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Electron-Transfer Bond-Breaking Processes. An Example of Nonlinear Activation–Driving Force Relationship in the Reductive Cleavage of the Carbon–Sulfur Bond

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The heterogeneous (electrode) and homogeneous electron transfer (ET) to triphenylmethyl *p*-cyanophenyl sulfide in *N,N'*-dimethylformamide is shown to involve the irreversible reductive cleavage of the C_{alkyl}–S σ-bond through a sequential charge-transfer/bond-breaking pathway. The intermediate formation of the sulfide anion radical, whose lifetime has been determined to be ca. 10 ns, evidences the outer-sphere nature of the initial ET. The kinetics of this step has been analyzed as a function of the reaction free energy. Heterogeneous rate constants have been determined as a function of the applied potential from voltammetric curves and their convolution. The kinetics of the homogeneous ET from a series of substituted azobenzene anion radicals has been investigated by voltammetric redox catalysis. Both the homogeneous and the heterogeneous reactions show a quadratic dependence of the activation free energy on the driving force. The rate constant data have been treated in terms of classical ET theories in order to obtain the corresponding thermodynamic and kinetic parameters. Noteworthy, the values of the standard potential for the sulfide/sulfide anion radical redox couple, derived in the treatment of the two independent sets of homogeneous and heterogeneous data, are practically coincident. Structural parameters, from semiempirical MO calculations on azobenzene and its anion radical have been used to evaluate the azobenzene contribution to the cross ET activation energy and consequently to estimate, by comparison with the experimental results, the electron-exchange activation energy for the sulfide. The transition from the neutral sulfide to its anion radical involves relevant variations of the internal coordinates, in agreement with the very fast anion radical fragmentation.

Introduction

The widespread interest for electron-transfer (ET) reactions has been greatly supported by the availability of several theoretical models,[1-4] ranging from relatively simple to more refined ones, which help to interpret experimental results at a molecular level. In this framework, electron exchange reactions ($\Delta G^\circ = 0$) are the most suitable to study the interplay between theory and experiment.[5] From a chemical point of view, however, reactions characterized by a net driving force ($\Delta G^\circ \neq 0$) are much more relevant to establish a link between kinetic and thermodynamic parameters.[6] In this regard, a quadratic dependence of the activation free energy on the reaction driving force for an outer sphere ET was derived since the early classical Marcus models[7,8] and generally confirmed by semiclassical and quantum mechanical treatments as well as by molecular dynamics calculations.[9] In bimolecular homogeneous ET reactions, the activation–driving force relationship was experimentally studied using families of compounds characterized by similar intrinsic parameters but with different standard potentials, as ET reagents toward a single acceptor or donor.[10] In heterogeneous electrode reactions, the variation of the reaction free energy for a single reactant can be simply achieved by varying the applied electrode potential. Therefore the electrochemical approach appears to be the best way for investigating kinetic–thermodynamic relationships. Actually, examples of quadratic variation have been reported in relatively few cases,[11-13] while linear activation-driving force relations such as the Butler–Volmer equation are generally assumed.

Tests on free energy relationships are possible also when the ET reactions are coupled with fast chemical steps. However, when the overall process is controlled by the ET kinetics, the instability of one of the products usually prevents the knowledge of the absolute ET driving force and therefore of the intrinsic kinetic parameters. A typical example of these irreversible processes is the inducement of a σ bond cleavage owing to the gain or loss of one electron by a substrate. Extensively studied is the one-electron addition to organic halides[13-16] where significant stability differences among the ensuing anion radicals are met, depending on the molecular structure. In some cases, for instance with alkyl,[13a,16b,d] benzyl,[16c,e] or fluorenyl[14b,16a] halides, the breaking of the bond is even concerted with the electron uptake. The theories developed for outer-sphere reactions, involving no bond formation or cleavage, cannot strictly be applied to such a dissociative ET. However, a treatment based on a Morse-like dependence of the potential energy upon the distance of the bond to be broken showed the validity of a similar quadratic activation–driving force relationship also in the case of dissociative ET.[17]

Similar problems are encountered in the reductive cleavage of other σ bonds. In particular, we have been investigating the role of structural effects on the reactivity towards the electron addition and the C–S bond cleavage, in asymmetric alkyl aryl sulfides, R_3CSPhX (R = H, Ph).[18,19] The systems previously investigated (X = H, NO_2) allowed us to clarify the key steps involved in the overall two-electron reduction. It was shown that the cleavage takes place at the level of the first ET and involves the alkyl C–S bond, giving rise to a thiophenoxide ion and an alkyl radical, followed by the reduction of the latter. When $R_3C^\bullet = Ph_3C^\bullet$, the reversible ET to the radical to form the anion was directly observed during a voltammetric scan[19b,c] so that its reduction parameters are unambiguously characterized in our reaction medium. The ET bond-breaking process is greatly different for X = H or NO_2 from both a thermodynamic and a kinetic point of view. Actually, whereas the behavior of the NO_2-substituted sulfides is characterized by a fast heterogeneous ET, the reductive cleavage of organic sulfides is usually controlled by the kinetics of the first ET.

We report in this paper the results of the irreversible heterogeneous and homogeneous ET to $Ph_3CSPhCN$ in *N,N'*-dimethylformamide (DMF). A triphenylmethyl derivative was

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selected both because the thermodynamics of the second ET was previously characterized (as noted above), and because the C–S reductive cleavage was shown to be the least complicated by side reactions. While the overall behavior of the sulfide can be considered as representative of an irreversible reductive cleavage, accurate measurements and favorable characteristics of the molecule allowed us to study in detail both the homogeneous and the heterogeneous ET reactions. In particular the results pointed to a clean quadratic dependence of the activation free energy on the reaction free energy, as predicted by current ET theories. Simple formulations of the latter were used to derive kinetic and thermodynamic information and to interpret the reactivity behavior on the basis of the structural features of the molecule.

