J. Am. Chem. Soc. **1998,** *120,* 5713−5722

Dependence of Intramolecular Dissociative Electron Transfer Rates on Driving Force in Donor−Spacer−Acceptor Systems

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Received December 4, 1997

Abstract: The voltammetric reduction of a series of phenyl-substituted 4-benzoyloxy-1-methylcyclohexyl bromides has been investigated in DMF. The reduction leads to the cleavage of the C−Br bond. On a thermodynamic ground, the direct reduction of the tertiary C−Br function is easier than that of the selected benzoates by at least 0.5 V. However, since the direct reduction of bromides is affected by a large activation overpotential, the electron is first located in the benzoate moiety. The rate constant for the following exergonic intramolecular dissociative electron transfer was determined by kinetic analysis of the cyclic voltammetry curves. The intermolecular rate constants for the reaction between the radical anions of methyl benzoates and 4-*tert*-butyl-1-methylcyclohexyl bromide were also determined and found to correlate very well with related literature data pertaining to *tert*-butyl bromide. The intramolecular rate constants were found to be more sensitive to variation of driving force than the corresponding intermolecular data. This result can be attributed to a shift of the center of the π^* orbital of the radical anion donor away from the acceptor moiety, the shift being larger for the most easily reduced donors. The resulting distance increase is therefore envisaged as responsible for a more rapid rate drop, compared to the intermolecular pattern, when smaller driving forces are considered.

Introduction

The distance dependence in electron transfer (ET) reactions within D−Sp−A systems, in which an electron donor (D) and electron acceptor (A) are separated by a saturated spacer (Sp), has been the subject of several studies.[1] Although A and D are usually chosen to be chemically stable during the ET process, some recent investigations have focused on acceptors designed to undergo fast and irreversible chemical reactions as a tool to provide further insight into the dynamics of intramolecular ET.[2] Dissociative ET processes, i.e., those reactions in which the acceptor molecule fragments synchronously with the electron uptake, represent the fundamental limiting case of a fast, irreversible follow-up reaction.[3,4] However, although very recent work has provided a clearer understanding of different aspects of intramolecular dissociative ETs,[5−8] no quantitative information concerning the distance dependence of such reactions in condensed media is available.[9] On these grounds and because of our interest in nonadiabatic dissociative ETs,[10] we have started to investigate the activation−driving force relationships ruling the intramolecular dissociative ETs in well-defined D−Sp−A systems (eq 1).

$$^{\bullet-}\mathrm{D{-}Sp{-}A} \rightleftharpoons \mathrm{D{-}Sp}^{\bullet} + \mathrm{A}^{-} \qquad (1)$$

Previous work on intramolecular dissociative ETs[5−8] focused on spacers consisting of either a single methylene group or a (partially) π-conjugated molecular backbone. Under these conditions, the free energy (ΔG°) of the intramolecular ET (eq 1) may be difficult to estimate. Since the standard potential for a dissociative ET ($E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}}$) can be expressed as a function of the bond dissociation free energy (BDFE) of the breaking σ bond (here, the Sp−A bond) and of the oxidation potential of the leaving group ($E^\circ_{\mathrm{A^\bullet/A^-}}$),[11,12] ΔG° may be expressed by eq 2

$$\Delta G^\circ = -F(E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}} - E^\circ_{\mathrm{DSpA/(DSpA)^{\bullet-}}}) = -F(E^\circ_{\mathrm{A^\bullet/A^-}} - E^\circ_{\mathrm{DSpA/(DSpA)^{\bullet-}}}) + \mathrm{BDFE} \qquad (2)$$

where $E^\circ_{\mathrm{DSpA/(DSpA)^{\bullet-}}}$ is the standard potential for the donor redox couple. In general, when D is varied while A is kept constant,

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(9) Some interesting results concerning the distance effects in gas-phase dissociative electron attachments have been published: Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Nachtigallova, D.; Jordan, K. D. *J. Phys. Chem.* **1995**, *99*, 12379.

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S0002-7863(97)04118-8 CCC: $15.00

the BDFE value and thus $E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}}$ also vary. In other words, by changing the donor, one varies ΔG° not only because of $E^\circ_{\mathrm{DSpA/(DSpA)^{\bullet -}}}$ but also through $E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}}$. As a consequence, if there is no practical way to know how the presence of different D groups affects the BDFE of the DSp−A bond, special caution must be exercised to deal with the result of an activation−driving force analysis. This complication can be minimized or even avoided by choosing a spacer that is not too short nor one that leads to a π-conjugated system. Therefore, along the lines described by the pioneering work by Closs, Miller, and their co-workers,[1a] we decided to focus on spacers formed by saturated and (relatively) rigid molecular frameworks.

In this study, the leaving group A has been selected to be a tertiary bromide since the reduction of *tert*-butyl bromide is by far the most studied molecule that undergoes a dissociative ET. As a matter of fact, for this experimental system data are available (homogeneous reduction in amide solvents) for an overall variation of the intermolecular rate constant by 13 orders of magnitude.[13] In this reaction (and also in the ET to other alkyl halides), the experimental data seems to fit almost equally well to a parabola, as predicted by the theory,[4] or to a straight line.[14,15] Consequently, the actual form of the activation−driving force relationship for ET to *tert*-butyl bromide and similar acceptors or the possible role of an inner-sphere component when the ET becomes more endergonic[15] are still an open matter for discussion. This is primarily because these reactions have large intrinsic barrier ($\Delta G_0^{\#}$) values. To better understand this point, one has to consider the Marcus-like parabola underlying the dissociative ET theory[4] and relating the activation free energy ($\Delta G^{\#}$) to ΔG° (eq 3). Whereas the first

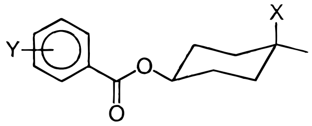
$$\Delta G^{\#} = \Delta G_0^{\#}\left(1 + \frac{\Delta G^\circ}{4\Delta G_0^{\#}}\right)^2 \tag{3}$$

$$\alpha = \frac{\partial \Delta G^{\#}}{\partial \Delta G^\circ} = 0.5 + \frac{\Delta G^\circ}{8\Delta G_0^{\#}} \tag{4}$$

$$\frac{\partial \alpha}{\partial \Delta G^\circ} = \frac{\partial^2 \Delta G^{\#}}{\partial (\Delta G^\circ)^2} = \frac{1}{8\Delta G_0^{\#}} \tag{5}$$

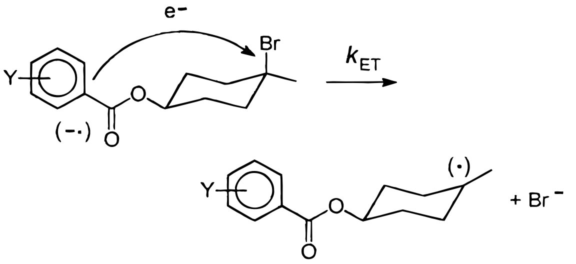
derivative of eq 3 provides the transfer coefficient (or symmetry factor) α of the reaction (eq 4), the second derivative (eq 5) yields the curvature of the parabola. Since the curvature is inversely proportional to $\Delta G_0^{\#}$, it follows that it might be difficult to detect the expected quadratic activation−driving force relationship for reactions characterized by large $\Delta G_0^{\#}$ values. Conversely, when the latter values are not too large, as it is for peroxides as a result of their small bond dissociation energy values,[16] the expected parabolic pattern is detectable beyond experimental error.[10,12,17,18] Therefore, if a quadratic rate-free energy law is in general better at describing dissociative ET processes, the mechanism of the reduction of halides deserves further investigation. We believe that a good way to tackle this problem is by using well-defined intramolecular D−Sp−A systems, where any inner-sphere contributions to the ET are precluded and where the distance and orientation of the electron-exchanging centers are controlled.

