The Role and Relevance of the Transfer Coefficient α in the Study of Dissociative Electron Transfers: Concepts and Examples from the Electroreduction of Perbenzoates

Sabrina Antonello and Flavio Maran*

Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, 35131 Padova, Italy

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Abstract: The electrochemical transfer coefficient α is shown to be a sensitive probe of the mechanism by which electron transfer and bond cleavage may be coupled in dissociative electron transfers. α is particularly useful in detecting the transition between stepwise and concerted dissociative electron transfers. Whereas linear potential dependencies of α are in agreement with either mechanism, a mechanism transition can be evidenced upon observation of a nonlinear α pattern. Under favorable circumstances, a wavelike potential dependence of α can be observed. This is a function of main parameters describing the mechanism competition such as, in particular, the difference between the two relevant standard potentials, the intrinsic barriers, and the preexponential factors of the two rate-constant equations. The analysis of α was applied to study the electroreduction of a series of perbenzoates, $XC_6H_4CO_3Bu^t$, in DMF. The reduction leads to the irreversible cleavage of the O−O bond. The α data were obtained by cyclic voltammetry followed by convolution analysis. For all compounds investigated, the experimental trend could be simulated satisfactorily by reasonable selection of the main parameters. Whereas the analysis showed that the reduction of the unsubstituted peroxide proceeds by a pure concerted mechanism, a stepwise mechanism holds when X = 4-NO$_2$. On the other hand, α-wave patterns were found for X = 4-COMe and 3-NO$_2$, as previously described for X = 4-CN. For the latter compounds, the α analysis is in agreement with a dissociative electron transfer process in which the mechanism changes from stepwise to concerted by increasing the applied potential. Finally, although the reduction of the 4-OCOMe perbenzoate basically occurs by a concerted mechanism, a transition pattern seems to emerge at the most negative potentials explored. Further support to the experimental outcome and conclusions was provided by studying the temperature effect on the reduction of the 4-COMe derivative, which led to the expected shift toward the stepwise mechanism by lowering the temperature.

Introduction

There are molecules that easily undergo σ-bond cleavage upon thermally induced or photoinitiated electron transfer (ET).[1−5] Usually, the dissociative mechanism entails ET to the acceptor compound (AB) to form a radical anion (AB$^{•−}$), followed by fragmentation to yield a radical (A$^•$) and an anion (B$^−$) (eqs 1,2). The electron donor, not indicated, may be a molecular

$$AB + e \rightleftharpoons AB^{•-} \qquad (1)$$

$$AB^{•-} \rightarrow A^{•} + B^{-} \qquad (2)$$

species or an electrode.

The fragmentation rate depends on the bond dissociation free energy (BDFE) of the A−B bond within the ET product AB$^{•−}$. As a consequence, the cleavage rate constant can span orders of magnitude, as found for example in studies on the reductive

cleavage of the C−S bond in sulfides,[6] the C−O bond in aryloxyacetophenones,[7,8] the C−C bond in diphenylethane derivatives,[4] and the C−halogen bond in some organic halides.[1] On the other hand, when the lifetime of the ET product is of the same order of magnitude as that of a vibrational period of the A−B bond, the process is better described as a single elementary step in which ET and fragmentation are concerted (eq 3).[9]

$$AB + e \rightarrow A^{•} + B^{-} \qquad (3)$$
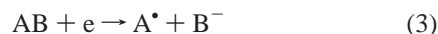
The concerted mechanism is better viewed as a possible reaction pathway independently of the fact that the AB$^{•−}$ radical anion might exist as a discrete intermediate species. Therefore,

(1) (a) Savéant, J.-M. *Adv. Phys. Org. Chem.* **1990**, *26*, 1. (b) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455.

(2) Savéant, J.-M. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI press: Greenwich, CT, 1994; Vol. 4, p 53.

(3) Schuster, G. B. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 1, p 163.

(4) Maslak, P. In *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1993; Vol. 168, p 1.

(5) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292.

(6) (a) Capobianco, G.; Farnia, G.; Severin, M. G.; Vianello, E. *J. Electroanal. Chem.* **1984**, *165*, 251. (b) Severin, M. G.; Arévalo, M. C.; Farnia, G.; Vianello, E. *J. Phys. Chem.* **1987**, *91*, 466. (c) Arévalo, M. C.; Farnia, G.; Severin, M. G.; Vianello, E. *J. Electroanal. Chem.* **1987**, *220*, 201. (d) Severin, M. G.; Farnia, G.; Vianello, E.; Arévalo, M. C. *J. Electroanal. Chem.* **1988**, *251*, 369. (e) Severin, M. G.; Arévalo, M. C.; Maran, F.; Vianello, E. *J. Phys. Chem.* **1993**, *97*, 150.

(7) (a) Andersen, M. L.; Mathivanan, N.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1996**, *118*, 4871. (b) Andersen, M. L.; Wayner, D. D. M. *J. Electroanal. Chem.* **1996**, *412*, 53. (c) Andersen, M. L.; Long, W.; N.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1997**, *119*, 6590.

(8) (a) Andrieux, C. P.; Savéant, J.-M.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1996**, *118*, 9788. (b) Andrieux, C. P., Savéant, J.-M.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 2420.

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

the actual formation (or nonformation) of $AB^{\bullet-}$ has always to be thought of as being a function of the competition between the stepwise and the concerted pathways. This aspect has been discussed as either a prediction[10a] or on the basis of actual experimental outcomes.[2,6d,10,11] An important issue is: How can we detect the transition between the two limiting mechanisms? Besides the free energy (ΔG°) values of ET 1 and ET 3, which are of course the first quantities to be compared, are there other parameters that should be taken into account? Finally, what theoretical and experimental tools do we have or can we conceive to improve our knowledge on this problem? This picture is something that is conceptually not very different from the problem of the S_N2 versus ET dichotomy[1a,12] or of other concerted-stepwise mechanism competitions,[13] although in the case of dissociative ETs less is known.

The rate constant for either ET 1 or ET 3 (k_{ET}) may be described in a simple way by eq 4

$$k_{ET} = Z \exp\left[-\frac{\Delta G^\ddagger}{RT}\right] \quad (4)$$

where Z is the preexponential factor, including the electron transmission coefficient, and $\Delta G^\ddagger$ is the activation free energy. According to the current theories of outersphere ET[14] and dissociative ET,[2,9] the dependence of $\Delta G^\ddagger$ on ΔG° can be expressed by a quadratic activation-driving force relationship (eq 5)

$$\Delta G^\ddagger = \Delta G_0^\ddagger\left(1 + \frac{\Delta G^\circ}{4\Delta G_0^\ddagger}\right)^2 \quad (5)$$

where $\Delta G_0^\ddagger$ is the intrinsic barrier.