Experimental Section

Samples. $Ph_3CSPhCN$ was synthesized from triphenylmethanol and *p*-cyanothiophenol in acetic acid with H_2SO_4, as previously described for other diphenylmethyl- and (triphenylmethyl)aryl sulfides.[18,19] It was recrystallized from ethanol; mp 162–162.5 °C. Elemental analysis (calculated/found): C 82.71/81.93; H 5.07/5.18; N 3.61/3.75; S 8.49/8.54. IR: band at 2200 cm^{-1} (CN).

p-Cyanothiophenol was obtained from *p*-cyanophenol through the intermediate *O*-(4-cyanophenyl)-*N*,*N*-dimethylthiocarbamate.[20]

N-Cyclohexyl isobutyramide, used as protonating agent, was kindly provided by Prof. F. D'Angeli.

Azobenzene (C. Erba) was recrystallized from 95% ethanol. 4,4′-Dimethoxyazobenzene was prepared from 4-methoxyaniline through the diazonium salt[21] and recrystallized from methanol and then from ether/*n*-pentane; mp 166–167 °C. 4-Methoxy-, 3,3′-dimethoxy-, and 4-methoxy-4′-ethoxyazobenzene were obtained by alkylation with dimethyl (diethyl) sulfate of the corresponding hydroxyazobenzenes, according to the method described for the former compound.[22] The required hydroxy azocompounds, in turn, were prepared as reported for 4-hydroxyazobenzene;[23] 3,3′-dihydroxyazobenzene was obtained from *m*-nitrophenol.[24] Melting points of the final products were as follows: 4-methoxyazobenzene, 56–57 °C (lit.[22] 56 °C) from petroleum ether (40–70 °C); 3,3′-dimethoxyazobenzene, 76–77 °C from *n*-hexane; 4-methoxy-4′-ethoxyazobenzene, 120–121 °C from ethanol.

3,3′-Dimethylazobenzene was prepared from *m*-nitrotoluene:[25] mp 55–56 °C (lit. 51 °C) from ethanol. 4-Methylazobenzene was obtained by condensation of 4-methylaniline and nitrobenzene;[26] it was purified by filtering a solution in *n*-hexane/ethyl ether through silica gel and then recrystallized from ethanol; mp 71–72 °C.

The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was prepared as previously reported.[27] *N*,*N*′-Dimethylformamide (DMF) was twice distilled at reduced pressure and stored under Ar. Bubbling of Ar was also used to deoxygenate the working solution.

Apparatus and Procedures. The working, reference, and counter electrodes used for the electrochemical measurements and their preparation and the procedures for activating the working electrodes and for determining their surface area were as previously reported.[18a] The potentials were measured against the reference redox system bis(biphenyl)chromium(I) tetraphenylborate (BBCr),[28] kindly provided by Prof. G. Gritzner. The potential of BBCr vs SCE (–0.626 ± 0.002 V) was checked after each experiment. All potentials are reported versus SCE.

HPLC analyses were performed with the same instrumentation, column, and solvents as previously described,[18c] only with a slightly different (60–100% CH_3CN) concentration gradient. An EG&G apparatus based on the 273 potentiostat was used for all electrochemical measurements.[18c] Ohmic drop losses between working and reference electrodes were compensated for with the positive feedback circuit built in the potentiostat. Voltammetric measurements performed on anthracene solutions, using the same experimental setup and in conditions otherwise identical to those utilized in the experiments with the investigated sulfide, have shown the behavior typical of a reversible process ($E_p^a - E_p^c = 59$ mV, E_p^c = const) thus confirming the correctness of the IR compensation.

The Nicolet 3091 oscilloscope used for electrochemical measurements was connected through a serial port to a PC (Olivetti, M24). The data were transferred from the oscilloscope to the computer by means of the Nicolet software. Subtraction of background current was usually made on the PC stored experimental curves.

Electrolyses and Product Analyses. Exhaustive controlled potential electrolyses were performed on DMF solutions of sulfide ($(5–7) \times 10^{-3}$ M) in the presence of *N*-cyclohexyl isobutyramide (4:1 ratio) at –1.7 V on a Hg pool electrode. Coulometric yields corresponding to 1.8 e/molecule were obtained. The electrolyzed solutions were acidified and analyzed by HPLC to establish the product yield and distribution. The sulfide was almost completely converted to triphenylmethane (84%) and *p*-cyanothiophenol (90%), only a small fraction of it (6%) suffering the hydrolysis of the CN group to give $Ph_3CSPhCONH_2$. The product yield and distribution were also determined for the homogeneous reaction between the sulfide and the azobenzene anion radical. The reaction was carried out by reducing azobenzene ($(5–6) \times 10^{-3}$ M, –1.35 V) on a Pt gauze electrode, in the presence of an excess of sulfide (2:1) and isobutyramide (8:1). The reduction was stopped after the supply of 1.1 electron per sulfide molecule. HPLC analysis on the acidified solutions shows the formation of 54% of both triphenylmethane and *p*-CN thiophenol, together with a 3% of the hydrolysis product. 40% of unreacted sulfide was recovered.

Computational Details. Elaboration of the computer stored voltammetric data were performed with a purposely written Basic program, running on a PC Olivetti M400.

Convolution of current/potential (time) curves,[29] obtained on a Hg microelectrode, with the time function characteristic of linear diffusion, $(t - \tau)^{-1/2}$, does not result in a plateau limiting value in the diffusion-controlled region. Instead, the linearly increasing trend expected when sphericity effects are involved was observed. The convolution was therefore performed with the time function characteristic of diffusion to and from a spherical electrode[30] which can be easily derived by application of Laplace transform to the diffusion equations:

$$I(t) = \frac{1}{\pi^{1/2}}\int_0^t \frac{i(\tau)\,d\tau}{(t-\tau)^{1/2}} - \phi\int_0^t i(\tau)\exp[\phi^2(t-\tau)] \times \operatorname{erfc}\,[\phi(t-\tau)^{1/2}]\,d\tau \quad (1)$$

were $\phi = D^{1/2}/r_0$ is the sphericity parameter (r_0 is the electrode radius, D is the diffusion coefficient) and erfc (z) is the complementary error function. Theoretical calculations for a system controlled by a slow charge transfer, with reasonable values of the pertinent parameters, showed that the convolution curve (1) should reach a limiting (plateau) value for i data taken at potentials ~0.25 V more negative than the peak potential. Therefore the sphericity parameter and the convolution limiting value, I_l, were determined, for each voltammetric curve, as those giving a constant convolution value (in the least square sense over 100 points minimum) for data at potentials ≤–0.25 V from the peak.