We report here the results obtained on the intramolecular ET rate in compounds **1** measured at 25 °C by cyclic voltammetry in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (TBAP). The free-energy dependence of the intramolecular ET rate constant (k_{ET}) in **1** (eq 6) was determined by varying D, which was chosen as the activated (i.e., reduced) form of an aromatic ester, while keeping constant a 1,4-cyclohexanediyl moiety as the spacer. To define the free energy of the process and the heterogeneous ET kinetics, we studied also the voltammetric reduction of the corresponding D−Sp−OH (**2**) and D−Sp−H (**3**) systems. 4-*tert*-Butyl-1-methylcyclohexyl bromide (**4**) served as a model to estimate the dissociative E° of the acceptor, using the convolution voltammetry approach. Information on the intermolecular counterpart of eq 6 was obtained by studying the ET between **4** and the radical anions electrogenerated from the esters Y−PhC(O)OMe (**5**), in comparison with the literature data on *tert*-butyl bromide.[13]



X = Br (**1**), OH (**2**), H(**3**)

Y = H (**a**), 3-OPh (**b**), 3-F (**c**), 2,3-benzo (**d**), 4-SO_2Me (**e**), 4-CN (**f**)



(6)

Experimental Section

Chemicals. *N,N*-Dimethylformamide (Janssen, 99%) and tetrabutylammonium perchlorate (TBAP, 99%, Fluka) were purified as previously described.[12] The following compounds were used as received: 4-*tert*-butylcyclohexanone (Fluka), methyl iodide (Acros), hydrobromic acid (48% aqueous, Fluka), 1,4-cyclohexanone monoethylene acetal (Fluka), sodium borohydride (Janssen), benzoyl chloride (Fluka), 3-fluorobenzoyl chloride (Aldrich), 3-phenoxybenzoic acid (Janssen), 1-naphthoyl chloride (Aldrich), 4-(methylsulfonyl)benzoic acid (Aldrich), 4-cyanobenzoyl chloride (Aldrich), thionyl chloride (Fluka), methyl benzoate (Janssen), methyl 4-cyanobenzoate (Aldrich).

4-Methylcyclohexanol was obtained by $NaBH_4$ reduction of 4-methylcyclohexanone (Aldrich). 3-Phenoxybenzoyl chloride and 4-(methylsulfonyl)benzoyl chloride were obtained by reaction of the acid with thionyl chloride. Compounds **3** were obtained by reacting 4-methylcyclohexanol with the pertinent aroyl chloride, in pyridine. The methyl esters **5b**−**e** were obtained by acid-catalyzed reaction of the aroyl acid with methanol. 4-*tert*-Butyl-1-methylcyclohexanol was obtained by

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[16] The intrinsic barrier $\Delta G_0^{\#}$, i.e., the activation free energy at zero driving force, is related[4] to the bond dissociation energy (BDE) and to the solvent reorganization energy λ_o by equation $\Delta G_0^{\#} = (\mathrm{BDE} + \lambda_o)/4$.

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Grignard reaction of 4-*tert*-butylclohexanone with methyl iodide. 4-*tert*-Butyl-1-methylcyclohexyl bromide[19] (**4**) was obtained as a 20:1 mixture of isomers by reaction of 4-*tert*-butyl-1-methylcyclohexanol with aqueous HBr: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 0.84 and 0.88 (3H, 2s, *t*-Bu), 1.61 and 1.63 (1H, 2s, Me).

The general synthetic scheme used to obtain the compounds **1** is as follows. Grignard reaction of 1,4-cyclohexanedione monoethylene acetal (Fluka) with methyl iodide gave 4-hydroxy-4-methylcyclohexanone monoethylene acetal[20] in about 80% yield. The ketone was then deprotected in acetone−aqueous 0.1 N HCl (5:1), at reflux for 1 h; after neutralization and extraction, 4-methyl-4-hydroxycyclohexanone[21] was obtained (about 85% yield). The latter was reduced with $NaBH_4$ in methanol to a mixture (ca. 80% yield) of isomeric diols.[22] The donor side of the system was introduced by reacting the diol mixture with the selected aroyl chloride in pyridine.[23] This reaction proceeded regioselectively onto the secondary alcohol group to give a mixture of stereoisomeric esters **2**, in 50−80% yield. The tertiary bromides **1a**−**f** were obtained by mixing the corresponding **2** with aqueous HBr (48%) and stirring the resulting slurry for ca. 12 h. The reaction usually gave similar amounts of two stereoisomers (75−85% overall yield) that were easily separated by chromatography. NMR {^{1}H}−^{1}H nuclear overhauser effect measurements and X-ray crystallography indicated that compounds **1a**−**f** have a cis equatorial−axial configuration, the bromine atom being axial. Full details of the spectroscopic and the structural analyses of both series of compounds will be published elsewhere.[24]

The melting points (uncorrected) and ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$, TMS) of bromides **1** are as follows. **1-Methyl-4-benzoyloxycyclohexyl bromide 1a**: mp 94−95 °C; ^{1}H NMR δ 1.89 (3H, s, Me), 4.97 (1H, m, CHO), 7.45−8.06 (5H, m, C_6H_5). **1-Methyl-4-(3′-phenoxybenzoyloxy)cyclohexyl bromide 1b:** mp 101−102 °C; ^{1}H NMR δ 1.88 (3H, s, Me), 4.94 (1H, m, CHO), 7.01−7.80 (9H, m, C_6H_5 and C_6H_4). **1-Methyl-4-(3′-fluorobenzoyloxy)cyclohexyl bromide 1c:** mp 56−57 °C; ^{1}H NMR δ 1.89 (3H, s, Me), 4.96 (1H, m, CHO), 7.26−7.85 (4H, m, C_6H_4). **1-Methyl-4-(1′-naphthoyloxy)-cyclohexyl bromide 1d:** mp 92−94 °C; ^{1}H NMR δ 1.90 (3H, s, Me), 5.08 (1H, m, CHO), 7.51−8.90 (7H, m, $C_{10}H_7$). **1-Methyl-4-(4′-methylsulfonylbenzoyloxy)cyclohexyl bromide 1e:** mp 152−153 °C; ^{1}H NMR δ 1.90 (3H, s, Me), 3.08 (3H, s, $MeSO_2$), 5.00 (1H, m, CHO), 8.04−8.25 (4H, m, C_6H_4). **1-Methyl-4-(4′-cyanobenzoyloxy)cyclohexyl bromide 1f:** mp 133−135 °C; ^{1}H NMR δ 1.89 (3H, s, Me), 4.99 (1H, m, CHO), 7.74−8.15 (4H, m, C_6H_4).

Electrochemistry. The glassy carbon (Tokai GC-20) electrode was prepared and activated before each measurement as previously described.[12] The reference electrode was a homemade Ag/AgCl,[25] calibrated after each experiment against the ferrocene/ferricinium couple and then against the KCl-saturated calomel electrode, SCE (in DMF/0.1 M TBAP, $E^\circ_{\mathrm{Fc/Fc^+}} = 0.464$ V vs SCE). In the following, all of the potential values will be reported against SCE. The standard potentials given in the text are actually formal potentials because concentrations were used instead of activities.[26] The counter electrode was a 1 cm^2 Pt plate. Electrochemical measurements were conducted in an all glass cell, thermostated at 25 ± 0.2 °C, and under an argon atmosphere. The voltammetric curves were obtained by using an EG&G-PARC 173 potentiostat, an EG&G-PARC 175 universal programmer, and a Nicolet 3091 12-bit resolution digital oscilloscope, using special precautions to reduce the electrical noise.[12] The feedback correction was applied in order to minimize the ohmic drop between the working and reference electrodes. In most of the experiments, the cyclic voltammograms were recorded in a selected potential range and for scan rates ranging from 0.1 to 200 V s^{-1} (first in the absence and then in the presence of the substrate) by the digital oscilloscope (digitalized 1 point/mV) and then transferred to a PC. The background-subtracted curves were analyzed by the conventional voltammetric criteria[26−28] or the convolution approach,[12,29] using our own laboratory software. Digital simulations of the cyclic voltammetry curves were performed by using the DigiSim 2.1 software by Bioanalytical Systems Inc.