The thermodynamics of the two ETs is the first parameter to be considered. Once we define the reducing properties of the medium (either the electrode potential or the standard potential of the solution electron donor), the chances for a concerted dissociative ET to provide the preferred reaction path are enhanced when the standard potential of ET 3 ($E^\circ_{AB/A^\bullet,B-}$) is significantly more positive than that of ET 1 ($E^\circ_{AB/AB^\bullet-}$). The condition $(\Delta G^\circ)_C < (\Delta G^\circ)_{ST}$ (hereafter, subscripts C and ST will be used to denote the parameters of ET 3 and ET 1), however, has to be mediated by the kinetic requirements of the two ETs, in terms of both the exponential and the preexponential factors in eq 4. The intrinsic barrier $\Delta G_0^\ddagger$ is best represented as the sum of solvent and inner contributions, i.e., $\Delta G_0^\ddagger = \Delta G_{0,s}^\ddagger + \Delta G_{0,i}^\ddagger$. Whereas $\Delta G_{0,s}^\ddagger$ ($\Delta G_{0,s}^\ddagger = \lambda_s/4$, where λ_s is the solvent reorganization energy) is expected to depend only slightly on the ET mechanism and thus can be expressed according to common procedures, $\Delta G_{0,i}^\ddagger$ is quite dependent on it. All of the inner reorganization contributions are expected to play a role in determining $\Delta G_{0,i}^\ddagger$. In the case of a concerted dissociative ET, $\Delta G_{0,i}^\ddagger$ contains also $^1/_4$ of the bond dissociation energy

(BDE) of the cleaving bond.[2,9] The intrinsic barrier of a concerted dissociative ET, $(\Delta G_0^\ddagger)_C$, is thus expected to be significantly larger than that of ET 1 no matter how significant is the $\Delta G_{0,i}^\ddagger$ component in $(\Delta G_0^\ddagger)_{ST}$. In fact, within typical dissociative-type systems, such as halides[1,2] and peroxides,[11,15-17] the contribution of the BDE term to $\Delta G_0^\ddagger$ is typically 70−80%. However, we should mention our recent results showing that there are molecular systems in which even for the ET of a stepwise mechanism the $\Delta G_{0,i}^\ddagger$ term can be very large. This is because of a significant AB-bond elongation in the formation of $AB^{\bullet-}$,[18] a concept that is being discussed also theoretically.[19-21] Alternatively, as suggested for the stepwise dissociative oxidation of oxalate ($^-O_2C-CO_2^- \rightarrow {}^-O_2C-CO_2^\bullet + e$), angle deformation also may contribute to $\Delta G_{0,i}^\ddagger$.[22] Although the result of bond elongation or angle deformation is to reduce substantially the gap between the stepwise and concerted intrinsic barriers, in most dissociative-type systems $\Delta G_0^\ddagger$ is still a relevant parameter in discriminating between the two ETs. As previously discussed,[11] because of the difference between $(\Delta G_0^\ddagger)_{ST}$ and $(\Delta G_0^\ddagger)_C$, ET 1 and ET 3 respond to changes in the driving force in a different way, and this may result in a smaller $(\Delta G^\ddagger)_{ST}$ relative to $(\Delta G^\ddagger)_C$, despite a less favorable reaction free energy for ET 1 than for ET 3. Besides the nuclear term of eq 4, Z_{ST} and Z_C might differ. For example, although the formation of $AB^{\bullet-}$ is most likely an adiabatic ET process, there is enough evidence indicating that nonadiabaticity[23] affects the concerted ET to peroxides.[15] This would result in Z_C being smaller than Z_{ST} and thus, at any given experimental condition, to a less relevant contribution (to the observed rate) of the rate of ET 3 relative to that of ET 1.

In this paper, by using a simple analysis based on the extensive use of the transfer coefficient $\alpha = \partial \Delta G^\ddagger/\partial \Delta G^\circ$, we will show how this problem can be approached in heterogeneous (electrochemical) ETs. The electrochemical approach has the advantages that the intrinsic barrier depends only on the acceptor molecule and, quite important, that the applied potential E, which is related to ΔG° ($\Delta G^\circ = F(E - E^\circ)$), can be varied continuously. Provided only one ET mechanism, obeying eq 5, takes place upon electroreduction of AB (i.e. either ET 1 or ET 3), α depends on the applied potential E according to eq 6

$$\alpha = 0.5 + \frac{F}{8\Delta G_0^\ddagger}(E - E^\circ) \quad (6)$$

where the effect of the double layer has been neglected.

An important aspect resulting from eq 6 is that $\alpha = 0.5$ when $E = E^\circ$. This offers a way to overcome a severe problem that affects the study of dissociative ETs, i.e., the estimation of the standard potential. In fact, being the dissociative ET reaction

(10) (a) Andrieux, C. P.; Savéant J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43. (b) Andrieux, C. P.; Robert, M.; Saeva, F. D.; Savéant J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 7864. (c) Andrieux, C. P.; Savéant J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1997**, *119*, 11546. (d) Costentin, C.; Hapiot, P.; Médebielle M.; Savéant J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 4451. (e) Pause, L.; Robert, M.; Savéant J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 7158.

(11) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 12595.

(12) (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Heidelberg, 1987. (b) Lund, H.; Daasbjerg, K.; Lund, L.; Pedersen, S. U. *Acc. Chem. Res.* **1995**, *28*, 313. (c) Marcus, R. A. *J. Phys. Chem. A* **1997**, *101*, 4072. (d) Kuznetsov, A. M. *J. Phys. Chem. A* **1999**, *103*, 1239.

(13) For example, see: Williams, A. *Chem. Soc. Rev.* **1994**, *23*, 93.

(14) For example, see: Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(15) (a) Workentin, M. S.; Maran, F.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 2120. (b) Donkers, R. L.; Maran, F.; Wayner, D. D. M.; Workentin, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 7239.

(16) Antonello, S.; Musumeci, M.; Wayner, D. D. M.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 9541.

(17) (a) Workentin, M. S.; Donkers, R. L. *J. Am. Chem. Soc.* **1998**, *120*, 2664. (b) Donkers, R. L.; Workentin, M. S. *J. Phys. Chem. B* **1998**, *102*, 4061.

(18) Daasbjerg, K.; Jensen, H.; Benassi, R.; Taddei, F.; Antonello, S.; Gennaro, A.; Maran, F. *J. Am. Chem. Soc.* **1999**, *121*, 1750.

(19) Benassi, R.; Taddei, F. *J. Phys. Chem. A* **1998**, *102*, 6173.

(20) Benassi, R.; Taddei, F.; Antonello, S.; Maran, F. et al., manuscript in preparation.

(21) German, E. D.; Kuznetsov, A. M. *J. Phys. Chem. A.* **1998**, *102*, 3668.

(22) Isse, A. A.; Gennaro, A.; Maran, F. *Acta Chem. Scand.*, in press.

(23) A nonadiabatic dissociative ET theory has been developed: German, E. D.; Kuznetsov, A. M. *J. Phys. Chem.* **1994**, *98*, 6120.

completely irreversible, the $E°_{AB/A•,B-}$ value cannot be calculated directly, say, by cyclic voltammetry. On the other hand, even though $E°_{AB/A•,B-}$ can be calculated, thanks to a thermochemical cycle, by eq 7
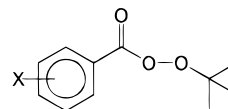
$$E°_{AB/A•,B-} = E°_{B•/B-} - BDFE/F \qquad (7)$$

where $E°_{B•/B-}$ is the standard potential for the leaving group couple B•/B⁻, the necessary data may not be available or accurate enough. In this case, use of eq 6 may allow one to obtain an estimate of $E°_{AB/A•,B-}$. Even though the sought potential at which $\alpha = 0.5$ is beyond the experimentally reachable range, $E°_{AB/A•,B-}$ can be estimated by linear regression analysis of the α data, provided a significantly large E range can be explored. This powerful application of eqs 5 and 6 has been shown to provide good estimates of $E°_{AB/A•,B-}$ by using mercury electrodes and by applying the corresponding correction for the electric double layer.[16] Along these lines, reasonable estimates of either $E°_{AB/A•,B-}$ or $E°_{AB/AB•-}$ (for ET 1 the same approach can be used when the cleavage rate is such that ET 1 is the rate determining step) can be made even by using glassy carbon electrodes.[11,17b,18,22,24,25]

A second application of α is that its value may allow discriminating between the two mechanisms.[1,2] Because of the large activation overpotential suffered by dissociative ET 3, the potentials at which the voltammetric peak for the reduction of AB occurs are much more negative, e.g., 1 V, than $E°_{AB/A•,B-}$. Equation 6 shows that values of α significantly lower than 0.5 are thus expected. On the other hand, if the initial ET leads to the formation of AB•⁻ that fragments only successively (eqs 1 and 2), the effect of the chemical reaction is, usually, to cause the peak to appear close or to be even more positive than $E°_{AB/AB•-}$. Therefore, α values close or larger than 0.5 are expected. This is not, however, an absolute criterion because there may be situations in which even in a stepwise dissociative ET the heterogeneous ET rate can be slow compared to the cleavage rate. Under this circumstance, the voltammetric peak is electrochemically irreversible and is pushed to more negative potentials than $E°_{AB/AB•-}$. α can thus be significantly lower than 0.5, even though the mechanism is stepwise.