Other calculations were made with Fortran programs running on a VAX 4000 computer (DEC). In particular, the theoretical analysis of the homogeneous redox catalysis was performed on the basis of the equations derived by Savéant and co-workers,[31] slightly modified to keep into account the different values of the diffusion coefficients of the two species involved. The partial derivative equations were solved by an implicit finite difference procedure,[32] with a second-order approximation for the flux and an exponentially expanding space grid.

Molecular orbital calculations at the semiempirical level were performed with a revised version of MOPAC.[33]

Results and Discussion

Electrode Reduction. The voltammetric reduction of $\mathrm{Ph_3CSPhCN}$ at both Hg and glassy carbon (GC) electrodes gives rise to a single irreversible peak at rather negative potentials (E_p = −1.680 V on a Hg electrode and −1.725 V on GCE, at the sweep rate v = 0.2 V s^{-1}). Exhaustive controlled-potential electrolyses of sulfide solutions at −1.7 V yields triphenylmethane and *p*-cyanothiophenol as the products with the consumption of ca. 2 e/molecule (see Experimental Section), in line with a two-electron reductive cleavage of the C–S bond,[18,19,34] involving the following steps:[35]

$$\mathrm{Ph_3CSPhCN} + e \overset{E^\circ_S, k^\circ_{het}}{\rightleftarrows} \mathrm{Ph_3CSPhCN^{\bullet -}} \tag{2}$$

$$\mathrm{Ph_3CSPhCN^{\bullet -}} \xrightarrow{k_2} \mathrm{Ph_3C^{\bullet}} + \mathrm{SPhCN^-} \tag{3}$$

$$\mathrm{Ph_3C^{\bullet}} + e \overset{E^\circ_R}{\rightleftarrows} \mathrm{Ph_3C^-} \tag{4}$$

$$\mathrm{Ph_3C^-} + \mathrm{H^+} \rightarrow \mathrm{Ph_3CH} \tag{5}$$

The linear variation of the voltammetric peak potential E_p with the logarithm of sweep rate, on both Hg and GC electrodes, and the rather high values of the pertinent slopes (∼52 and ∼64 mV/log v for the Hg and GC, respectively) suggest that the electrode process is controlled by the first electron addition, with transfer coefficients $\bar{\alpha}$ = 0.57 on Hg and $\bar{\alpha}$ = 0.46 on GC. However, a scrutiny of the voltammetric data shows that the peak current, normalized with respect to the sweep rate, decreases on rising v. Also the shape of the peak, measured by the half-peak width $E_{p/2} - E_p$, is sweep rate dependent, an increase being observed on rising v. Such an outcome[36] is not consistent with the behavior expected for a slow charge transfer described by the Butler–Volmer rate law,[37] according to which the above parameters should be independent of v. Since the reduction curve is shifted toward more negative potentials by increasing the sweep rate, the behavior that we observed points to a potential dependence of the transfer coefficient.[12]

With the assumption that the first ET is the rate-determining step of the process and that the backward ET reaction can be neglected, which is justified by the fast follow-up decay of the ET product (vide infra), the voltammetric data obtained on Hg were analyzed on the basis of the kinetic law for an elementary irreversible electrode reaction. In other words the rate, i.e., the current, $i(E)$, is expressed as the product of the electrode concentration of the substrate, times a potential-dependent constant, $k_{het}(E)$. Under the conditions of diffusional mass transport, the concentration at the electrode was conveniently obtained by the method of convolution voltammetry. This allowed us to avoid any hypothesis on the actual k_{het}/E functional relationship. The experimental values of the heterogeneous rate constant at different applied potentials were derived from the individual voltammetric i–E curves at different sweep rates according to[11a]

$$\frac{RT}{F}\ln\frac{k_{het}(E)}{D_S^{1/2}} = \frac{RT}{F}\ln\frac{i(E)}{I_l - I(E)} \tag{6}$$

where D_S is the sulfide diffusion coefficient, and $I(E)$ and I_l are the convoluted current and its limiting plateau value, respectively.

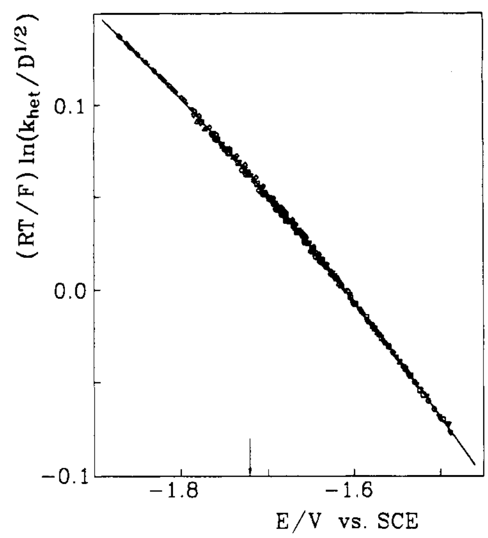

Figure 1. Heterogeneous ET to $\mathrm{Ph_3CSPhCN}$ at a Hg electrode in DMF + 0.1 M TBAP. Variation of the heterogeneous ET rate constant with the applied potential, from the spherical convolution of the voltammetric curves (see text). C_S = 2.5 × 10^{-3} M; T = 25.0 °C. v (V s^{-1}): (▽) 0.5; (○) 1.0; (□) 2.0; (△) 5.0; (▼) 10; (◇) 20. The solid line is the best fitting according to the quadratic eq 7. The arrow indicates the sulfide standard potential obtained by the fitting.

The diffusion coefficient itself was obtained by the convolution limiting value, $D_S = (I_l/2FAC_S)^2$, where C_S is the sulfide concentration, according to a stoichiometric coefficient n = 2, and results in D_S = (3.7 ± 0.3) × 10^{-6} cm^2 s^{-1}. The same value was obtained from chronoamperometric measurements at potentials corresponding to diffusion control. A plot of $(RT/F)\ln(k_{het}(E)/D_S^{1/2})$ as a function of the applied potential, obtained at sweep rates varying between 0.5 and 20 V s^{-1} is shown in Figure 1. A definite curvature can be detected well beyond the experimental error. Since $\alpha = -(RT/F)\, \mathrm{d}\ln k_{het}(E)/\mathrm{d}E$, the observed curvature corresponds to a potential dependence of the transfer coefficient.

