obtained with both series of compounds. It was verified that the intramolecular DET rate obeys the same rules already highlighted for the intermolecular and heterogeneous processes. To predict the rate equally well, however, one has to make

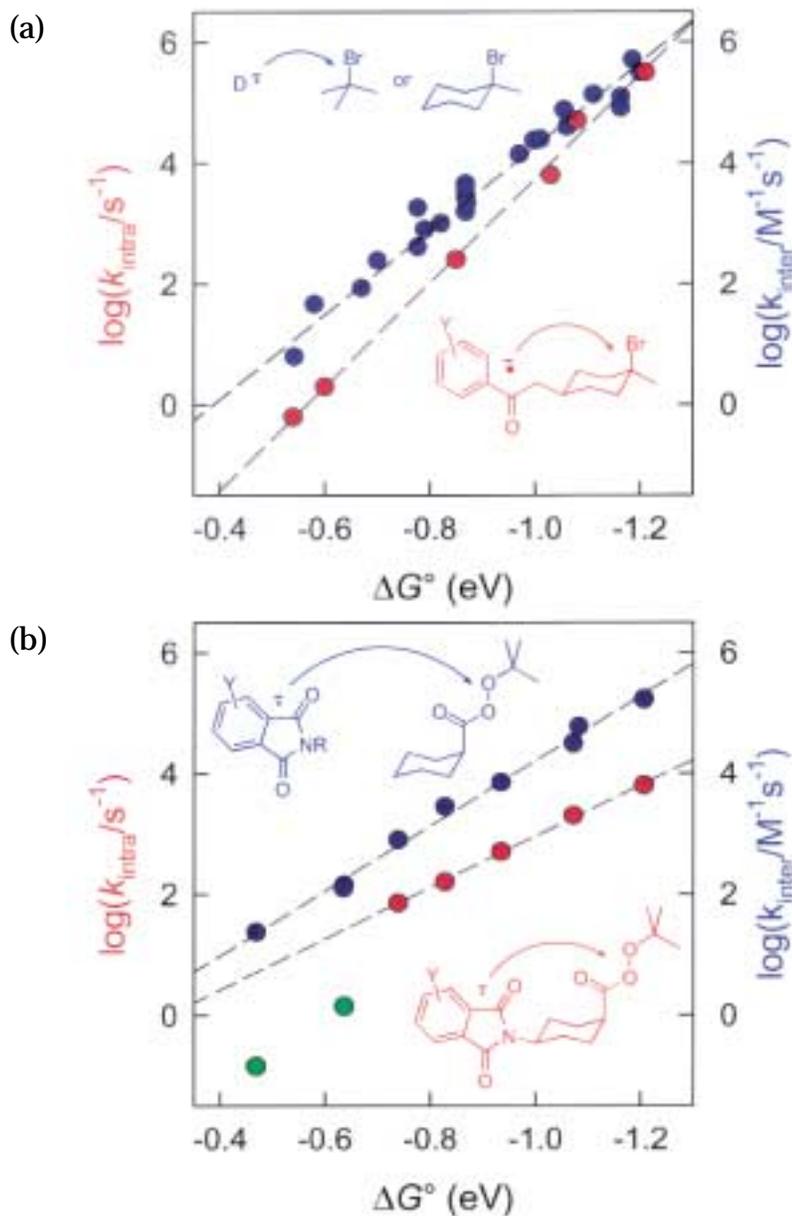


Fig. 5. Free energy dependence of the logarithm of the intramolecular (● and ●) and intermolecular (●) ET rate constants for reduction of either a tertiary bromide (graph a) or a perester (graph b) acceptor in DMF at 25 °C. The data are taken from Refs. 42 and 43; The dashed lines are the fits of the intramolecular and intermolecular data. The substituents in the intramolecular reaction are as follows: (right to left, graph a, ●) Y = H, 3-OPh, 3-F, 2,3-benzo, 4-SO₂Me, and 4-CN; (right to left, graph b, ●) Y = H, 3-F, 3,6-difluoro, 3,4,5,6-tetrafluoro, and 3,4,5,6-tetrachloro, or (●) Y = 3-NO₂ and 4-NO₂.

sure that the donor and acceptor orbitals are kept essentially unaffected by driving force variations.

The final proof to these findings is provided by the effect of introducing strong electron-withdrawing groups on the donor moiety. In fact, with two nitro-phthaloyl derivatives we found, both experimentally and theoretically, that the effective D/A distance increases and thus that the intramolecular rate constant is much smaller than expected. The intermolecular rates are perfectly in line with the results obtained with the other donors because the intermolecular

rate is a consequence of random distance and orientation distributions in the encounter complex. Further research is now underway to investigate the distance dependence of the DET rate, particularly, by using biologically-relevant molecular bridges.⁴⁴ Other nonelectrochemical studies (e.g., photoinduced DET) on similar problems are expected to provide complementary information on this important issue.

Conclusions

The DET concept is continuously growing and its relevance in many areas

is only now being realized. Several applications in the area of synthetic organic chemistry are obviously possible, as these reactions may yield powerful nucleophiles or reactive radicals. A variety of such examples may be found in a recent article by Lund⁴⁵ and a chapter by Peters.⁴⁶ DETs may be employed in the context of the hydrogenation versus electron transfer/protonation issue, as a test of heterogeneous reduction mechanisms.⁴⁷ DET processes have been also used as probes of the electrocatalytic mechanisms in microemulsions.⁴⁸ The usefulness of the stepwise-to-concerted mechanistic transition has been shown to be instrumental to explain the activation mechanism of the so-called thermal SRN1 reactions.⁴⁹

The concept of DET can be extended to the problem of concerted electron and proton transfer, as recently proposed.⁵⁰ Very recently, applications of the DET concepts may be found in the area of biologically relevant systems.^{44,51-53} Applications in surface chemistry can also be imagined³⁸ by taking advantage of the fact that, upon electroreduction of suitable compounds, reactive radicals can be generated directly near the electrode, as shown for example in the case of the dissociative reduction of aryl diazonium salts on carbon surfaces.⁵⁴ It is also worth mentioning the growing interest in the mechanisms of photoinitiated DET and their relationship with the corresponding thermally-activated processes.⁵⁵⁻⁵⁷ As we and Wayner concluded in a recent account on DETs,⁶ significant progress has been made in this area over the last few years. On the basis of the increasing interest in the area, we believe that other key challenges will be addressed in the coming years, particularly in view of useful applications of the concepts described above. ■

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About the Authors

Flavio Maran is with the Department of Physical Chemistry at the University of Padova, Padova, Italy. His main research interests are molecular electrochemistry and electron transfer mechanisms. He may be reached by e-mail at f.maran@chfi.unipd.it.

Mark Workentin is with the Department of Chemistry at the University of Western Ontario, London, Ontario, Canada. His main research interests are in the area of mechanistic organic electrochemistry and photochemistry. He may be reached at mworkent@uwo.ca.