α is very sensitive to the ET mechanism[11] and, in our opinion, provides the best way to detect a possible mechanism transition. This is because α, being the derivative of the activation-driving force relationship (experimentally, α is calculated from $RT\ \partial \ln k_{ET}/\partial \Delta G°$), is particularly useful in revealing deviation from the parabolic behavior expected on the basis of eq 5. The analysis described in this paper origins from our recent finding that the electrochemical reduction of *tert*-butyl-*p*-cyanoperbenzoate in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAP) provides data in agreement with a clear-cut case of transition between stepwise and concerted dissociative ETs. The α patterns expected for different values of the relevant thermodynamic and kinetic parameters are now described. The mechanism transition is represented in a simple way by assuming competitive reaction trajectories leading to the two transition states of ET 1 and ET 3.[26] The α analysis is then applied to experimental data pertaining to the representative series of perbenzoates **1a–f**, selected along criteria that will be outlined below.

The results were obtained by voltammetry in DMF/0.1 M TBAP at the glassy carbon electrode followed by convolution analysis.

(24) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1998**, *120*, 5713.
(25) Preliminary data suggest that the double layer properties of glassy carbon in DMF are qualitatively similar to those of mercury: Arévalo, M. C., Maran, F., work in progress.


1, X = H (**a**), 4-OCOMe (**b**), 4-COMe (**c**), 4-CN (**d**), 3-NO₂ (**e**), 4-NO₂ (**f**)

Convolution voltammetry is a powerful electrochemical tool, using all the kinetic information contained in a cyclic voltammetry curve and is thus liable to allow one to collect a huge amount of $\ln k_{ET} - E$ data.[11,16,27] The data were then analyzed in comparison with the electrochemical reduction of the corresponding *tert*-butyl benzoates **2a–f**, taken as the best experimentally available model systems for the formation of the putative radical anions of perbenzoates **1**.

Experimental Section

Chemicals. *N,N*-Dimethylformamide (Janssen, 99%) and tetrabutylammonium perchlorate (Fluka, 99%) were treated as previously described.[16] *tert*-Butylperbenzoate (Aldrich, 98%) was used as received. The syntheses of perbenzoates **1** and benzoates **2** were carried out as previously reported for **1d** and **2d**, i.e., by reacting the pertinent aryloyl chloride with either *tert*-butyl hydroperoxide or *tert*-butyl alcohol, respectively.[11] Methyl 4-acetoxybenzoate was purchased from Aldrich. The reagents used for the syntheses were commercially available; *p*-acetoxybenzoyl chloride and *p*-acetylbenzoyl chloride were prepared from the corresponding acids. Perbenzoates **1c**, **1e**, and **1f** are known and characterized compounds.[28,29] A purified sample of **1b** gave the following data: mp 58 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.41 (9H, s, C₄H₉), 2.33 (3H, s, CH₃) 7.19–8.00 (4H, AA′BB′, C₆H₄); ¹³C NMR (400 MHz, CDCl₃, TMS) δ 21.14 (CH₃CO), 26.25 (C(CH₃)₃), 84.13 (*C*(CH₃)₃), 121.97, 125.24, 130.77, 154.58 (Ph: C3, C4, C2, C1), 163.66 (Ph*C*O), 168.78 (CH₃*C*O).

Electrochemistry. The working electrode material was a 3 mm diameter microdisk glassy carbon electrode, prepared as previously described.[16] Before each set of measurements, the electrode was polished with a 0.25 μm diamond paste (Struiers) and ultrasonically rinsed with ethanol for 5 min. Electrochemical activation was carried out in the background solution by means of several cycles at 1 V s⁻¹ in a wide potential range. The area was calculated with reference to the diffusion coefficient of ferrocene in DMF/0.1 M TBAP, 1.13 × 10⁻⁵ cm² s⁻¹.[30] The reference electrode was a homemade Ag/AgCl.[16] Its potential was always calibrated after each experiment by adding ferrocene as an internal standard; the standard potential for ferrocene oxidation in DMF/0.1 M TBAP is 0.464 V against the KCl saturated calomel electrode, SCE. In the following, unless otherwise stated, all of the potential values will be reported against (SCE). The counterelectrode was a 1 cm² Pt plate. The electrochemical apparatus and the feedback correction procedure were as previously described.[11,16] The electrochemical measurements were conducted at 25 °C, except for some experiments carried out at −40 °C. The cyclic voltammograms were recorded by digital oscilloscope and then transferred to a PC. The background-subtracted curves were analyzed by conventional

(26) This representation is, of course, an oversimplification of the actual system because the reaction coordinates describing the two ET reactions are most probably similar (being related in both cases to the elongation of the breaking bond and to solvent reorganization). Theoretical work seems to be necessary to shed some light onto this problem, as recently reported for the relation between S_N2 and ET.[12c,d] However, as the comparison with the experimental data presented in this paper will show, the mechanism transition is conveniently describable as a simple competition problem, at least at a first level of approximation.
(27) (a) Imbeaux, J. C.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *44*, 169. (b) Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1975**, *65*, 57.
(28) Filliatre, C.; Maillard, B.; Villenave, J. J. *Thermochim. Acta* **1980**, *39*, 195.
(29) (a) Blomquist, A. T.; Berstein, J. *J. Am. Chem. Soc.* **1951**, *73*, 5546. (b) Plesnicar, B.; Exner, O. *Collect. Czech. Chem. Commun.* **1981**, *46*, 490.
(30) Curtis, N.; Donkers, R. L.; Isse, A. A.; Leist, D. G.; Maran, F.; Workentin, M. S., to be published.
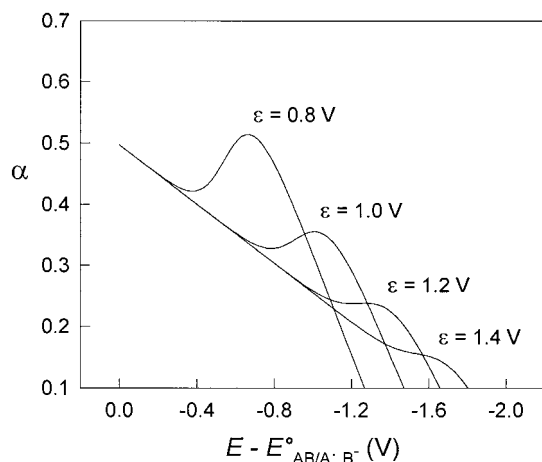
Figure 1. Typical effect of the parameter ϵ, $E°_{AB/A\bullet,B-} - E°_{AB/AB\bullet-}$, on the potential dependence of the apparent transfer coefficient α for a mixed dissociative ET mechanism obeying eq 8. $\zeta = Z_{ST}/Z_C = 1$, $\beta = (\Delta G_0^{\ddagger})_C/(\Delta G_0^{\ddagger})_{ST} = 3.5$, BDE = 34 kcal mol^{-1}.

voltammetric criteria[31] and the convolution approach,[16,27] using purposely designed laboratory software. Digital simulations of the cyclic voltammetry curves were performed by using the DigiSim 2.1 software by Bioanalytical Systems Inc.