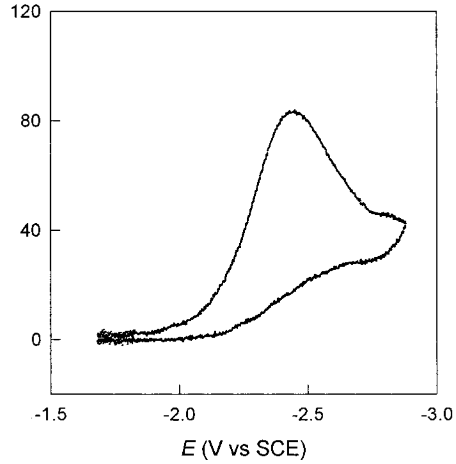

Figure 1. Cyclic voltammetry of bromide **4** (3 mM) in DMF/0.1 M TBAP obtained at a glassy carbon electrode, $v = 0.2$ V s^{-1}, $T = 25$ °C.

Results and Discussion

Standard Potentials and Heterogeneous ET Kinetics. The free energy of the intramolecular dissociative ET between the donor and the acceptor (eq 6) is related to the difference between the two relevant E°s (eq 2). Whereas the E° values for the donor side of compounds **1** can be easily determined (see below), the estimation of $E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}}$ is complicated because dissociative ETs are highly irreversible reactions. In fact, it has been shown that the direct reduction of alkyl halides suffer a large activation overpotential;[13c] for example, although the voltammetric peak potential (E_p) for the reduction of *tert*-butyl bromide is −2.51 V (0.1 V s^{-1}, glassy carbon, DMF, 10 °C), thermochemical calculations bracket the dissociative ET E° ranging from −0.93 to −1.05 V (eq 7, R = *t*-Bu).[3,4b,30] Since

$$\mathrm{RBr} + e^- \rightarrow \mathrm{R}^\bullet + \mathrm{Br}^- \qquad (7)$$

tert-butyl bromide mimics satisfactorily the acceptor side of compounds **1**, such E° values could be used in eq 2. However, although thermochemical calculations can provide, under favorable conditions, remarkably precise data, we tried to obtain an independent check of $E^\circ_{\mathrm{DSpA/DSp^\bullet,A^-}}$ and studied the direct reduction of 4-*tert*-butyl-1-methylcyclohexyl bromide **4** by cyclic voltammetry, using a glassy carbon electrode. Compound **4** has the advantage of being structurally similar to the actual D−Sp−A systems and possesses the tertiary halide character of *tert*-butyl bromide.

The irreversible, dissociative electroreduction of **4** (eq 7, RBr = **4**) leads to a voltammetric peak (Figure 1) located at −2.47 V (0.2 V s^{-1}), i.e., at essentially the same E_p observed with *t*-BuBr.[13c] When the scan rate is increased, the peak shifts toward more negative values by 116 mV/log v, leading to an average value of α of 0.255;[26] correspondingly, the peak width

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[30] The two limiting values arise by either neglecting or by taking into account in the calculation a different solvation of the halide relative to the corresponding radical. For details, see refs 3 and 4b.

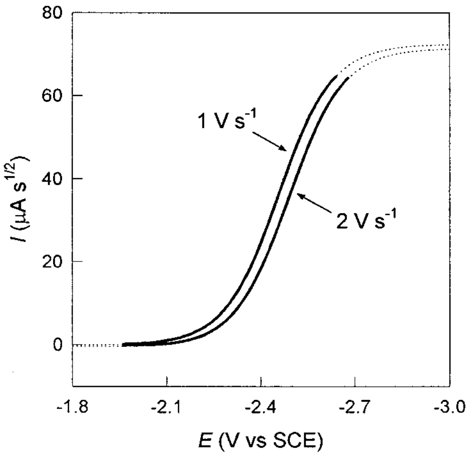

Figure 2. Convolution curves of the background-subtracted voltammetric curves for the reduction of **4** (3 mM) in DMF/0.1 M TBAP at the glassy carbon electrode, $T = 25$ °C. The dotted lines were obtained by sigmoidal fitting of the experimental data, according to equation[12] $I = a_0 + a_1/\{1 + \exp[-(E - a_2)/a_3]\}$.

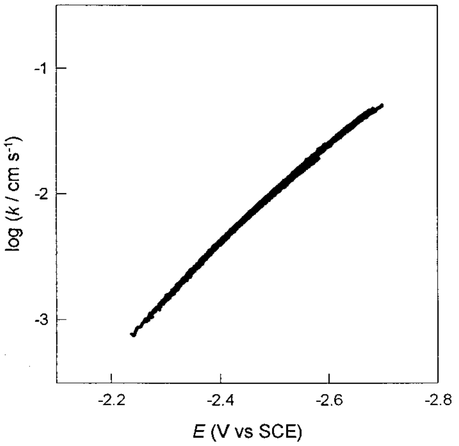

Figure 3. Potential dependence of the logarithm of the heterogeneous rate constant for the reduction of **4** in DMF/0.1 M TBAP at the glassy carbon electrode, $T = 25$ °C.

$\Delta E_{p/2}$ (difference between the potential measured at half-peak height and E_p) increases, in agreement with a potential dependence of α.[12] To obtain an estimate of the $E°$ for the dissociative ET to **4**, we carried out the convolution analysis.[12,29] The background-subtracted curves obtained in different experiments and for scan rates in the 0.2−2 V s^{-1} range were subjected to convolution followed by logarithmic analysis to obtain the heterogeneous ET rate constant (k) as a function of the potential E. The logarithmic equation valid for an irreversible electrode process is $\ln k = \ln D^{1/2} - \ln[(I_l - I(t))/i(t)]$, where real ($i$) and convoluted ($I$) current values are combined; a limiting convolution current (I_l) is reached when the electrode process becomes diffusion controlled.[29] Only low scan rates could be employed because of the proximity of the solvent−electrolyte discharge. In addition, since I_l was reachable only at potentials too close to the cathodic discharge, therefore leading to unacceptable uncertainty in its evaluation, we used an approach in which the rising part of the convolution curves was fitted by a sigmoid equation.[12] I_l values were thus estimated for each scan rate and found to agree with each other within 3%. While Figure 2 shows typical examples of convolution curves and fitting, Figure 3 provides the final results of the logarithmic analysis. The potential dependence of the apparent value of α, i.e., $\alpha_{app} = -(RT/F)\ d(\ln k)/dE$, was obtained by quadratic fitting of the whole series of $\ln k$ data followed by derivatization. By taking into account the double-layer effect, the $E°$ of **4** was finally estimated to be about −1.06 V.[31] Although reliable experimental data could only be collected in a limited potential range (0.5 V), causing the error on $E°$ to be about ±0.1 V, the agreement with the thermochemical estimates pertaining to *t*-BuBr[3,4b] is very good and thus strengthens the reliability of the electrochemical estimate.[32] Consequently, the value −1.06 V will be used in the following discussion.