The ET rate constant data on Hg were least-squares fitted to a quadratic equation in the potential:

$$\frac{RT}{F}\ln\frac{k_{het}(E)}{D_S^{1/2}} = c(1) + c(2)(E - E^*) + c(3)(E - E^*)^2 \tag{7}$$

where E^* = −1.7 V is approximately the middle potential of the investigated range. The individual coefficients result in

$$\begin{aligned} c(1) &= (5.065 \pm 0.007) \times 10^{-2} \\ c(2) &= -0.5495 \pm 0.0007 \\ c(3) &= -0.229 \pm 0.006 \end{aligned} \tag{8}$$

To evaluate some intrinsic parameters for the heterogeneous ET under investigation, we have used heterogeneous ET theories[8,38] predicting a quadratic dependence of the ET activation free energy on the heterogeneous driving force, ΔG°_{het}:

$$-\frac{\Delta G^{\ddagger}_{het}}{F} = \frac{RT}{F}\ln\frac{k_{het}(E)}{A_{het}} = -\frac{\Delta G^{\ddagger\circ}_{het}}{F}\left(1 + \frac{\Delta G^\circ_{het}}{4\Delta G^{\ddagger\circ}_{het}}\right)^2 \tag{9}$$

In (9) A_{het} is the heterogeneous frequency factor, $\Delta G^{\ddagger\circ}_{het}$ is the standard activation free energy and ΔG°_{het}, the difference in standard electrochemical free energy between products and reagents in their preactivation state, is related to the potential difference between the electrode and the actual reaction site, $\Delta G^\circ_{het} = F[E - \varphi_r(E) - E^\circ_S]$. This site is usually identified with the outer Helmholtz plane (OHP). Its potential referred to that of the solution, $\varphi_{OHP}(E)$, for the Hg/DMF + 0.1 M TBAP interphase, varies in a roughly linear way with the applied potential[18a] in the investigated range (∼−1.49 to −1.88 V vs SCE) with a slope $s = 0.0164$.

On the basis of eq 9, the curvature of the plot is inversely proportional to the standard activation free energy:

$$c(3) = -\frac{(1-s)^2}{16\Delta G^{\ddagger\circ}_{\mathrm{het}}/F} \qquad (10)$$

while the first- and zeroth-order coefficients depend, besides $\Delta G^{\ddagger\circ}_{\mathrm{het}}$, on the standard potential and on the standard potential and standard rate constant, respectively. These parameters can therefore be obtained from the fitting coefficients: $\Delta G^{\ddagger\circ}_{\mathrm{het}} = 25.5 \pm 0.7$ kJ mol^{-1}, $E^\circ_S = -1.721 \pm 0.004$ V vs SCE, $k^\circ_{\mathrm{het}} = 0.18 \pm 0.01_5$ cm s^{-1}.

Since the φ_{OHP} value is of the order of −100 mV, most of the experimental rate constant data correspond to positive (or nearly zero) standard reaction free energies, in agreement with α values greater than 0.5 on an average. Furthermore, positive or nearly zero values of $\Delta G^\circ_{\mathrm{het}}$ point to an outer-sphere character for the heterogeneous ET, and thus to the intermediacy of the anion radical. The thermodynamically unfavored reaction is driven by the fast follow up bond cleavage (see below). The concerted ET-bond breaking reaction

$$\mathrm{Ph_3CSPhCN + e \rightarrow Ph_3C^\bullet + SPhCN^-} \qquad (11)$$

recently found for alkyl, benzyl, and fluorenyl halides,[13-16] can therefore be excluded in the present case since it would correspond to a highly exoergonic process. The value of k°_{het} or, equivalently, of $\Delta G^{\ddagger\circ}_{\mathrm{het}}$, also shows that the charge transfer step is not intrinsically very slow. It results in being the slow step because it is driven under thermodynamically unfavored conditions by the fast follow-up reaction.

The observation of a quadratic dependence of the activation free energy on the reaction free energy allowed us to determine both the standard rate constant and the standard potential, an impossible task when the slow ET is the rate-determining step and a linear dependence of ln $k_{\mathrm{het}}(E)$ on $\Delta G^\circ_{\mathrm{het}}$ is found.

Homogeneous Reduction. The kinetics of the homogeneous reduction of the sulfide by a series of substituted azobenzene anion radicals was also investigated by voltammetric measurements at a GC electrode. According to the principles of homogeneous redox catalysis,[31,39] the electron transfer agents ($\mathrm{Az^{\bullet-}}$) are electrogenerated from the corresponding azobenzenes (Az) during a voltammetric run in the presence of sulfide. Simultaneously, the extent of the reaction is followed by measuring the relative increase of the Az cathodic peak current, at different sweep rates (v), Az (C_{Az}), and sulfide (C_S) concentrations.

The process corresponds to the indirect sulfide reduction leading, in the first step, to the formation of its radical anion:

$$\mathrm{Az + e \overset{E^\circ_{Az}}{\rightleftarrows} Az^{\bullet-}} \qquad (12)$$

$$\mathrm{Az^{\bullet-} + Ph_3CSPhCN \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Az + Ph_3CSPhCN^{\bullet-}} \qquad (13)$$

The C–S bond cleavage, eq 3, does occur as a separate step, as indicated for the heterogeneous process, and is followed by the further ET from $\mathrm{Az^{\bullet-}}$ to the neutral radical $\mathrm{Ph_3C^\bullet}$:

$$\mathrm{Ph_3CSPhCN^{\bullet-} \xrightarrow{k_2} Ph_3C^\bullet + SPhCN^-} \qquad (3)$$

$$\mathrm{Az^{\bullet-} + Ph_3C^\bullet \xrightarrow{k_3} Az + Ph_3C^- \xrightarrow{+H^+} Ph_3CH} \qquad (14)$$

The mechanism described by reactions 12, 13, 3, and 14 is the one usually considered in most cases of homogeneous reductive cleavage,[39] and in particular for the homogeneous ET to aryl halides.[14] The ET reactions from the radical anion to both the sulfide and the neutral radical, eqs 13 and 14, respectively, regenerate the starting azobenzene, with a catalytic increase in its reduction current. The increase generally depends on the rates of all reactions 13, 3, and 14. The theoretical treatment of the voltammetric response for this catalytic mechanism, the limiting situations arising from it, and the way of deducing the relevant kinetic parameters by comparing experimental and computed data has been extensively discussed.[31,39,40]