Results and Discussion

Potential dependences of α**.** The above description of the properties of the transfer coefficient α concerns the two individual stepwise and concerted mechanisms. Both eqs 5 and 6 depend on specific $E°$ and $\Delta G_0^{\ddagger}$ values and are thus determined by the particular ET mechanism taking place. In the case where both the concerted and the stepwise processes may take place to some extent at the same potential, we may express the heterogeneous rate constant as the sum of the rate constants of the two competitive ETs, k_C and k_{ST}:[26]

$$k_{ET} = Z_C \exp\left\{-\frac{(\Delta G_0^{\ddagger})_C}{RT}\left[1 + F\frac{E - E°_{AB/A\bullet,B-}}{4(\Delta G_0^{\ddagger})_C}\right]\right\} +$$
$$Z_{ST} \exp\left\{-\frac{(\Delta G_0^{\ddagger})_{ST}}{RT}\left[1 + F\frac{E - E°_{AB/AB\bullet-}}{4(\Delta G_0^{\ddagger})_{ST}}\right]\right\} \quad (8)$$

Since the experimental quantity that is used to calculate α is

$$\alpha = -\frac{RT}{F}\frac{\partial \ln k_{ET}}{\partial E} \quad (9)$$

the predicted potential dependence of α for the mixed mechanism is obtained by using eqs 8 and 9 for different values of the relevant parameters. There are three main parameters worth considering: (a) the difference between the two standard potentials, $\epsilon = (E°_{AB/A\bullet,B-} - E°_{AB/AB\bullet-})$; (b) the ratio between the two preexponential factors, $\zeta = Z_{ST}/Z_C$; (c) the ratio between the two intrinsic barriers $\beta = (\Delta G_0^{\ddagger})_C/(\Delta G_0^{\ddagger})_{ST}$. The dependence of α on the applied potential, best expressed as $E - E°_{AB/A\bullet,B-}$, is depicted for different values of ϵ, ζ, and β in Figures 1–3. The following default parameters were used: $\epsilon = 1.4$ V, $\zeta = 1$ ($Z = 5000$ cm s^{-1}), $\beta = 3.5$ (BDE = 34 kcal mol^{-1}).
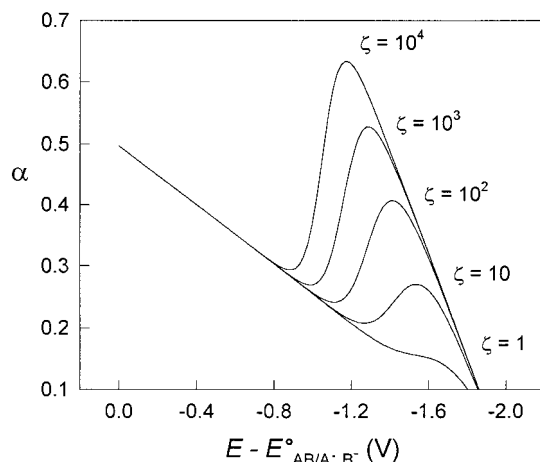
(31) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113. (c) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980.

Figure 2. Typical effect of the parameter ζ, Z_{ST}/Z_C, on the potential dependence of the apparent transfer coefficient α for a mixed dissociative ET mechanism obeying eq 8. $\epsilon = E°_{AB/A\bullet,B-} - E°_{AB/AB\bullet-} = 1.4$ V, $\beta = (\Delta G_0^{\ddagger})_C/(\Delta G_0^{\ddagger})_{ST} = 3.5$, BDE = 34 kcal mol^{-1}.
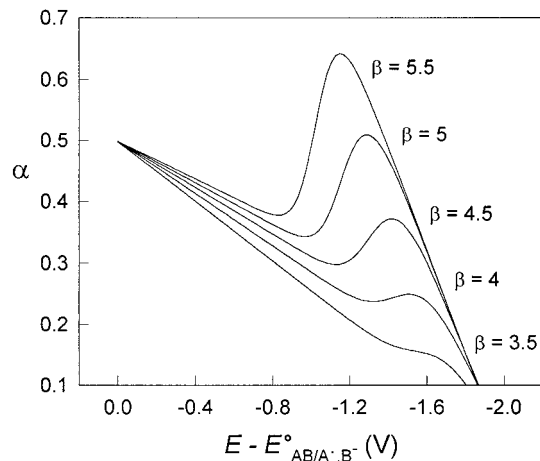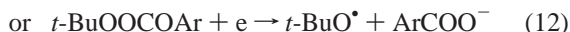

Figure 3. Typical effect of the parameter β, $(\Delta G_0^{\ddagger})_C/(\Delta G_0^{\ddagger})_{ST}$, on the potential dependence of the apparent transfer coefficient α for a mixed dissociative ET mechanism obeying eq 8. $\epsilon = E°_{AB/A\bullet,B-} - E°_{AB/AB\bullet-} = 1.4$ V, $\zeta = Z_{ST}/Z_C = 1$. The curves corresponding to $\beta = 3.5$, 4, 4.5, 5, 5.5 were obtained by using BDE = 34, 40.8, 47.6, 54.4, 61.2 kcal mol^{-1}, respectively.

Figure 1 shows that for $\epsilon > 1.4$ V the ET is a pure concerted dissociative ET ($\zeta = 1$, $\beta = 3.5$). In fact, considering α values lower than ~0.2 is pointless because those values can hardly be measured and are usually affected by a large error. For smaller values of ϵ, a wavelike potential dependence of α is evident. This effect magnifies as ϵ decreases because we are now exploring E values where the contribution of k_{ST} to k_{ET} (eq 8) becomes increasingly significant. Accordingly, the apparent α detects the fact that when E is positive to $E°_{AB/AB\bullet-}$ the stepwise-type α contribution is larger than 0.5 (eq 6). Figure 2 shows how also the relative value of the two preexponential factors, ζ, may affect the α pattern. The α wave moves to less negative E values and the maximum α value increases as ζ increases. Focusing only on $\zeta \geq 1$ is more practical because there are more chances that a concerted dissociative ET, instead of ET 1, is nonadiabatic. The effect of increasing BDE and thus β, illustrated in Figure 3, is similar from a qualitative point of view to that of ζ. It should be noted that considering an increase of BDE is more interesting from an experimental point of view because the BDEs of peroxides are the smallest among those of dissociative-type compounds. The main significance of Figure 3 is thus to suggest that the effect of ET 1 should show up at

Table 1. Electrochemical and Thermochemical Data for the Dissociative ET to **1a−f**

1	$E_p(\mathbf{1})^a$ (V)	$E°(\mathbf{2})^b$ (V)	$E_{p,red\ B\bullet/B^-}{}^a$ (V)	$E_{p,ox\ B\bullet/B^-}{}^a$ (V)	BDE^c (kcal/mol)	$E°_{AB/A\bullet,B^-}{}^d$ (V)	$E°_{AB/A\bullet,B^-}{}^e$ (V)
a	−1.38	−2.29	f	1.43	32.6	0.07	−0.20
b	−1.35	−2.20^g	f	1.48	33.7	0.07	−0.12
c	−1.25	−1.58	−2.09	1.50	33.3	0.11	0.02
d	−1.26	−1.63	−2.27	1.56	36.1	0.04	0.02
e	−0.88	−1.01	−1.24	1.57	35.3	0.22	0.12
f	−0.76	−0.89	−1.20	1.58	35.4	0.23	0.09

^{a} $v = 0.2$ V s^{-1}. ^{b} Obtained from the reversible reduction peaks at 0.2, 10, and 100 V s^{-1} for **2c−f**, **2a**, and **2b** (methyl ester), respectively. ^{c} See ref 33. ^{d} Estimated on the basis of thermochemical and peak potential data: see text and refs 33 and 34. ^{e} From convolution analysis: see text. ^{f} Beyond the solvent/electrolyte discharge. ^{g} Methyl ester: The $E°$ of the *tert*-butyl ester can be estimated to be −2.25 V; see ref 24 and: Wagenknecht, J. H.; Goodin, R. D.; Kinlen, P. J.; Woodard, F. E. *J. Electrochem. Soc.* **1984**, *131*, 1559.

more positive potentials and α should reach larger values for those compounds having larger BDE values, all other conditions (ϵ, ζ, and $\Delta G_{0,s}^{\ddagger}$) being the same. For example, if the experimental α data can be collected only from −1.2 to −1.6 V (on the scale of Figure 3), it would be quite difficult to detect a mechanism transition for β equal to 3.5 or 5.5. In conclusion, Figures 1−3 suggest that there is always a specific E window, function of ϵ, ζ, and β, where experimental α data may provide evidence of a mechanism transition.