The standard potentials of the candidate donors ($E°_{D/D^{\bullet -}}$) were selected to have no competition between the direct reduction of the donor and of the bromide.[33] A homogeneous series of substituted benzoates was chosen as the pro-donors, i.e., as those groups able to provide the active form of the donor upon one-electron reduction. The resulting radical anions are convenient donors in that their formation is often reversible on the time scale of cyclic voltammetry, which means that their lifetimes are longer than a few seconds. This was checked with the series of the cyclohexyl benzoates, **2** and **3**, and the methyl benzoates, **5**.[34] Table 1 shows the $E°$ values of compounds **2**, **3**, and **5**, obtained from the reversible reduction peaks. In general, the $E°$ undergoes a slightly negative shift upon varying the alkyl substituent from methyl to cyclohexyl and this shift tends to vanish when going to more easily reducible substrates. On the other hand, comparison between the $E°$ values of **2** and **3** indicates that the remote cyclohexyl susbtituent does not affect the reduction of the benzoate aryl moiety, within experimental error. Conversely, the ease of the reduction is strongly affected by the substituents on the aryl ring. In the last column of Table 1, the diffusion coefficients of **2**, calculated from the peak current values obtained at low scan rates, are also reported. As

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[31] According to the dissociative ET theory,[4] the electrochemical transfer coefficient α should be given by eq 4, where $\Delta G° = F(E - E°)$ and thus $\alpha = (\partial \Delta G^{\#}/\partial E)/F$. Accordingly, $\alpha = 0.5$ when $E = E°$. However, when the electron donor is an electrode instead of a soluble species, $\Delta G°$ is best written as $F(E - E° - \phi^{\#})$, where $\phi^{\#}$ is the difference between the potential at the reaction site (average distance from the electrode at which the substrate is located when the ET takes place) and the potential of the bulk solution. Therefore, α is related to α_{app} through equation $\alpha = \alpha_{app}/(1 - \partial \phi^{\#}/\partial E)$. The problem is that the reduction of halides is best performed by using glassy carbon, the double-layer properties of which are unknown. On the other hand, by using a mercury electrode (for which the double-layer correction is feasible), we have recently shown that when α_{app} is used in place of α, a negative error of 60−70 mV in the estimate of $E°$ ensues.[12] In the hypothesis that the double-layer effects of glassy carbon and mercury are similar, we applied the same correction to the results obtained with **4** (the uncorrected $E°$ is −1.13 V). We believe, however, that the error estimated for $E°$ (±0.1 V) takes into account also possible double-layer differences.

[32] Taking into account that the dissociative ET $E°$ can be expressed[11,12] as $E°_{A^{\bullet}/A^{-}}$ − BDFE/F, our results would suggest that differences in the BDFEs of the two bromides are essentially undetectable. Our analysis would also support the correctness of the solvation free energy correction,[30] which led to ca. −1.05 V.[3,4b]

[33] Since the peaks of the donors in **1** were expected to appear at more positive potentials than the reversible E_p value, owing to the kinetic effect of the intramolecular follow-up reaction,[26−28] and also because the bromide peak shifts consistently toward more negative potentials upon increasing v (116 mV/log v), the condition $E°_{D/D^{\bullet -}} - E_{p(\mathbf{4})} > 0.2$ V proved to be adequate.

[34] We tried other benzoate-type donors and found that the presence of certain substituents led to labile radical anions, as indicated by either the absence or the reduced height of the anodic peak corresponding to the reoxidation of the radical anion during the backward voltammetric scan. For example, we encountered this situation with the methyl esters of pyrazinecarboxylic acid ($E° = -1.58$ V) or nicotinic acid ($E° = -1.98$ V) and, with compounds **2**, for Y = 2-CF_3 ($E° = -1.95$ V), 4-CF_3 ($E° = -1.84$ V), 2-C(O)OMe ($E° = -1.98$ V), or 3-CN ($E° = -1.89$ V). The decay rate of the radical anion can be rather high, such as for the latter compound where a first-order rate constant of 26 s^{-1} was determined by studying the anodic-to-cathodic peak current ratio as a function of the scan rate.[27a] Since it is not completely clear how these decays take place (Wagenknecht, J. H.; Goodin, R. D.; Kinlen, P. J.; Woodard, F. E. *J. Electrochem. Soc.* **1984**, *131*, 1559), the above radical anions were discarded as candidate electron donors.

Table 1. Voltammetric Data for the Reduction of Substituted Benzoates in DMF/0.1 M TBAP at $T = 25$ °C

Y in Y-PhC(O)OR	$E°_{(2)}$[a] (V)	$E°_{(3)}$[a] (V)	$E°_{(5)}$[a] (V)	$k°_{(2)}$[b] (cm s^{-1})	$D_{(2)}$[b,c] (cm^2 s^{-1})
H (**a**)	−2.27	−2.26	−2.22	0.12 ± 0.01	5.5×10^{-6}
3-OPh (**b**)	−2.15	−2.14	−2.12	0.081 ± 0.007	4.2×10^{-6}
3-F (**c**)	−2.09	−2.08	−2.06	0.11 ± 0.01	4.5×10^{-6}
2,3-benzo (**d**)	−1.91	−1.92	−1.89	0.15 ± 0.015	4.3×10^{-6}
4-SO_2Me (**e**)	−1.66	n.d.[d]	−1.65	0.057 ± 0.006	3.9×10^{-6}
4-CN (**f**)	−1.61	−1.61	−1.60	0.088 ± 0.006	4.8×10^{-6}

[a] Potentials are against SCE; uncertainty is 5−10 mV. [b] Average of two or three independent experiments. [c] The uncertainty is $\pm 0.2 \times 10^{-6}$ cm^2 s^{-1}. [d] Not determined.

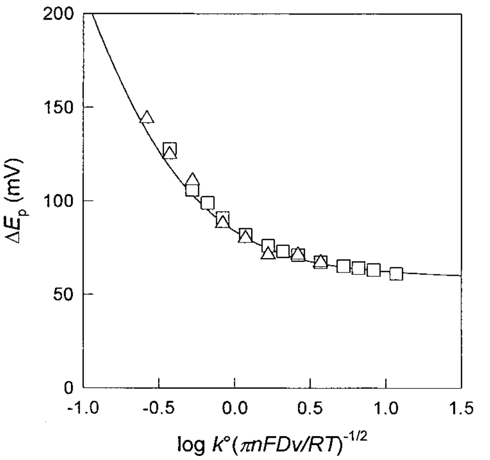

Figure 4. Scan rate dependence of the separation between the cathodic and the anodic peak potentials for the reduction of 1.4 mM **2f** (□) or **1f** (△) in DMF/0.1 M TBAP at the glassy carbon electrode, $T = 25$ °C. The plot is the best fit ($k° = 0.088$ cm s^{-1}) of the data to the theoretical curve describing the competition between diffusion and electron transfer ($\alpha = 0.5$).[28] The same D value (4.8×10^{-6} cm^2 s^{-1}) has been used for substrates and radical anions.

Table 2. Rate-Driving Force Data for the Indirect Dissociative ET to **4** in DMF at 25 °C

Pro-donor Y in Y-PhC(O)OMe or ArH	$E°_{D/D^{\bullet-}}$ (V)	$\Delta G°$ (eV)	log k_{ET} (M^{-1} s^{-1})
H (**5a**)	−2.22	−1.16	5.1
3-OPh (**5b**)	−2.12	−1.06	4.6
3-F (**5c**)	−2.06	−1.01	4.4
2,3-benzo (**5d**)	−1.89	−0.83	3.0
1-cyanonaphthalene	−1.85	−0.79	2.9
4-CN (**5f**)	−1.60	−0.54	0.8

expected because of the negligible difference between the radii of the corresponding **2** and **3**, the D values of the corresponding benzoates **3** were found to be equal within experimental uncertainty.

