Electrochemically Induced $\mathrm{S_{RN}1}$ Aromatic Nucleophilic Substitution. Absolute Reactivities of Phenyl Derivatives in Liquid Ammonia

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Abstract: Homogeneous redox catalysis of the electrochemical reductive cleavage of diphenyl sulfide is used for determining the absolute reactivity of phenyl radicals toward benzenethiolate and diethyl phosphite ions in liquid ammonia. Other redox catalysis data obtained with chlorobenzene as the substrate as well as the direct electrochemistry of the two substrates appear to be consistent with these determinations. The cleavage rate constants of the anion radicals of PhSPh and PhCl and the standard potentials of the corresponding redox couples were also determined. Phenyl radicals appear to be significantly less reactive than most of the other aryl radicals, giving rise to nucleophilic attack rate constants that are well below the diffusion limit. $\mathrm{PhS^-}$ is shown to be markedly less reactive toward phenyl radicals than the other usual $\mathrm{S_{RN}1}$ nucleophiles. The observed reactivities are discussed in terms of transfer of the unpaired electron from the σ^* carbon–nucleophile bond orbital to the π^* orbital of the aromatic ring during the addition reaction.

$\mathrm{S_{RN}1}$ aromatic nucleophilic substitution belongs to the general class of electron-transfer-induced reactions. The substrate, ArX, is first activated by injection of an electron producing the anion radical $\mathrm{ArX^{-}\cdot}$ which then cleaves giving rise to the aryl radical $\mathrm{Ar\cdot}$:

$$\mathrm{ArX + e \rightleftarrows ArX^{-}\cdot} \tag{0}$$

$$\mathrm{ArX^{-}\cdot \overset{k_1}{\rightleftarrows} Ar\cdot + X^{-}} \tag{1}$$

$$\mathrm{Ar^{\cdot} + Nu^{-} \overset{k_2}{\rightleftarrows} ArNu^{-}\cdot} \tag{2}$$

$$\mathrm{ArNu^{-}\cdot - e \rightleftarrows ArNu} \tag{3}$$

and/or:

$$\mathrm{ArNu^{-}\cdot + ArX \rightleftarrows ArNu + ArX^{-}\cdot} \tag{3'}$$

$\mathrm{Ar\cdot}$ is the actual electrophile leading, upon attack of the nucleophile, $\mathrm{Nu^-}$, to the anion radical of the substituted product, $\mathrm{ArNu^{-}\cdot}$. The latter is ultimately oxidized yielding the final substitution product, ArNu. Electron-transfer induction can be effected photochemically[2a–c], by alkali metals dissolved in liquid ammonia,[2a–c] electrochemically,[2d] or by exogeneous one-electron reducing agents which can themselves be produced electrochemically.[2e–g] The overall reaction appears as a chain process when (3′) is the major oxidation step.[2a,e] Under conditions where the mechanism depicted by eq 0–3′ is fully operating, there is no net consumption of electrons and the reaction therefore appears as a true electrocatalytic process. This is actually not often the case since the $\mathrm{Ar\cdot}$ radical may undergo other reactions which decrease the substitution yield and increase the consumption of electrons. In poor H-atom donor solvents, such as liquid ammonia, these side reactions consist of the electron-transfer reduction of the aryl radical by the source of electrons which has caused its production, or by the anions radicals involved in the chain process[2d,3]:

$$\mathrm{Ar^{\cdot} + e \rightleftarrows Ar^{-}} \tag{4}$$

$$\mathrm{Ar^{\cdot} + ArX^{-}\cdot \rightleftarrows Ar^{-} + ArX} \tag{4'}$$

$$\mathrm{Ar^{\cdot} + ArNu^{-}\cdot \rightleftarrows Ar^{-} + ArNu} \tag{4''}$$

completed by the protonation of $\mathrm{Ar^-}$ into ArH by the strongest proton donor present in the medium (usually residual water).

In usual organic solvents, H-atom transfer from the solvent to the aryl radicals is an additional mode of deactivation of the aryl radicals:[3b,4]

$$\mathrm{Ar^{\cdot} + SH \rightarrow ArH + S^{\cdot}} \tag{5}$$

These side reactions are the termination steps competing with the propagation reactions in the homogeneous chain process.[2e]

Both types of side reactions, electron transfer and H-atom abstraction, are rapid owing to the fact that the aryl radicals are much easier to reduce[5] than the substrates commonly used in $\mathrm{S_{RN}1}$ substitution and that they are good H-atom abstractors toward most of the organic solvents.

The existence of these side reactions is an obvious drawback as far as good substitution yields are concerned. It is, however, an advantage for unravelling the reaction mechanism on kinetic grounds. This has been done in the context of electrochemical induction using the previously acquired knowledge of the side reactions.[2d,3,6] Liquid ammonia appears to be a particularly attractive solvent both because it is a very poor H-atom donor solvent which eliminates one of the two types of side reaction and its acidity is low, allowing the use of quite powerful nucleophiles.

At the beginning of these mechanistic investigations, sparse determinations of the reactivity of aryl radicals toward nucleophiles

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(4) (a) According to the nature of SH, S· can be further reduced at the electrode or in the solution at the potential where the reaction is carried out. This is the case for dimethyl sulfoxide and acetonitrile[3b,4b] which implies that the H-atom abstraction side reaction possesses a two-electron stoichiometry. With other solvents such as dimethylformamide, S˙ may undergo other follow-up reactions leading to an overall one-electron stoichiometry.[4c] (b) M'-Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. (c) Andrieux, C. P.; Combellas, C.; Savéant, J. M.; Thiébault, A.; Zann, D., unpublished results.