Voltammetric Behavior. The reduction of perbenzoates **1a−f** was studied in DMF/0.1 M TBAP at 25 °C using a glassy carbon electrode. The electrochemical measurements were carried out in the presence of an equivalent of a weak acid (acetanilide) to ensure protonation of the electrogenerated *tert*-butyloxy anion. As previously shown for **1d**,[11] this was necessary to avoid the interference of the parent-child reaction[32] between *t*-BuO$^-$ and the perbenzoate **1**, leading to the corresponding ester **2**. The voltammetric peak potential (E_p) values obtained at 0.2 V s^{-1} are given in Table 1. As expected for peroxides, the initial one-electron reduction proceeds with O−O bond cleavage leading to the formation of *t*-BuO$^\bullet$ and ArCOO$^-$ (eqs 10,11 or eq 12). At the working potentials, *t*-BuO$^\bullet$ is reduced (eq 13) to the anion *t*-BuO$^-$ ($E° = -0.23$ V),[15] and thus the overall process is a two-electron reduction.

$$t\text{-BuOOCOAr} + e \rightarrow t\text{-BuOOCOAr}^{\bullet-} \quad (10)$$

$$t\text{-BuOOCOAr}^{\bullet-} \rightarrow t\text{-BuO}^\bullet + \text{ArCOO}^- \quad (11)$$

$$\text{or} \quad t\text{-BuOOCOAr} + e \rightarrow t\text{-BuO}^\bullet + \text{ArCOO}^- \quad (12)$$

$$t\text{-BuO}^\bullet + e \rightarrow t\text{-BuO}^- \quad (13)$$

Besides the main reduction peak, a second reversible peak is observable at more negative potentials for compounds **1c−f**. The peak is the reduction of the carboxylate anion ArCOO$^-$, as verified in comparison with experiments carried out using authentic solutions. The formation of ArCOO$^-$ is detectable also through the irreversible oxidation of the latter, which occurs at very positive potential values. The redox data for ArCOO$^-$ are reported in Table 1 together with the $E°$ of the esters **2**, $E°(\mathbf{2})$.

The perbenzoates **1** were selected and synthesized mostly on the basis of the expected ϵ, approximated as the difference between $E°_{AB/A\bullet,B^-}$ and $E°(\mathbf{2})$. The former was estimated through eq 7, using either reported[28] or estimated BDE[33] and $E°_{B\bullet/B^-}$ values.[34] Since the voltammetric peaks for the oxidation of most of the carboxylates were not of the quality required to carry out a reliable analysis, we focused on the estimation of the $E°_{B\bullet/B^-}$ of the carboxylate arising from **1a**, which appeared to

provide the most reproducible results at low to moderate scan rates. The estimation was carried out starting from the experimental $E_{p,ox\ B\bullet/B^-}$ and $\Delta E_{p/2}$ values ($\Delta E_{p/2}$ is the peak width, defined as the difference between the potential measured at half-peak height and the peak potential), by assuming Marcusian kinetics for the heterogeneous ET, and by using $Z = (k_B T/ 2\pi M)^{1/2}$, where M is the molecular mass. Since the inner component to the intrinsic barrier for the oxidation of carboxylates is expected to be large, because of both C−C bond elongation and O−C−O angle deformation, we assumed $\Delta G_0^{\ddagger}$ to be ∼10 kcal mol^{-1}. This value takes into account our recent data on the formation of fast-cleaving radical ions, including the results on oxalate oxidation.[18,22] This allowed us to estimate the relevant standard heterogeneous rate constants, to reproduce $\Delta E_{p/2}$ within a few mV and, by using the experimental $E_{p,ox\ B\bullet/B^-}$ values, to estimate $E°_{B\bullet/B^-}$ to ∼1.22 V. Although there are other reasons to consider this value as a rather crude estimate,[35] it is worth mentioning the agreement with a previous thermochemical estimate, 1.24 V.[36] The $E°_{B\bullet/B^-}$ of the other carboxylates were then estimated by using 0.21 V for the difference $E_{p,oxB/B^-} - E°_{B\bullet/B^-}$. The resulting $E°_{AB/A\bullet,B^-}$ estimates are reported in Table 1. The uncertainty, related to both the BDFE and $E°_{B\bullet/B^-}$ values, is likely of the order of ± 0.2− 0.3 V. $E°_{AB/A\bullet,B^-}$ does not appear to depend significantly on the substituent, which could be the result of the mild but also opposing substituent effect on BDE and $E°_{B\bullet/B^-}$. On the other

(32) In particular, see: (a) Arévalo, M. C.; Farnia, G.; Severin, M. G.; Vianello, E. *J. Electroanal. Chem.* **1987**, *220*, 201. (b) Maran, F.; Roffia, S.; Severin, M. G.; Vianello, E. *Electrochim. Acta* **1990**, *35*, 81.
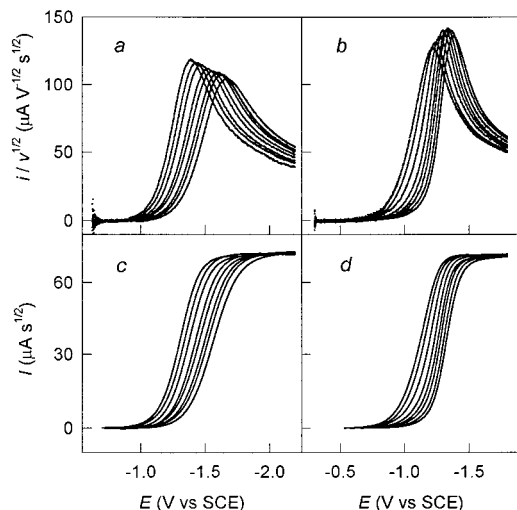
(33) The enthalpies of activation for the thermal decomposition of the perbenzoates[28] were used for the BDE values. Since the data for **1b** and **1e** were lacking, we used the correlation BDE = (32.41 ± 0.68) + (4.05 ± 0.61) σ, based on the data pertaining to 11 perbenzoates. The BDE values were then transformed into BDFE values by using a 6 kcal mol^{-1} correction. This correction takes into account that, although a more correct value (in condensed phase) seems to be 8.5 kcal mol^{-1},[15b] the reported activation entropies of perbenzoates lead to 0.4−7.1 kcal mol^{-1}.[28,29a]

(34) The estimation of $E°_{B\bullet/B^-}$ was carried out in an approximate way, as previously attempted for the carboxylate of **1d**.[11] The oxidation of ArCOO$^-$, chemically generated in DMF from the corresponding acid, was studied by digital simulation of the experimental voltammetric curves. Measurements were in agreement with the heterogeneous ET being the rate determining step of the oxidation. The rate constant for the chemical decay of ArCOO$^\bullet$ was taken as 10^7 s^{-1}.[11] Further measurements carried out with the carboxylate arising from **1d** led to the same oxidation picture, allowing us to refine the previous estimate of $E°_{B\bullet/B^-}$.[11]

(35) The voltammetric oxidation of carboxylates can be studied also by running a positive going scan after reducing either the dibenzoyl peroxide, (ArCO$_2$)$_2$, or **1**. With reference to the oxidation behavior of the chemically generated anion, whereas the peak does not change when starting from (ArCO$_2$)$_2$ (we tried X = H, *p*-CN, and *p*-NO$_2$), the oxidation peak becomes sharper and less positive when starting from **1**. This seems to be related to the presence of acetanilide, as checked by experiments in which the latter was added to a solution of (ArCO$_2$)$_2$. For the carboxylate of **1a** analysis of the oxidation peak obtained in the presence of acetanilide led to $E°_{B\bullet/B^-}$ = 1.10 V, i.e., a value not too far from 1.22 V. Although the problem of ArCOO$^-$ oxidation would require a specific study, it should be noted that only rough $E°_{B\bullet/B^-}$ estimates were required in the present investigation.