TABLE I

	azobenzenes	$D_{\mathrm{Az}} \times 10^6$ [a]	E°_{Az} [b]	$\Delta G^\circ_{\mathrm{hom}}$ [c]	log k_1 [d]
1	4,4′-di($\mathrm{OCH_3}$)	5.5	−1.493	22.0	4.81
2	4-$\mathrm{CH_3}$,4′-$\mathrm{OC_2H_5}$	5.4	−1.436	27.5	4.20
3	4-$\mathrm{OCH_3}$	5.5	-1.380_5	32.8	3.45_5
4	4-$\mathrm{CH_3}$	5.7	−1.325	38.2	2.86
5	3,3′-di($\mathrm{CH_3}$)	5.5	-1.312_5	39.4	2.60
6	H	7.4	−1.277	42.8	2.18
7	3,3′-di($\mathrm{OCH_3}$)	5.4	−1.242	46.2	1.72

[a] cm^2 s^{-1}; deviation ±0.1 ± 10^{-6}. [b] V vs SCE; deviation ±0.002. [c] kJ mol^{-1}; deviation ±0.5. [d] k_1: mol^{-1} L s^{-1}; deviation ±0.01.

The azobenzenes (Table I) were selected so as to have a series of ET agents with slightly different standard potentials, always positive to the sulfide reduction potential. In the absence of sulfide, all of them produce anion radicals which are stable in the time scale of the voltammetric experiments, as witnessed by the unity ratio between their anodic and cathodic peak currents, even at the lowest sweep rates employed. In the same way it was also verified that N-cyclohexyl isobutyramide, added to prevent CN hydrolysis,[35b] does not react significantly with the anion radicals of the azobenzenes used as ET reagents. As a matter of fact, such amide was selected within a series of proton donors,[41] as the most suited to fulfil the above requirements. The results of controlled potential electrolyses on solutions of azobenzene in the presence of the sulfide (see Experimental Section) show that the homogeneous reduction substantially follows the stoichiometry predicted by the above scheme even in the time scale of macroscale reduction.

At low Az concentrations ($C_{\mathrm{Az}} = 4 \times 10^{-4}$–$2 \times 10^{-3}$ M) the extent of catalysis, as measured by the i_p/i_p^d ratio of the voltammetric peak current in the presence and in the absence of sulfide, depends on the ratio C_{Az}/v, and on the molar ratio γ between sulfide and azobenzene. This corresponds to the first ET (13) being the rate-determining step. The experimental data fit rather well the theoretical curves calculated for the above scheme[31,39,40] only in the case of the most easily reducible catalysts where the catalytic increase $i_p/(i_p^d\gamma)$ is low. Differences can be observed with the least easily reducible azobenzenes when high extents of catalysis can be achieved. We have found that under the latter conditions the computed i_p/i_p^d ratio is strongly sensitive to differences in the catalyst and substrate diffusion coefficients (in the standard approach the coefficients are assumed to be equal). Theoretical working curves for the i_p/i_p^d ratio as a function of the dimensionless kinetic parameter $RTC_{\mathrm{Az}}k_1/Fv$ were computed by using for each catalyst the corresponding γ factors and the experimentally determined d ratio ($d = D_S/D_{\mathrm{Az}}$).[42] In such a way sensible improvements in the fitting was achieved (Figure 2). The rate constants, k_1, obtained for each azobenzene are reported in Table I.

An alternative mechanism would involve the direct electrode reduction of $\mathrm{R^\bullet}$, eq 4, instead of reaction 14. However the theoretical treatment[40] has shown that, when the first ET is the rate-determining step, the homogeneous reduction prevails over the heterogeneous one approximately when the parameter $k_3/k_1\gamma > 4$. Under our experimental conditions this parameter can be estimated[43] to vary between 6×10^6 for the most positive azobenzenes and 3×10^5 for the most negative ones, i.e., well above that limiting value. The assumption of the above scheme is therefore correct.[44]

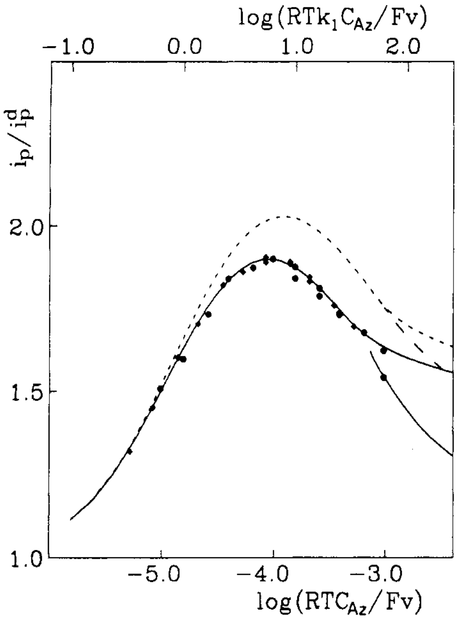

Figure 2. Homogeneous ET to $Ph_3CSPhCN$ from 4,4′-di(OCH_3) azobenzene (Az 1) anion radical in DMF + 0.1 M TBAP. Relative increase of the voltammetric peak current of Az 1 in the presence of the sulfide, at two different C_{Az} ((◆) 0.817 × 10^{-3} M; (●) 1.512 × 10^{-3} M) and different sweep rates ranging between 0.04 and 4.0 V s^{-1}. T = 25.0 °C; γ = 0.5. The lines are the theoretical variation of the relative increase as a function of the dimensionless kinetic parameter (upper scale). Dashed line: computed with d = 1.0; solid line: computed with d = 0.67.