An important parameter to study chemical reactions following an heterogeneous ET is the apparent standard rate constant ($k°$). Accordingly, the $k°$ values of **2a**−**f** were determined by studying the scan rate dependence of the separation between the cathodic and the anodic peak potentials (ΔE_p).[27b] Figure 4 illustrates a typical plot showing how, upon increasing the scan rate v, ΔE_p increases relative to its reversible value (59 mV at 25 °C[26]). In the figure, ΔE_p is plotted against a kinetic parameter describing the competition between diffusion and electron transfer. For each compound, an excellent fit to the Nicholson theoretical curve[27b] was achieved in the whole scan rate range investigated (0.1 to 100 V s^{-1}). This outcome, and also because quasi-reversible behavior was detectable starting from relatively low scan rates (see Figure 4), led to good determinations of $k°$ (Table 1). The rather small values of $k°$ reported in Table 1 are comparable with the values obtained with other carbonyl compounds in the presence of a tetrabutylammonium salt as the supporting electrolyte, using glassy carbon electrodes.[5e] It is also relevant to add that differences in the heterogeneous behavior among compounds **1**−**3** were not detectable. For example, as shown by Figure 4, the ΔE_p values of **1f** (whose reduction is chemically reversible for $v > 1$ V s^{-1}; see below) cannot be distinguished from those of **2f** within experimental error.

Intermolecular ET. The homogeneous ET to **4** was studied to gain information on the effect of intermolecular processes on the electroreduction of compounds **1**. The indirect reduction of **4** was accomplished by using electrogenerated radical anions as homogeneous electron donors (mostly obtained from compounds **5**), according to the homogeneous redox catalysis approach.[35] The reversible reduction peak of the mediator is transformed into an irreversible peak upon addition of suitable amounts of **4**; the peak is catalytic because in the exergonic ET to **4** the neutral form of the donor is regenerated and thus can be reduced again at the electrode. The corresponding ET rate constant values were determined by simulation of the experimental curves, using the DigiSim 2.1 software. The cyclic voltammograms were obtained by using a glassy carbon electrode, different potential scan rates (in the 0.02−20 V s^{-1} range), and three molar ratios between mediator and substrate. In the simulation, the ET and coupling reactions already focused in studies on the intermolecular dissociative ET to alkyl halides were taken into account.[36] Because of the selected donor−acceptor systems, we carried out measurements for reactions characterized by driving forces in the 0.5−1.2 eV range. Table 2 shows the k_{ET} values resulting from this analysis. The uncertainty of the measured k_{ET} values is estimated to be 10−15%, as found in analogous studies.[13,37]

Electroreduction of 1 and Intramolecular ET Rates. The voltammetric reduction of **1a**−**e** is characterized by an irreversible peak, followed by a reversible component for **1a**−**c** (Figure 5). The splitting of the peaks becomes progressively less evident by increasing v or going to more easily reducible substrates. At 0.1 V s^{-1}, only the reduction peak of **1f** is partially reversible, indicating that the chemical reaction of the ensuing radical anion is rather slow. A similar situation holds for **1e**, for which an anodic peak corresponding to the main reduction peak appears

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(35) (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant J.-M. *J. Electroanal. Chem.* **1980**, *113*, 19. (b) Andrieux, C. P.; Savéant J.-M. *J. Electroanal. Chem.* **1986**, *205*, 43.

(36) The reactions between electrogenerated electron donors ($D^{\bullet-}$) and alkyl halides (RX) are given by following equations[13,15]

$$D + e \rightleftharpoons D^{\bullet-}$$

$$D^{\bullet-} + RBr \longrightarrow D + R^{\bullet} + Br^{-}$$

$$D^{\bullet-} + R^{\bullet} \longrightarrow D + R^{-}$$

$$D^{\bullet-} + R^{\bullet} \longrightarrow DR^{-}$$

where the last two reactions describe the competition reactions (ET and coupling with the radical anion donor) destroying the radical $R^{\bullet}$.

(37) Daasbjerg, K.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1991**, *45*, 424.

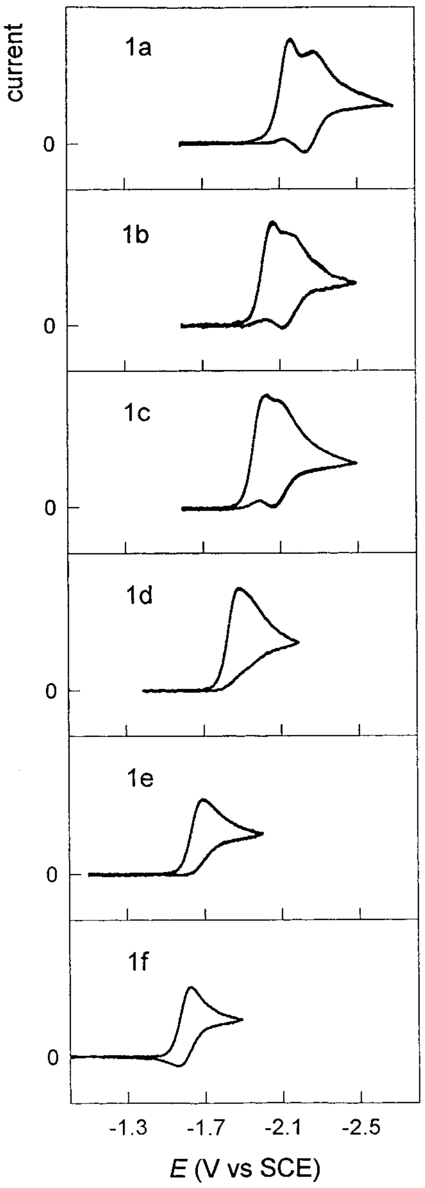

Figure 5. Comparison of the cyclic voltammograms of 1.8−2.0 mM **1a**−**f** in DMF/0.1 M TBAP obtained at the glassy carbon electrode, $v = 0.1$ V s^{-1}, $T = 25$ °C.

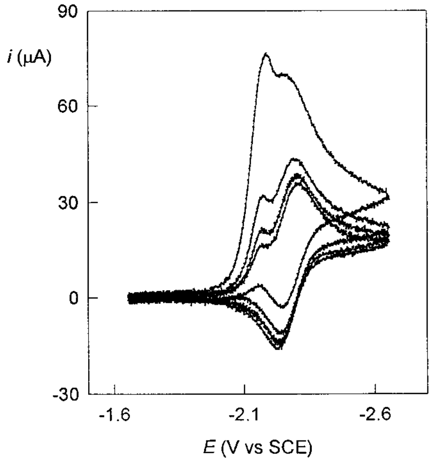

Figure 6. Multiscan (4 cycles) voltammetry of 1.8 mM **1a** obtained in DMF/0.1 M TBAP. Glassy carbon electrode, $v = 0.2$ V s^{-1}, $T = 25$ °C.

Scheme 1

$\text{D-Sp-Br} + e \rightleftharpoons {}^{\bullet -}\text{D-Sp-Br}$ (a)

${}^{\bullet -}\text{D-Sp-Br} \xrightarrow{k_{ET}} \text{D-Sp}^{\bullet} + \text{Br}^{-}$ (b)

$\text{D-Sp}^{\bullet} + e \rightleftharpoons {}^{\bullet -}\text{D-Sp}^{\bullet}$ (c)

${}^{\bullet -}\text{D-Sp}^{\bullet} \longrightarrow \text{D-Sp}^{-}$ (d)

$\text{D-Sp}^{-} \xrightarrow{H^{+}} \text{D-Sp-H}$ (e)

$\text{D-Sp-H} + e \rightleftharpoons {}^{\bullet -}\text{D-Sp-H}$ (f)

${}^{\bullet -}\text{D-Sp-X} + \text{D-Sp-Br} \longrightarrow \text{D-Sp-X} + \text{D-Sp}^{\bullet} + \text{Br}^{-}$ (g)

${}^{\bullet -}\text{D-Sp-X} + \text{D-Sp}^{\bullet} \longrightarrow \text{D-Sp-X} + \text{D-Sp}^{-}$ (h)