(36) See footnote 19 in ref 8b.

Role and Relevance of the Transfer Coefficient α

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Figure 4. Background-subtracted linear scan voltammetries and corresponding convolution curves for the reduction of 1.97 mM **1a** (graphs a and c) and 2.10 mM **1c** (graphs b and d) in DMF/0.1 M TBAP at the glassy carbon electrode. The voltammetric current *i* is reported in its *v*-normalized form. The scan rates were (left to right): **1a**: 0.2, 0.5, 1, 2, 5, 10, 20, and 50 V s⁻¹; **1c**: 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 V s⁻¹. *T* = 25 °C.

hand, a substituent effect is quite evident with esters **2**, where a gap of as much as 1.4 V is covered from **2a** to **2f** (Table 1). Therefore, even though the error on $E°_{AB/A•,B-}$ is large, there is little doubt that ϵ decreases significantly by increasing the electron-withdrawing properties of the aryl substituent.[37]

Compounds **1a** and **1b** are characterized by an irreversible reduction peak controlled by slow heterogeneous kinetics. $\Delta E_{p/2}$ is 170 and 190 mV respectively, leading to α values of 0.281 and 0.251, respectively, for $v = 0.2$ V s⁻¹. When v is increased, E_p shifts toward more negative values by 126 and 137 mV/decade, leading to α values of 0.234 and 0.216, respectively ($\partial E_p/\partial \log v = 1.15\ RT/F/\alpha$). The normalized peak current, $i_p/v^{1/2}$, is not independent of the scan rate but instead decreases as v increases, particularly for **1a** as illustrated in Figure 4. As previously discussed,[16] this is because of the broadening of the peak caused by a decrease of α when the scan rate is increased and thus the peak moves toward more negative E values. On the other hand, for compound **1f** the value of $\partial E_p/\partial \log v$ is ca. 47 mV/decade at low scan rates, leading to an apparent α of 0.632. The peak is sharper than that of **1a** and **1b** and thus α is larger (0.2 V s⁻¹: $\Delta E_{p/2} = 69$ mV, $\alpha = 0.687$). Perbenzoate **1e** gives raise to a voltammetric peak that is as sharp as that of **1f** (0.2 V s⁻¹: $\Delta E_{p/2} = 68$ mV, $\alpha = 0.702$) and $\partial E_p/\partial \log v$ is roughly 45 mV/decade. The voltammetric peaks of both **1e** and **1f** are thus under kinetic control by both the heterogeneous ET and a following chemical reaction.[31] Concerning compound **1c**, the situation is qualitatively similar to that recently described for **1d**,[11] i.e., sharpening of the peak (and thus α increase) when v is increased up to moderately high values (Figure 4) and nonlinear dependence of E_p on $\log v$.

Convolution Analysis. Quantitative information on the potential dependence of the electrode kinetics of the reduction

(37) It should be noted, however, that the decrease is not quantitatively predictable. In fact, both E_p(**1**) and $E°$(**2**) data correlate very poorly with the Hammett σ constants (Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165). In particular, the nitro-substituted compounds are characterized by rather positive potential values, in line with the fact that the latter compounds are to be considered as substituted nitro compounds rather than nitro-substituted perbenzoates or benzoates. On the other hand, columns 3 and 4 (the σ_p of COO⁻ is 0) allow one to predict that the voltammetric pattern of **1c** and **1d** should not be very different, despite the difference of the corresponding σ values, 0.50 and 0.66, respectively.
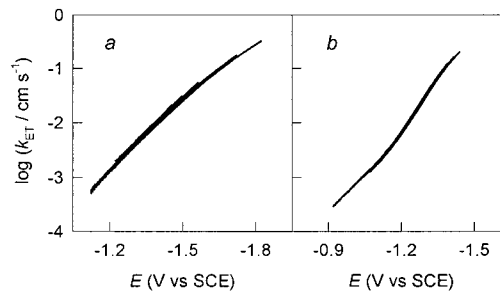

Figure 5. Potential dependence of the logarithm of the heterogeneous rate constant for the reduction of **1a** (graph a) and **1c** (graph b). Experimental conditions as in Figure 4.

of **1a**−**f** was obtained by treating the same voltammetric curves by convolution analysis.[16,27] The background-subtracted voltammetric curves were convoluted to yield convoluted current *I* vs E plots.[38] The limiting convoluted currents, I_l, were independent of the scan rate, within 1−2%, as expected. Graphs c and d of Figure 4 provide two typical examples. The electronicity of the electrode process was successfully checked by comparing the I_l values of compounds **1** with those of the corresponding esters **2** (one-electron process), taking into account the small difference between the diffusion coefficients (e.g., for **1a** and **2a** D is 1.08×10^{-5} and 1.12×10^{-5} cm² s⁻¹, respectively).

The logarithmic analysis was carried out by using the equation holding for irreversible processes.[38] For compounds **1a** and **1f** the overall plot originated by overlapping the series of $\ln k_{ET} - E$ plots obtained at several scan rates and different experiments in the range 0.1−50 V s⁻¹ could be fitted very nicely by a second-order regression ($r^2 = 0.998$ and 0.997, respectively). The pattern is parabolic also for **1b**. However, for **1c** and **1e** the $\ln k_{ET} - E$ plots present neither a parabolic nor a linear pattern, as already observed for **1d**.[11] Nevertheless, even for these compounds the $\ln k$ values obtained at different scan rates, but at the same E value, were equal within error.[39] An example is provided in Figure 5, in which the $\log k_{ET}$ vs E plots of **1c** is compared to that of **1a**. The apparent α values were obtained from the $\ln k_{ET} - E$ plots of **1a**−**f** by derivativation (eq 9). As expected on the basis of the corresponding $\ln k_{ET} - E$ plots, for compounds **1a** and **1f** the double-layer uncorrected transfer coefficient α was found to depend linearly on E (Figure 6). On the other hand, some tendency to a nonlinear behavior is displayed by **1b** (Figure 7). The low values of α (**1a**: $\alpha = 0.19-$ 0.26; **1b**: $\alpha = 0.19-0.25$) obtained in the experimentally