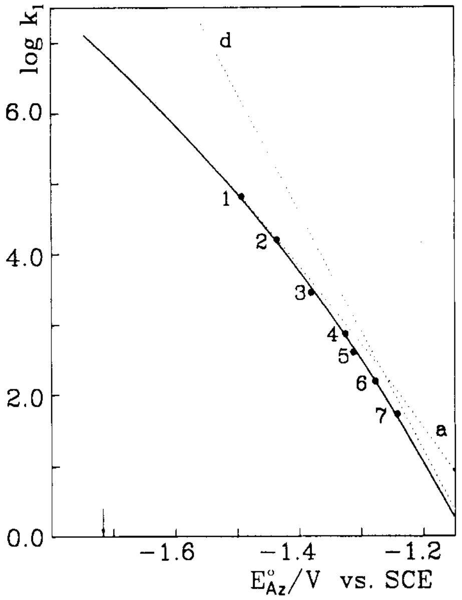

Figure 3. Homogeneous ET to $Ph_3CSPhCN$ from the family of Azobenzene anion radicals (see Table) in DMF + 0.1 M TBAP. Variation of the cross ET rate constant with the substituted azobenzenes standard potentials. T = 25.0 °C. The solid line is the best fitting according to eqs 16 and 17 with the parameters reported in the text. The dotted lines show the behavior of the "counter-diffusion" (d) and of the activation (a) components of the rate constant. The arrow indicates the sulfide standard potential obtained by the fitting.

Under these experimental conditions, the fragmentation (3) of the sulfide anion radical is much faster than its oxidation by Az (backward reaction 13). With azobenzene itself, however, by increasing the concentration ($C_{Az} \geq 2 \times 10^{-2}$ M), it was possible to accelerate the radical anion reoxidation relative to its fragmentation, up to the point where the total process was depending, at least partially, on the C–S cleavage rate. Experimentally, this results in an i_p/i_p^d ratio lower than expected for given C_{Az} and γ values, or equivalently, in a smaller apparent rate constant. Under such a mixed control, the competition parameter $k_2/C_{Az}k_{-1}$ can be obtained by computing the theoretical i_p/i_p^d values as functions of log ($k_2/C_{Az}k_{-1}$) at fixed values of γ and RTk_1C_{Az}/Fv, and comparing with them the pertinent experimental i_p/i_p^d value. Different values of γ, C_{Az} and v were used corresponding to the different experimental data; the value derived at low concentrations was employed for k_1. The average k_2/k_{-1} ratio, determined for two azobenzene concentrations C_{Az} = 2 × 10^{-2} and 4 × 10^{-2} M and for several sweep rates and γ's, results in (2.6 ± 0.9) × 10^{-2} M. Since the k_{-1} value can be obtained from that of k_1 and the difference of sulfide and azobenzene standard potentials:

$$k_{-1} = k_1 \exp\frac{\Delta G^\circ_{\mathrm{hom}}}{RT} = k_1 \exp\left[-\frac{F(E^\circ_{\mathrm{S}} - E^\circ_{\mathrm{Az}})}{RT}\right] \qquad (15)$$

this yields the actual value of $k_2 = (1.2 \pm 0.5) \times 10^8\ s^{-1}$. Besides allowing us to determine the lifetime of the sulfide anion radical, this result indicates that the ET between the sulfide and the different azobenzene anion radicals is indeed an outer sphere ET reaction, during which no bond cleavage occurs. The sulfide anion radical is generated together with the Az inside the solvent cage (encounter complex), but its lifetime, being greater than the half-life of the encounter complex (~0.1 ns for our systems), is long enough to allow it to diffuse away. The same is true in the heterogeneous case. On the other hand, the high value of k_2 confirms the validity of neglecting the backward ET reaction in our treatment of the heterogeneous data, eq 6, as previously indicated.

The ET rate constants for the series of substituted azobenzenes (Table I) show a decreasing dependence on the reaction free energy, $\Delta G^\circ_{\mathrm{hom}}$, as expected for a more and more unfavored reaction. An approximate value of 0.7 can be taken for the transfer coefficient $\bar{\alpha}_{\mathrm{hom}} = -RT\,\mathrm{d}\ln k_1/\mathrm{d}\,\Delta G^\circ_{\mathrm{hom}}$ which indicates that the uphill reaction is not under "counter-diffusion control" (the rate constant of the backward downhill reaction has not yet reached the diffusive limiting value, which is of the order of 10^{10} mol^{-1} L s^{-1} for our system, see below). Therefore the rate constant for the ET must be expressed in terms of both the activation and the diffusion components as

$$\frac{1}{k_1} = \frac{1}{k_{\mathrm{d}}}\left(1 + \frac{k_{\mathrm{d}}}{k_{\mathrm{act}}} + \exp\frac{\Delta G^\circ_{\mathrm{hom}}}{RT}\right) \qquad (16)$$

A quadratic law, similar to that experimentally found in the heterogeneous case, relating the activation to the reaction free energy, was assumed for the activated ET step, as theoretically predicted:[7]

$$-\Delta G^{\ddagger} = RT\ln\frac{k_{\mathrm{act}}}{A_{\mathrm{hom}}} = -\Delta G^{\ddagger\circ}\left(1 + \frac{\Delta G^\circ_{\mathrm{hom}}}{4\Delta G^{\ddagger\circ}}\right)^2 \qquad (17)$$

The practical use of the relationships 16 and 17 for fitting our experimental data requires some assumptions. The standard activation free energy $\Delta G^{\ddagger\circ}$ is considered to be constant along the series of substituted azobenzenes (indeed they were selected so similar one to the other with this goal in mind). The same is considered to be true for the diffusive rate constant, k_{d}, and the homogeneous preexponential factor, A_{hom}. Finally, it is assumed that the electron is transferred at a fixed distance between the two reagents.[45]

Instead of using the value of the sulfide standard potential obtained by heterogeneous data, to derive the individual homogeneous driving forces, we decided to treat it as a fitting parameter in order to obtain an independent check of its value. The experimental homogeneous k_1 data were therefore fitted to eqs 16 and 17 by a nonlinear-least-squares procedure, with the two parameters $\Delta G^{\ddagger\circ}$ and E°_{S}. Average values of $k_{\mathrm{d}} = (8.7 \pm 0.3) \times 10^9$ mol^{-1} L s^{-1} and $k_{\mathrm{d}}/A_{\mathrm{hom}} = (1.45 \pm 0.14) \times 10^{-2}$ were calculated[46] and used in the equations. The intrinsic activation free energy results $\Delta G^{\ddagger\circ} = 28.0 \pm 0.5$ kJ mol^{-1}, and the sulfide standard potential $E^\circ_S = -1.717 \pm 0.004$ V. As can be seen, this latter value is in amazingly good agreement with the independently found heterogeneous result of -1.721 V, also considering that some approximations are necessarily involved in the treatment of both homogeneous and heterogeneous data. In turn, the almost coincidence of the two values shows a posteriori the goodness of our correction for double-layer effects.