${}^{\bullet -}\text{D-Sp-X} + \text{D-Sp}^{\bullet} \longrightarrow \text{coupling product}$ (i)

for $v > 0.2$ V s^{-1}. Some reversibility is detectable also for compounds **1d** and **1c** when v is increased to ca. 10 and 200 V s^{-1}, respectively, whereas the lifetimes of the radical anions of **1a** and **1b** is too short relative to our experimental time window. By using sufficiently high scan rates, the $E°$ of **1f**, **1e**, and **1d** were thus calculated to be −1.60, −1.66, and −1.92 V, respectively, and that of **1c** estimated to be ca. −2.08 V. In line with the above conclusions, these values are equal to the $E°$ values of **2** and **3** (Table 1), within experimental error. Peak current measurements showed that the apparent number of electrons characterizing the irreversible reduction of **1a**−**d** is greater than 1.5 at low scan rate and tends to 2 upon increasing v. This was verified by comparison of the irreversible peaks with the reversible peaks of **2a**−**d**. Only the peaks of compound **1f** and **1e** correspond to a one-electron process, at relatively low scan rates. Further information on the overall process was gained by multiscan voltammetry experiments, in which the disappearance of the irreversible reduction peak and the appearance of a well-defined steady voltammogram was observed (for example, see Figure 6). The resulting reversible peak is due to the reduction of the product accumulating near the electrode, in the diffusion layer, and is coincident to that of an authentic sample of **3**. Although the above experiments were carried out in DMF by using a glassy carbon electrode, which is known to provide an inert electrode surface for halogen-containing substrates, we observed a similar voltammetric behavior (compound **1a**) either by using a mercury electrode, provided that v was higher than 2 V s^{-1}, or in acetonitrile. Also, in both DMF and acetonitrile, the addition of either a weak acid, such as *N*-benzylisobutyramide or formanilide ($\text{p}K_a^{\text{DMF}} = 25.8$ and 20.3, respectively[38]), or an H-atom donor (2-propanol, 60 equiv) did not change significantly the voltammetric pattern.

The voltammetric behavior can be interpreted by the mechanism shown in Scheme 1. The first step involves the reduction of the benzoate moiety (reaction a). In fact, although the direct reduction of the alkyl bromide is more facile on a thermodynamic ground, it suffers a large activation overpotential. The electron is then transferred dissociatively to the accepting bromide function in a second step (reaction b = eq 6), with a k_{ET} value that is a function of the reducing power of the

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[38] Maran, F.; Celadon, D.; Severin, M. G.; Vianello, E. *J. Am. Chem. Soc.* **1991**, *113*, 9320.

benzoate, i.e., **1a** > **1b** > **1c** > **1d** > **1e** > **1f**. Therefore, the benzoate function acts as an ET antenna shuttling the electron from the electrode to the bromide in the same way, though now intramolecularly, as in the above intermolecular reactions. Once the intramolecular ET takes place, the radical formed can accept an electron from the electrode, the benzoate moiety acting again as the antenna (reaction c). This is in fact the most likely heterogeneous pathway because, although the $E°$ for the reduction of a tertiary carbon radical is per se not very negative (its value can be bracketed between −1.5 and −1.8 V),[39,40] it has been shown that the direct reduction of alkyl radicals is controlled by a significant activation overpotential (the direct reduction of the *tert*-butyl radical takes place at ca. −2.6 V).[39] As a result, the electrode reduction tends to become a two-electron process, provided k_{ET} is large enough. A second intramolecular ET then takes place (reaction d), and the ensuing carbanion is protonated to form **3**, which is the species to which the reversible component of the cyclic voltammetry curves can be assigned (reactions e−f). This sequence for the direct reduction is paralleled by intermolecular reactions in which the radical anions of **1** and **3** can act as electron donors toward **1** (reactions g, X = Br or H). The second electrode reduction (reaction c) has no direct homogeneous counterpart. However, the ET and coupling reactions between D−Sp$^•$ and the radical anions of **1** and **3** must be considered (reactions h and i, X = Br or H), in analogy to that found in mediated ET processes.[15,36] The protonation of the carbanion (reaction e) is probably by a parent molecule undergoing a 1,2-elimination to form a cyclohexene derivative (self-protonation mechanism). This reaction might be the origin of the scan rate dependence of the apparent number of exchanged electrons.[41] Hydrogen atom abstraction by D−Sp$^•$ can be regarded as negligible in the overall electrode process because no appreciable effects were brought about on the cyclic voltammetry by addition of a good H-atom donor (2-propanol) or by changing DMF with acetonitrile (a poorer H-atom donor than DMF).

Kinetic analysis of the reduction peaks of compounds **1** was carried out along similar lines as recently described for the similar mechanisms occurring in the electroreduction of a-substituted acetophenones.[5d,e,6] In general, except for those compounds where it is possible to outrun the intramolecular ET by increasing the scan rate until reversible behavior is reached, the knowledge of the $E°$ corresponding to the initial heterogeneous ET often requires assumptions and estimates. Whereas this holds, e.g., for many α-substituted acetophenones,[5d,e,6] the accepting bromide in compounds **1** is located at an appreciable distance from the ET antenna that the $E°$ values of donor and acceptor are not coupled. In fact, we observed that the $E°$ of the corresponding **1**, **3** (equations a,f) and **2** are equal (Table 1), leading us to use the same value also for the reduction of the donor side of D−Sp$^•$ (Scheme 1, equation c). The same holds for $k°$, which is insensitive of the remote substitution at the cyclohexyl spacer, although it depends to some extent on the substituent on the aryl group (Table 1).

Table 3. Rate-Driving Force Data for the Intramolecular Dissociative ET in Compounds **1** in DMF at 25 °C

D−Sp−Br	$E°_{D/D^{•-}}$ (V)	$\Delta G°$ (eV)	log k_{ET} (s^{-1})
1a	−2.27	−1.21	5.5
1b	−2.15	−1.09	4.7
1c	−2.09	−1.03	3.8
1d	−1.91	−0.85	2.4
1e	−1.66	−0.60	0.3
1f	−1.61	−0.55	−0.2

The reduction of compounds undergoing relatively fast follow-up reactions and characterized by not very high $k°$ values is known to be to a large extent under mixed kinetic control by the heterogeneous ET and the follow-up chemical reaction.[6b,28,42,43] Under these circumstances, $\Delta E_{p/2}$ and $E_p - E°$ constitute the parameters of choice to determine the rate constant of the chemical step (e.g., k_{ET}). Also, of great help to the analysis is the knowledge of both $E°$ and $k°$, as it is for the compounds here investigated. Therefore, the scan rate dependence of $\Delta E_{p/2}$ and $E_p - E°$ was used to obtain k_{ET} values for compounds **1a**−**c**. The analysis was accomplished by fitting working curves, obtained from tabulated data[28] using k_{ET} as a parameter and $E°$ and $k°$ as the known inputs, to the experimental data. The effect of the reversible peak following the main reduction peak was taken into account (the presence of the second peak causes the first peak potential to be slightly more negative than in its absence), and thus, more weight was given to the data points obtained at the lowest scan rates, where the peak separation is larger. Since the use of tabulated data[28] involves a simplification of the mechanism of Scheme 1, the k_{ET} results were checked by simulation (DigiSim 2.1) of the cyclic voltammetry curves. However, no relevant differences were obtained. Finally, by simulation, it was possible to determine the k_{ET} value of **1d**−**f** and to have an idea of the relative contribution of the intermolecular reactions corresponding to the above scheme. Table 3 shows the final results of the voltammetric analysis. Because of the complexity of the analysis, the error in log k_{ET} depends on the actual experimental case, as indicated by the error bars in the semilogarithmic plot of Figure 7. In particular, the error reduces to ca. ±0.15 when either the two peaks are sufficiently separated (**1a**) or the radical anions are relatively stable (**1e** and **1f**).