(38) *I* is related to the actual current *i* through the convolution integral[27]

$$I = \pi^{-1/2} \int_0^t \frac{i(u)}{(t-u)^{1/2}}\, du$$

The *I* vs *E* plot is a wavelike curve. The plateau value is reached when the applied potential is sufficiently negative. Under these conditions (diffusion control), *I* reaches its limiting value, I_l, defined as $I_l = nFAD^{1/2}C^*$, where n is the overall electron consumption, A the electrode area, D the diffusion coefficient, and C^* the substrate concentration. Since *I* is related to the surface concentration of reactant and product, an equation relating k_{ET} to i and *I* ensues. When the back electrode reaction is either absent (because the dissociative ET is concerted) or negligible (thanks to the occurrence of a fast reaction destroying the reduction product, such as in the stepwise mechanism), the electrode kinetics is related to the experimental data by equation

$$\ln k_{ET} = \ln D^{1/2} - \ln \{[I_l - I(t)]/i(t)\}$$

(39) This represents a good indication that under our experimental conditions the ohmic-drop effect was satisfactorily accounted for.[11,16] In fact, unproper ohmic-drop compensation leads to both negative shift and broadening of the voltammetric curves. As a consequence, this results in poor agreement of $\ln k_{ET}$ data obtained at different scan rates.
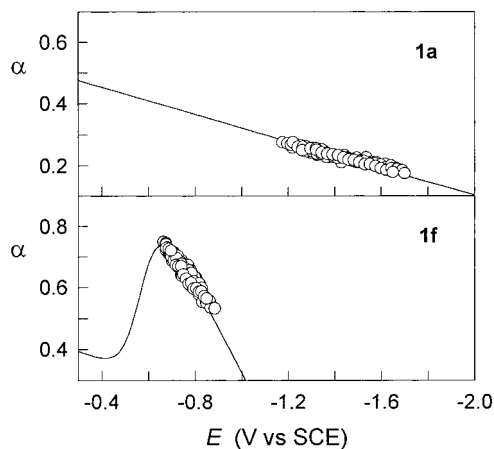
Figure 6. Experimental (○) and calculated (solid line) potential dependencies of the apparent transfer coefficient α for the electroreduction of **1a** and **1f** in DMF/0.1 M TBAP at 25 °C. The solid curves were obtained by using a mixed dissociative ET rate law (eq 8). By using the BDE value of Table 1, best fit was obtained for the following values of $E°_{AB/A•,B-}$ (V), $E°_{AB/AB•-}$ (V), ζ, λ (kcal mol^{-1}): **1a**, −0.2, −2.29 ($\equiv E°(\mathbf{2})$), 10^2, 20; **1f**, 0.09, −0.89, 70, 8. In the case of **1a**, the fit to the experimental α data does not change as long as $E°_{AB/AB•-} <$ −1.8 V.
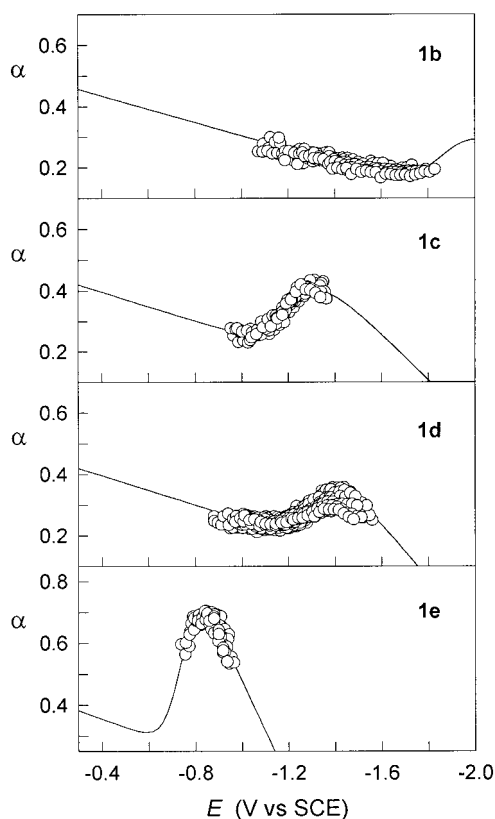

Figure 7. Experimental (○) and calculated (solid line) potential dependencies of the apparent transfer coefficient α for the electroreduction of **1b**–**e** in DMF/0.1 M TBAP at 25 °C. The solid curves were obtained by using a mixed dissociative ET rate law (eq 8). By using the BDE value of Table 1, best fit was obtained for the following values of $E°_{AB/A•,B-}$ (V), $E°_{AB/AB•-}$ (V), ζ, λ (kcal mol^{-1}): **1b**, −0.12, −1.78, 10^2, 19; **1c**, 0.02, −1.30, 70, 15; **1d**, 0.02, −1.35, 13, 12; **1e**, 0.12, −1.00, 10^2, 7.

available range with **1a** and **1b** point to ET reactions occurring at large overpotentials, in agreement with a pure (**1a**) or almost pure (**1b**) concerted mechanism. In contrast, the apparent α values obtained with **1f** are much larger, being in the range

0.53−0.75 in the explored E range. This points to a clear-cut case of stepwise mechanism. On the other hand, markedly curved $\alpha - E$ plots were obtained with **1c** and **1e**, as previously found with **1d** (Figure 7). At difference with **1a** and **1f**, the experimental trend cannot be accommodated by either dissociative ET mechanism. It can be added, however, that whereas for **1e** the α values are in the range 0.54−0.68, i.e., not too different from those of **1f**, for **1c** and **1d** smaller values are found (0.24−0.43 and 0.23−0.35, respectively).

ET Mechanism. The solid lines of Figures 6,7 result from the best-fit analyses of the experimental data on the basis of eqs 8,9. The starting point of the fitting procedure was the data of Table 1. This includes the estimates of the $E°$ values for both the concerted and the stepwise mechanisms (the ϵ parameter) and of the intrinsic barriers ($\Delta G_0^\ddagger$)$_C$ and ($\Delta G_0^\ddagger$)$_{ST}$. The latter energies were obtained by using the BDE values of Table 1 and the $\Delta G_{0,s}^\ddagger$ values obtained by using the Stokes radii of **1a**−**f**.[40] As discussed above, these estimates lead to the parameter β. The reorganization energy was varied to allow for some variation of β. The ζ parameter was then adjusted to the experimental data. By admitting the correctness of the BDE values of Table 1, it was possible to fit the calculated α curve to the experimental data only by using a preexponential Z_C value much smaller than the corresponding Z_{ST} value. While Z_{ST} was taken as the adiabatic value, the Z_C value was eventually estimated to be ∼2 orders of magnitude smaller than Z_{ST}. Despite the simplicity of the adopted model, it was possible to reproduce satisfactorily the experimental trend for each compound. The final parameters deriving from the best fitting procedure are provided in the captions to Figures 6,7 and in Table 1 ($E°_{AB/A•,B-}$).

The analysis shows that in the experimentally available potential range three of the selected compounds provide data in agreement with a mixed mechanism behavior. The trend is less evident for **1b**. As previously shown with **1d**,[11] the concerted-pathway contribution to the overall rate increases as E is rendered more positive. By using scan rates of 0.1−50 V s^{-1}, the E range in which α data are experimentally measurable is usually of the order of 0.5−0.7 and 0.2−0.3 V for the concerted and the stepwise mechanism, respectively. This means that full transition from one mechanism to the other cannot be observed; in fact, Figures 1−3 show that full transition from one linear behavior to the other would require no less than 0.7 V. However, one may be able to observe either a mixed kinetic regime where one of the two mechanism prevails, such as with **1e**, or a completely mixed kinetic regime, such as with **1c** and **1d**. Because of experimental constraints, we observed that in general the E_p value measured at 0.2 V s^{-1} lies more or less in the middle of the investigated E range.[11,16,18,22,24] By using this simple but useful information together with estimates of $E°_{AB/A•,B-}$ and $E°_{AB/AB•-}$, the type of α pattern and thus the degree of stepwise versus concerted pathway experimentally observable can be predicted to some extent within a family of related compounds. Let us focus, e.g., on compounds **1c**−**f**. According to our best fit analysis, the E range over which α data can be obtained includes $E = E°_{AB/AB•-}$, the estimated difference $E_p(\mathbf{1}) - E°_{AB/AB•-}$ for **1c**−**f** being very similar (∼0.1 V). However, the estimated difference $E°_{AB/A•,B-} - E_p(\mathbf{1})$ increases in the order **1f** < **1e** < **1d** ≈ **1c**. Despite the crudeness of the numerical comparison, this order reproduces correctly