A comparison of our present results with those previously obtained for the p-NO$_2$-substituted[19c] and the unsubstituted[18c] triphenylmethyl phenyl sulfide reveals some trends. The anion radical lability increases on decreasing the electron-withdrawing character of the substituents, i.e., the bond breaking rate constant values are 4.1×10^5, 1.2×10^8, and 8×10^{11} s^{-1} for the p-NO$_2$-, p-CN-, and unsubstituted phenyl sulfide, respectively. As regards the latter unsubstituted compound, the anion radical decays before it can diffuse away from its ET partner, whether it be a molecular species as in the homogeneous process or the electrode as in the heterogeneous reduction. In particular, by simply decreasing the driving force of the ET step, the sequential mechanism is overwhelmed by the concerted ET bond-breaking process,[18c] a transition that although theoretically foreseen[47] was never observed before.[48] A further trend is that the increase of the cleavage rate is matched by a decrease of the pertinent standard potentials (E° values are -1.00, -1.72, and -2.16 V, for the NO$_2$, CN, and H derivative, respectively). An analogous relationship between stability of closely related anion radicals and thermodynamic easiness of their formation was found with substituted aryl halides.[14b,15] In all cases a trend of this type can be attributed to the different stabilizing effect brought about by the substituents on the π^* molecular orbital initially occupied by the unpaired electron.

Electron Exchange (EE) Standard Activation Free Energy. Some considerations can be made on the standard activation free energy for the homogeneous cross ET process, $\Delta G^{\ddagger\circ}$. It can be expressed as the half sum of the standard activation free energies for the homogeneous EE processes of the two partners:[1,7]

$$\Delta G^{\ddagger\circ} = \frac{\Delta G^{\ddagger\circ}{}_{S} + \Delta G^{\ddagger\circ}{}_{Az}}{2} \tag{18}$$

where $\Delta G^{\ddagger\circ}{}_{Az}$ can be taken as an average value of the EE activation free energy in the series of substituted azobenzenes. From the experimental $\Delta G^{\ddagger\circ}$ result, the value for the sulfide homogeneous EE process can be obtained, if the contribution of $\Delta G^{\ddagger\circ}{}_{Az}$ is known. Unfortunately, no experimental data are available on the homogeneous EE for any of the compounds in the series. Therefore we have tried to evaluate it on a theoretical ground. Unsubstituted azobenzene itself was selected as a representative model of the series.

The activation free energy can be separated, according to the classical or semiclassical treatment,[1,45] into an "inner" contribution due to fluctuations of the molecular coordinates of reagents and products and an "outer" term due to fluctuations of the orientational coordinates of solvent molecules. The simple expression usually given for changes in polarization of the solvent (in the continuum dielectric approximation) around the two reagents represented as conducting spheres at their contact separation,[7] is known to overestimate the outer contribution in the case of organic molecules, where neither the shapes are spherical nor the charge density is uniformly distributed. Several attempts were made to improve the theoretical evaluation.[49]

Very recently an approximated multisphere model has been proposed,[50] where each bond in both the oxidized and reduced species is represented by a sphere, centered halfway between the bonded atoms. Each sphere, having a diameter a_i slightly larger than the length of the corresponding bond, bears a partial charge ρ_i taken as the sum of the charge contributions of the two bonded atoms. Such a model seems to provide a good estimate of the solvent repolarization free energy.[50] The corresponding relation is

$$\Delta G^{\ddagger\circ}{}_{Az,out} = \frac{1}{4}\frac{N_A e^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\sum_i (\Delta\rho_i)^2\left(\frac{1}{a_{i,o}} + \frac{1}{a_{i,r}} - \frac{1}{R_{hom}}\right) \tag{19}$$

where $a_{i,o}$ and $a_{i,r}$ are the diameters of each sphere in the neutral molecule and the anion radical, respectively, $\Delta\rho_i = \rho_{i,r} - \rho_{i,o}$ is the partial charge variation between reduced and oxidized form in the ith bond and the summation is extended to all the bonds. R_{hom} is the average distance between the two reactants (products) in the encounter complex.

The bond length and the partial charges on each atom were obtained by semiempirical (AM1)[51] molecular orbital calculations with complete geometry optimization on both azobenzene and its anion radical. The outer contribution to the EE free energy results $\Delta G^{\ddagger\circ}{}_{Az,out} = 9.6$ kJ mol^{-1} when R_{hom} is taken as twice the van der Waals radius perpendicular to the aromatic rings (the shortest principal molecular axis) and $\Delta G^{\ddagger\circ}{}_{Az,out} = 10.7$ kJ mol^{-1} with $R_{hom} = 6.6$ Å (the intermediate principal molecular axis). Both data are much smaller than the value obtained by the approximation of conducting spheres, $(\Delta G^{\ddagger\circ}{}_{Az,out})_{sf} = 21.7$ kJ mol^{-1}, with a spherical radius of 3.7 Å estimated by the experimental diffusion coefficient.

Quantum chemical calculations with the semiempirical AM1 Hamiltonian were also used to obtain the force constant matrix for both the oxidized and the reduced state in order to estimate the inner contribution to the EE free energy. The usual expression for the internal reorganization free energy, $\Delta G^{\ddagger\circ}{}_{in}$, in terms of normal coordinate variations is correct only if there is no change in the normal modes between the two oxidation states.[52] This was not the case for our system neutral azobenzene/azobenzene anion radical. Therefore we followed the approach suggested by Goetz[50a] also for the inner contribution. This contribution (in the high temperature limit) was evaluated on the basis of the atom-atom force constant matrix, $K_{lm} = \partial^2 E_{pot}/\partial r_l\, \partial r_m$, and of the separation r_l between any atom pair:

$$\Delta G^{\ddagger\circ}{}_{Az,in} = \frac{1}{2}\sum_l \sum_{m<l} \frac{K^{o}{}_{lm} K^{r}{}_{lm}}{K^{o}{}_{lm} + K^{r}{}_{lm}} \Delta r_l \Delta r_m \tag{20}$$

with $\Delta r_l = r^{eq}_{l,o} - r^{eq}_{l,r}$ the change of equilibrium distance between the lth atom pair in the two oxidation states. The effect of incomplete population of the high frequency vibrational modes and of nuclear tunneling at the working temperature was approximately taken into account through the Holstein correction[53] by using the average frequency of 1300 cm^{-1} for our system. The resulting inner contribution to the activation free energy amounts to $\Delta G^{\ddagger\circ}{}_{Az,in} = 3.4$ kJ mol^{-1} and is not negligible with respect to the solvent polarization contribution.