Comparison of Tables 2 and 3 shows that, at a given concentration (voltammetric experiments were run with 1−2 mM substrate concentrations), the intermolecular ET rates are slower than the corresponding intramolecular rates by at least 2 orders of magnitude. During the voltammetric scan, however, the concentrations of substrate and electrogenerated species change in the layer adjacent to the electrode surface.[26] While the concentration of DSpBr decreases, that of DSpH builds up. Simulation of the mechanism of Scheme 1 indicates that when the concentration of DSpBr in the reaction layer is low enough relative to that of DSpH and for potentials more negative than E_p, the effect of the intermolecular reactions becomes evident. Also, it results that the intermolecular reactions of the DSpBr radical anion are less important than those of the DSpH radical anion. Although the intermolecular reactions have no relevant

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[39] Andrieux, C. P.; Gallardo, I.; Savéant, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 1620.

[40] Occhialini, D.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1990**, *44*, 715.

[41] (a) Maran, F.; Vianello, E.; D'Angeli, F.; Cavicchioni, G.; Vecchiati, G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 33. (b) Maran, F.; Roffia, S.; Severin, M. G.; Vianello, E. *Electrochim. Acta* **1990**, *35*, 81. (c) By acting as a proton donor, part of the starting material is transformed into a species that is not reducible at the working potentials. Accordingly, the number of exchanged electrons is less than expected. An increase of v tends to outrun the effect of self-protonation reactions. We are currently investigating the relevance of this reaction and of radical coupling reactions in the overall process.[24.]

[42] Evans, D. H. *J. Phys. Chem.* **1972**, *76*, 1160.

[43] When an electrode process is affected by a follow-up reaction, the two limiting cases are when the heterogeneous ET is in equilibrium (nernstian ET) and the follow-up reaction is the rate-determining step or when the kinetic control is by the heterogeneous charge transfer.[28, 42] For example, $\partial E_p/\partial \log v$ varies form 29.6 mV/log v to 59.1 mV/log v (25 °C, $\alpha = 0.5$) when the system passes from the former to the latter kinetic control. In the intermediate situation (ca. 6 orders of magnitude in v), a nonlinear peak potential shift connects the two limiting zones.

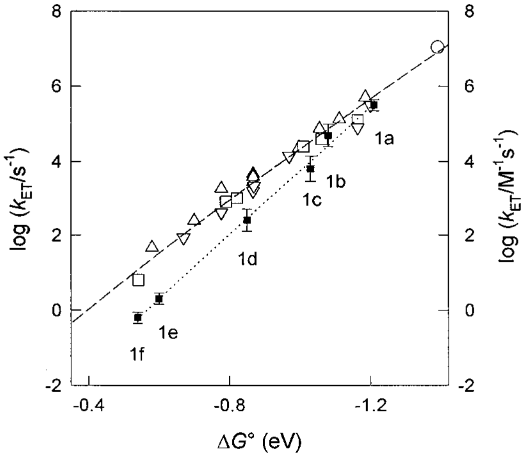

Figure 7. Plot of the logarithm of the first-order intramolecular (■) and the second-order intermolecular (□), this work; △, ref 13a,b; ▽, ref 13c; ○, ref 13d) ET rate constants for the reduction of tertiary bromides against the reaction free energy. For the sake of better comparison, the free energy window has been restricted to ca. 1.1 eV. The dashed line is that obtained by nonlinear least-squares fitting of the intermolecular data; the dotted line is the linear fitting of the intramolecular data.

influence on either $\Delta E_{p/2}$ or $E_p - E°$, they affect markedly the shape of the cyclic voltammetry past the reduction peak, in particular during the backward scan.[24]

Activation−Free Energy Relationships. Figure 7 shows the intermolecular and intramolecular dissociative ET rate constants as a function of the driving force; for the sake of comparison, the literature data pertaining to the homogeneous reduction of *t*-BuBr[13] are also shown. Two aspects are worth noting in Figure 7. First, there is no difference, within error, between the activation driving force relationships describing the reduction of the tertiary bromide **4** and that of *t*-BuBr. This is in agreement with a common $E°$ for these tertiary bromides and with similar preexponential factors and sensitivities on $\Delta G°$ variations. On the other hand, the second outcome is that the inter- and the intramolecular kinetic results display different sensitivities to the driving force, as illustrated by the independent fittings we carried out on the two series of experimental values. It is not our intent to discuss the difference between the intra- and the intermolecular log k_{et} data; in fact, in addition to the distance effect, the pertinent frequency factors are expected to play a role in determining such a difference. We wish to focus here on the intriguing difference between the *local slopes* of the two semilogarithmic plots. In this context, a point that should be stressed is the remarkable consistency of the intermolecular data shown in Figure 7 although the intermolecular ET is the result of random distance and orientation distributions between donors and acceptor. On the other hand, for the intramolecular ET data the distance factor is controlled in well-defined way, and therefore, by comparison, there are good reasons to believe that the trend of the resulting log $k_{ET} - \Delta G°$ contains elements of particular interest.

The best way to compare the data is via the corresponding values of the ET coefficient α (eq 4). Concerning the intermolecular data, α values in the range of 0.38−0.41 can be calculated by assuming either a linear[13d,37] or a quadratic[4,44] log $k_{ET} - \Delta G°$ relationship. These α values are in agreement with exergonic dissociative ETs, as discussed on many occasions.[3,4,10,13−15,37] Instead, a value for α of 0.51 is obtained by linear regression of the intramolecular data, a result which would be expected only if $\Delta G° \approx 0$ (see eq 4), i.e., at a driving force significantly smaller than those in the investigated range (0.5−1.2 eV). As a first hypothesis, the reasons for such a difference may come from the definition of α (eq 4); an intrinsic barrier for the intramolecular ET much larger than that pertaining to the intermolecular process could indeed account for the above difference between the α values. In particular, because of the compounds considered, differences in $\Delta G_0^{\#}$ must be related essentially to differences in the solvent reorganization energies; a bond energy of 66 kcal mol^{-1} [4b] can be used as a common value for the C−Br bond of the above tertiary bromides.[16,32] It is known that the solvent (or outer) reorganization energy (λ_o), is a function of the donor−acceptor distance.[45,46] Equation 8 can be used to evaluate the λ_o values of both the intermolecular ET, at van der Waals contact in the solvent cage, and the intramolecular ET within the radical anion of **1**, where donor and acceptor further separated by the spacer. In eq 8, N_A is

$$\lambda_o = \frac{N_A e^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{DA}}\right) \qquad (8)$$

Avogadro's number, e is the charge of the electron, ϵ_0 is the permittivity of vacuum, ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent, r_D and r_A are the radii of the donor and the acceptor (assumed as spherical), and R_{DA} is the distance between their centers; R_{DA} is equal to $r_D + r_A$, for the intermolecular ET, or to $r_D + r_A + r_{Sp}$, for the intramolecular ET, where r_{Sp} is the edge-to-edge distance of the spacer (3.88 Å, for 1,4-cyclohexanedyil). For DMF and considering radii of the donors in the 3.6−3.9 Å range and an effective radius of the acceptor of 2.83 Å,[4b] λ_o can be estimated to be 24−25 and 32−33 kcal mol^{-1} for the inter- and intramolecular processes, respectively. Equation 8, however, tends to overestimate λ_o,[47,48] and the distance-independent term in the right-hand side of eq 8 should be adjusted according to experimental data.[47] An alternative and probably[4b] better way to estimate λ_o is to make use of a correlation based on self-exchange data in DMF.[48] This procedure leads to values of λ_o of ca. 15 and 20−21 kcal mol^{-1} for the inter- and intramolecular processes, respectively. Whichever way is adopted to calculate λ_o, the presence of the spacer causes the intramolecular λ_o to increase by 30−40% relative to the intermolecular values while the intrinsic barrier increases by no more than 10%. This is not as much as would be required to obtain $\alpha \approx 0.5$, within error, at the negative $\Delta G°$ explored: In fact, even if one uses the largest of the intramolecular λ_o estimates, for the investigated range of driving forces (0.5−1.2 eV) an α increase of only 0.01 would be expected as a consequence of the presence of the spacer.