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(40) The equation employed, λ_s(kcal mol^{-1}) = 55.7/r(Å),[16] derives from an extensive set of experimental data: Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

Role and Relevance of the Transfer Coefficient α
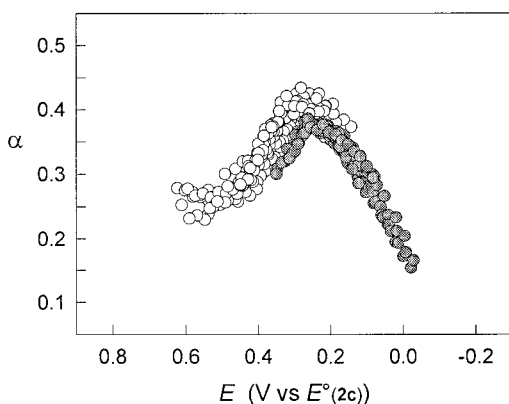
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Figure 8. Potential dependencies of the apparent transfer coefficient α for the electroreduction of **1c** in DMF/0.1 M TBAP at 25 (white circles) and −40 °C (gray circles). The data are reported against $E°$ (**2c**), as obtained at the working temperature.

the picture arising from the sets of α data, where we have the passage from a stepwise mechanism (**1f**), to a mixed mechanism having a pronounced stepwise character (**1e**), to a mixed mechanism where both ET components are significant (**1c,1d**).

Let us hypothesize that the various fits indeed provide a reasonable representation of the actual experimental systems and analyze the significance of the final values of the parameters employed to fit the experimental α data in Figures 6,7. For **1a** the actual value of $E°_{AB/AB•−}$ is not relevant because this compound undergoes a clear-cut case of concerted mechanism. Under this circumstance, $E°_{AB/AB•−}$ can be more positive than that of the corresponding ester **2** without affecting the α pattern in the region where the experimental data were collected (see Figures 1, 4, 5 and the caption to Figure 6). It is not so, however, for the other compounds. Concerning the two nitro derivatives, they constitute a peculiar case because in the formation of the radical anion the unpaired electron is mostly localized onto the nitro group, no matter whether the other substituent is CO_3-Bu-*t* or CO_2Bu-*t*. This is supported by the observation that the same $E°$ as that of the corresponding ester **2** is obtained by analyzing the "stepwise" linear component of the E dependence of α (see the pertinent plots in Figures 6 and 7). However, the $E°_{AB/AB•−}$ values resulting from the analysis of the potential dependence of α for **1c** and **1d** are almost 0.3 V more positive than those of **2c** and **2d**. That of **1b**, although affected by a larger uncertainty, seems to be ∼0.4 V more positive than that of **2b**. In principle, this could be attributed either to an experimental artifact (an unlikely event because three different compounds led to a similar outcome) or to an indirect indication that the effect of the CO_3Bu-*t* group is to lower the energy of the π* orbital with respect to the corresponding CO_2Bu-*t* substituted molecule. We approached this problem by studying the reduction of **1c** at −40 °C, in comparison with that of **2c**. In fact, by studying the dissociative electroreduction of a sulfonium salt it was shown that a temperature decrease favors the stepwise mechanism over the concerted one.[10c] This is because of the kinetically induced negative shift of the experimental peak, which moves closer to the pertinent $E°_{AB/AB•−}$. The result of this approach is shown in Figure 8, where it can be noted that the trend observed at 25 °C changes into the expected direction, leading to an α pattern displaying a pronounced stepwise character.[41] By making the reasonable assumption that the standard entropy ruling $E°_{AB/AB•−}$ is the same as that of the $E°$ of the very similar ester **2c**, the E scale was referred to the latter $E°$ value, as obtained under the same experimental conditions. From the linear part of the α pattern,

a standard potential of 0.30 V vs $E°$(**2c**) was estimated. In Figure 8, the trend observed at 25 °C is also reported on the same potential scale for the sake of comparison. The agreement between the two sets of data thus supports the above hypothesis on the orbital stabilization effect.

It is also interesting to note that our analysis is in agreement with some dependency of the reorganization energy on the X substituent and with a preexponential factor Z_C significantly smaller than Z_{ST}. Concerning the first point, this can be attributed to an increasing contribution of the inner component to the overall reorganization λ when going from **1f** to **1a**, as found for the stepwise reduction of disulfides.[18,20] Concerning the low Z_{ST}/Z_C ratios, this would mean that the concerted dissociative ET to perbenzoates is essentially nonadiabatic. However, it is not clear why this would be so. We have recently analyzed the homogeneous reduction of dialkyl peroxides in connection with nonadiabaticity problems and obtained evidence for unusually low preexponential factors.[15b] By comparing the ET data with those of an adiabatic dissociative ET (reduction of *tert*-butyl bromide), it appeared reasonable to think that while the stretching of the C-halogen bond results in a change in the dipole moment of the bond because of electron redistribution, the corresponding change in symmetrical peroxides is smaller. This would lead to poor electronic coupling between the reactant and the product surfaces. This argument, however, should be less relevant for perbenzoates, which are nonsymmetrical acceptors, and this calls for further experimental and theoretical studies.

Conclusions

The analysis here presented points to a relevant role of the transfer coefficient α as a probe of stepwise-to-concerted mechanism transitions. Linear potential dependencies of α are in agreement with either mechanism. The type of mechanism can be assessed by the value of the slope, which is significantly larger for the stepwise case. On the other hand, a mechanism transition may be detected by the observation of a nonlinear α pattern. In fact, under favorable circumstances, a wavelike potential dependence of α pattern is expected. The shape and position of these α waves can be modulated by relevant parameters describing the mechanism transition: The difference between the two relevant standard potentials, the two intrinsic barriers, and the two preeponential factors.

We applied this analysis to the dissociative electroreduction of six perbenzoates. Whereas the reduction of **1a** proceeds by a concerted ET and that of **1f** by a stepwise mechanism, a stepwise-to-concerted mechanism transition was observed by increasing the applied potential in the other cases, particularly with **1c−e**. Despite the relatively large number of parameters involved and the poor quality of some of the data required for the analysis, the experimental α trends could be reproduced fairly well for each compound. Although this required some adjustment of the initial input parameters, the final picture seems to be reasonable. In addition, it appears that, at least within a family of related compounds, a transition behavior can be predicted on the basis of relatively simple considerations.

(41) We studied also the effect of increasing the temperature on the reduction of **1e**. Although for practical reasons the temperature could be raised only to 50 °C and thus the resulting effect was not as evident as in Figure 8, the shift was in the expected direction. In fact, since a temperature increase closes the gap $E°_{AB/A•,B−} − E_p(1)$ and increases $E_p(1) -E°_{AB/AB•−}$, the mechanism shifts to one in which the concerted component becomes more important than that observed at 25 °C. A similar temperature effect has been recently described (Reference 10e. We are grateful to Professor Savéant for providing us an advanced copy of the manuscript).

Among the qualitative observations stemming from the analysis, one concerns the indirect evidence of the effect of the O$-$O bond in lowering the π^* orbital of perbenzoates relative to that of the corresponding benzoates, provided these molecules are not nitro derivatives. This experimental observation is interesting because the direct determination of $E^\circ_{AB/AB\bullet-}$ would be unfeasible owing to the short lifetime of the radical anion. In this framework, an important support is provided by the temperature effect on the potential dependence of α. By studying the reduction of **1c**, we have shown that the transition is shifted toward a stepwise pattern by lowering the temperature and thus by shifting the voltammetric peak closer to $E^\circ_{AB/AB\bullet-}$ and away

from $E^\circ_{AB/A\bullet,B-}$. This confirms very nicely the very recent observation of Savéant and co-workers of an analogous transition shift by studying by conventional voltammetry the reduction of a completely different compound, a sulfonium salt,[10c] and further enforces the overall picture of dissociative ETs.