According to eq 18, the homogeneous EE standard activation free energy for the sulfide can be estimated as $\Delta G^{\ddagger\circ}{}_S \sim 42.9$–44 kJ mol^{-1}. The outer contribution to the sulfide activation free energy can be evaluated by using the charge distribution and bond length variation between neutral molecule and anion radical computed by AM1 quantum mechanical calculations[54] on the parent compound CH$_3$SPhCN and its reduction product. This amounts to neglect the effect of the three phenyl groups on the alkyl carbon. The resulting $\Delta G^{\ddagger\circ}{}_{S,out}$ value, according to (19), is 14.8 kJ mol^{-1}, for the minimum reactants separation in the encounter complex roughly equivalent to twice the van der Waals radius of the sulfur atom[55] and 16.6 kJ mol^{-1} when $R_{hom} = 6.9$ Å, corresponding to a coplanar arrangement of benzene rings. The value obtained by using the Marcus' relation with a mean spherical radius (3.3 Å) would be 24.0 kJ mol^{-1}. If the spherical radius of Ph$_3$CSPhCN (derived by the experimental diffusion coefficient), $r_S = 7.4$ Å, were used in the Marcus approximation, a much smaller value of 10.8 kJ mol^{-1} would be obtained owing to the implicit assumption of charge delocalization over a very large molecule. The above estimate based on the theoretical MO data for CH_3SPhCN corresponds to assuming that the negative charge in the reduced form is preferentially localized on the –SPhCN moiety. As a matter of fact, MO calculations for $Ph_3CSPhCN$ show that the two LUMO's are π^*-type molecular orbitals with probability density largely present (~80%) in this part of the molecule.

The value of $\Delta G^{\neq\circ}_S$ shows therefore that the fluctuations in intramolecular coordinates must play a prominent role for obtaining the activated complex configuration in the homogeneous EE for the sulfide ($\Delta G^{\neq\circ}_{S,in} \simeq 26.3$–$29.2$ kJ mol^{-1}). This would imply also a rather large difference in the internal structure of the neutral molecule and the anion radical. In view of the high value for the rate constant of the C–S bond cleavage in the anion radical, one can think that a strong contribution should come from a sensible lengthening of this bond and an increase of the ∠PhCPh angles, which would favor the subsequent fragmentation into $Ph_3C^\bullet$ and $SPhCN^-$.

Conclusions

Although the full characterization of an irreversible ET reaction involving bond breaking or formation is usually rather difficult, this goal was achieved for the reductive cleavage of $Ph_3CSPhCN$ as a result of the combined investigation of the homogeneous and heterogeneous reactions. The determination of the lifetime of the sulfide anion radical clearly indicated the outer sphere character of the ET reaction. The convolution analysis of the voltammetric curves allowed us to determine the heterogeneous ET rate constants in a wide potential range. Thanks to the relatively low value of the standard activation free energy for the ET step and of the suitable value of fragmentation rate constant, a clear-cut case of quadratic activation–driving force relationship was observed, in agreement with the theoretical predictions.

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(35) (a) The standard potential for the fast ET to $Ph_3C^\bullet$ ($E^\circ_{R^\bullet/R^-} = -1.10$ V[19b]), is more positive than the sulfide reduction potential so that step (4) is much favored at the working potentials. (b) When the proton transfer agent of reaction 5 is residual water, OH^- anions are formed, which are responsible for CN hydrolysis in the parent compound. This reaction, yielding the corresponding amide, is fast enough to be detected even in the voltammetric time scale.[35c] For this reason all experiments were carried out in the presence of a small excess of a mild proton donor, such as *N*-cyclohexyl isobutyramide, which competes efficiently with water in the protonation of the carbanion Ph_3C^-, without substantially modifying the voltammetric behavior. An observable effect of isobutyramide addition was the disappearance of the oxidation peak of Ph_3C^- (reaction 4 backward), while that of the anion $SPhCN^-$ was unaffected. As to the controlled-potential electrolysis results, the effect of the added proton donor is to minimize the yield of the amide (<6%) and to increase that of the expected products up to a quantitative level. (c) Arévalo, M. C.; Maran, F.; Severin, M. G.; Vianello, E., manuscript in preparation.

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(43) (a) An estimate of k_3 can be made by using the theoretical relationship (18, see below) even if the intrinsic activation energy for the EE of both the azobenzenes' and the triphenylmethyl radical is not known. We can use an average value typical of other aromatic molecules showing similar heterogeneous EE standard rate constant[43b] and/or theoretical evaluation of the EE activation free energy (see below). In the less favorable situation (3,3′-di-(OCH_3)azobenzene, where $\Delta G^\circ = -F(E^\circ_{R^\bullet} - E^\circ_{Az}) = -13.7$ kJ mol^{-1}) the rate constant amounts at least to 80% of the limiting diffusion value, k_d, and practically coincides with it for the most negative catalyst. (b) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317. Kapturciewicz, A.; Jaenicke, W. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2727. Grampp, G.; Kapturkiewicz, A.; Jaenicke, W. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 439.

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(45) (a) This assumption is quite useful from a practical point of view, although a whole series of local ET reactions, each at different reactant separations, have been suggested as a more realistic representation of the process.[45b] (b) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

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(48) An example of passage from a sequential to a concerted mechanism has been recently reported in a study concerning the electrochemical reductive cleavage of benzyl halides.[16c] In that case, however, the passage was achieved upon changing the ring substituent from NO_2 to the weaker electron-withdrawing CN group.

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(55) This separation would be valid also for the bulkier $Ph_3CSPhCN$ if the head-to-tail "sandwich" structure is assumed for the latter encounter complex. Such a geometry would be obviously consistent with an antiparallel alignment of the two dipoles.