These arguments may lead to the attractive hypothesis that the observed intramolecular α value is actually the result of an increase of the *effective* distance between the two redox sites on going progressively along the series from **1a** to **1f**. This hypothesis derives from the following considerations. The intramolecular dissociative ET consists of the transfer of one electron from the π^* orbital of the donor to the σ^* orbital localized on the acceptor side of the D−Sp−A molecule. While the latter is kept constant along the investigated series, the orbital

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[44] α was calculated by the derivative of both the quadratic fit to the experimental data and the parabola deriving from the theoretical treatment,[4] both derivatives being calculated at the midpoint of the explored $\Delta G°$ range.

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initially occupied by the unpaired electron strongly depends on the substitution on the aryl group. A less negative $E°$ is also associated with a shift of the center of the π^* orbital of the donor away from the acceptor and is predictable if we go from, e.g., **1a** to **1f** and consider the effect of the electron-withdrawing competition between CN and COOR in the latter. This is also supported by the decrease of the sensitivity of the benzoate $E°$ on the alkyl substituent at oxygen on going from **1a** to **1f** (Table 1). The shift can be detectable only in the intramolecular ET, because of the geometric constrains of the D−Sp−A framework. According to the apparent value of α (or by comparison with the plot of the intermolecular data), it appears that the k_{ET} value pertaining to **1f** is lower than expected on the basis of the value of **1a** and of a "normal" α value by about 1 order of magnitude. Taking into account the exponential decrease of the coupling energy between the electronic wave functions of donor and acceptor with the distance, the activated process ET rate constant k_{ET} can be described in a classical form by eq 9[49]

$$k_{ET} = \nu_n \kappa_{el} \exp[-\beta(r - r_0)] \exp\left(-\frac{\Delta G^{\#}}{RT}\right) \qquad (9)$$

where ν_n is the effective frequency for motion along the reaction coordinate, κ_{el} is the electron transmission coefficient at the van der Waals separation r_0 between the donor and acceptor centers, r is the actual distance at which ET takes place, and β is the exponential decay parameter. The second exponential is distance dependent through the link between $\Delta G^{\#}$ and the intrinsic barrier (eq 3) and thus λ_o.[16] A simple calculation can be carried out through eq 9 by using β values in the range 0.8−1.2 Å^{-1}, as found with several non dissociative-type systems.[1a,47,50] Accordingly, a rate drop of ca. 80−90% is accounted for by an increase of, e.g., 1.4 Å (half the distance of a benzene ring) in the effective distance between the two centers exchanging the electron, an increase that is not unlikely on the basis of the electron-withdrawing properties of the *p*-cyano group in **1f**. The rate drop is mainly due (60−80%) to the effect of λ_o on the nuclear factor, through $\Delta G_0^{\#}$.[51,53]

Conclusions

The reduction of the compounds **1** has been investigated by electrochemical methods to obtain information on the distance effect in dissociative ETs within well-defined D−Sp−A molecular systems. To define the reaction free energy of the intramolecular dissociative ET from benzoate radical anions to the tertiary bromide acceptor group, the standard potential for the reduction of the bromide has been estimated by convolution analysis. The $E°$ was found to be about −1.06 V, in very good agreement with literature thermochemical calculations pertaining to *tert*-butyl bromide. The standard potential for the reduction of the benzoate-type function to the corresponding radical anion was easily determined by cyclic voltammetry and shown to be independent of the substitution at the other side of the spacer. This led to a free-energy picture more easily defined than in previous investigations on intramolecular dissociative ETs. The rate constants for the intramolecular ET between the donors and the tertiary bromide moieties have been determined by cyclic voltammetry analysis for an overall variation of the free energy of ca. 0.7 eV. The analogous intermolecular ETs have been determined by homogeneous redox catalysis and found to be indistinguishable from the available literature data on the reduction of *tert*-butyl bromide.

The comparison of the intramolecular and the intermolecular kinetic data reveals that for the latter ETs the transfer coefficient α is distinctly smaller than 0.5 (namely, 0.38−0.41), as expected for such exergonic processes (comparison is made for driving forces of 0.5−1.2 eV), and the intramolecular rates are significantly more sensitive to driving force changes. The intramolecular α value is 0.51, although such a value would be expected at $\Delta G° \approx 0$. The experimental outcome can be explained by considering that the effective distance at which the intramolecular ET takes place changes in the D−Sp−A series when the driving force is varied. An increase of the effective distance when the reaction becomes less exergonic is accounted for by a shift of the π^* orbital away from the acceptor. As a consequence, the intramolecular ET rate is also decreased. Simple calculations aimed to evaluate the rate drop expected for an increase of the effective distance at which the ET takes place, in comparison with the experimental results, support this hypothesis.

Even though a quantitative understanding of this problem requires further experimental and theoretical work, the significance of these intramolecular results would be useful in a more detailed interpretation of the distance effect on ETs. This is particularly true when relatively short spacers are considered and thus when differences in the shape of the donor orbital are significant compared with the spacer length. This is consistent with the fact that previous kinetic studies, aimed to determine the activation driving force relationships of (stable) D−Sp−A systems (in which the spacer was kept constant), could not reveal the secondary distance effect suggested here most likely because of the length of the spacer and, also, the very large driving force increments considered.[1a]

Our data do not provide an answer to the problem[14,15] of the shape of the activation driving force relationship describing the dissociative ET to alkyl halides. However, the observed linear dependence of the intramolecular rates on $\Delta G°$ can be explained (mostly) on the basis of the effect of λ_o on $\Delta G^{\#}$, using the quadratic relationship of eq 3. An interesting aspect is that the ET mechanism proposed here involves the concept that an intramolecular ET system contains useful features that can be revealed thanks to a more controlled molecular framework. At the same time this may lead to anomalous driving force

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(51) The adiabaticity degree of the ET is expected to have a role in this framework. For example, if the intramolecular dissociative ET process is best described as nonadiabatic ($\kappa_{el} \ll 1$), the preexponential factor becomes a function of both λ_o and the elongation of the C−Br bond at the transition state.[52] On the other hand, if the dissociative ET is adiabatic ($\kappa_{el} \approx 1$), the preexponential factor might be determined by solvent relaxation in a similar way as in nondissociative ETs (for example, see: Bixon, M.; Jortner, J. *Chem. Phys.* **1993**, *176*, 467) and thus, again, might depend on λ_o, although in a different way. At this stage, it is impossible to settle this issue for the investigated reactions, and in fact, there is no doubt that in general the problem of adiabaticity vs nonadiabaticity in dissociative ETs awaits further investigation. Some research in this direction is currently underway with dialkyl peroxides.[10b.]

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(53) Interesting improvements of the adiabatic dissociative ET are underway (Andrieux, C. P.; Savéant, J.-M.; Tardy, C. *J. Am. Chem. Soc.* **1998**, *120*, 4167; we are grateful to Prof. Savéant for providing us an advanced copy of the manuscript). One of them is that λ_o is described as dependent on the stretching of the breaking bond at the transition state. In particular, λ_o would increase when the driving force is decreased (the transition state is now relatively more product-like), with the consequence that k_{ET} decreases more rapidly than expected. However, this is common to both the inter- and the intramolecular ETs and thus cannot be considered as a relevant factor in determining the difference between the observed α values.

dependencies (in a not too large $\Delta G°$ range) relative to intermolecular ETs, where random distance and orientation distributions in the encounter complex yield an average ET rate constant. We are now exploring different D-Sp-A systems in order to verify these conclusions together with other aspects of the intramolecular dissociative ET in well-defined molecular systems. At this stage, however, it is relevant to add that preliminary experiments carried out with the trans isomers of **1** led to an experimental sensitivity to driving force analogous to that described above, although the rates are significantly different.[24]

Acknowledgment. Dedicated to Prof. Ferruccio D'Angeli on the occasion of his retirement. This work was financially supported by the Consiglio Nazionale delle Ricerche (CNR) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST).

JA9741180