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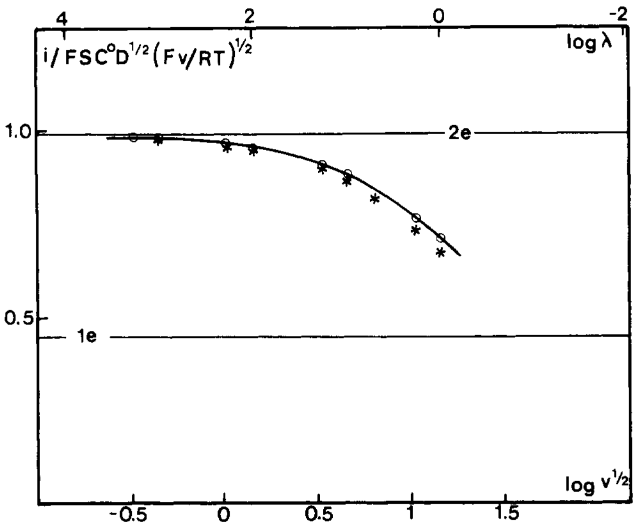

Figure 1. Cyclic voltammetry of PhSPh in liquid NH_3 + 0.1 M KBr at −38 °C. Variations of the cathodic peak current (i_p) with this sweep rate (v in V s^{-1}): (O) without addition of PhS^-, PhSPh conc (C^0) = 3 mM. (*) in the presence of 0.11 M PhS^-, PhSPh conc (C^0) = 2.8 mM. The solid line is the DIPS1 working curve represented as a function of the dimensionless kinetic parameter $\lambda = RTk_1/Fv$ (upper horizontal scale). Lower horizontal scale: v in V s^{-1}. i = current intensity, S = electrode surface area, C^0 = concn. of PhSPh, D = diffusion coefficient. $i/FS\,C^0D^{1/2}\,(Fv/RT)^{1/2}$ is a dimensionless quantity.

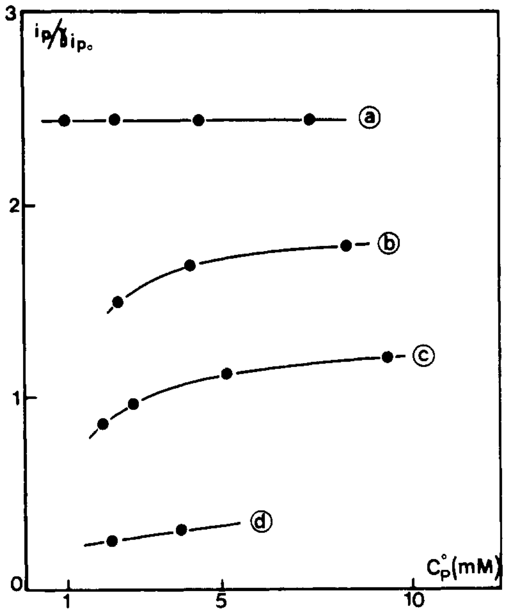

Figure 2. Homogeneous redox catalysis of the reduction of PhSPh and PhCl in liquid. NH_3 + 0.1 M KBr at −38 °C. Variations of the catalytic efficiency $i_p/\gamma i_p^0$ (i_p, peak current of the catalytic wave; i_p^0, peak current of the catalyst in absence of substrate; γ, excess factor concn of substrate/concn of catalyst) with the catalyst concentration, C_p^0, at constant values of the excess factor for v (sweep rate) = 0.115 V s^{-1}. Substrate, catalyst, and γ for a–d respectively follow: (a) PhSPh, naphthalene, 1; (b) PhCl, 2-methylnaphthyl ether, 1.83; (c) PhCl, diethyl phenyl phosphite, 1; (d) PhCl, naphthalene, 5.3.

were reported.[2d,e,g,3a,b,6] More systematic investigations of this problem have been carried out recently. One of these dealt with the relative reactivities of phenyl radicals toward a series of nucleophiles in liquid NH_3 using a competition method under photochemical stimulation.[7a] The other was an electrochemical investigation using direct and indirect methods which allowed determination of the absolute reactivities of nine aryl radicals toward a series of three nucleophiles: benzenethiolate, diethyl phosphite and acetone enolate.[7b] However, owing essentially to its relatively low reactivity, the phenyl radical has escaped thus far characterization of its absolute reactivity toward nucleophiles. This is particularly unfortunate because it is the simplest aryl radical and also because the rate constants of its reaction with nucleophiles are significantly below the diffusion limit, as will be demonstrated below, at variance with most other aryl radicals.[7b] The work described hereafter was intended to fill this gap. Homogeneous redox catalysis of the electrochemical-inducing reaction was the main method we used for this purpose. Additional electrochemical experiments were also carried out to check the values thus obtained. In addition, other interesting data such as characteristic standard potentials and anion radical cleavage rates of the substrates have been determined.

Results

Thermodynamic and Kinetic Characteristics of the Reduction of Diphenyl Sulfide and Chlorobenzene. Diphenyl Sulfide is an interesting molecule in the context of $S_{RN}1$ substitution in the sense that it may both act as a substrate for the replacement of PhS^- by another nucleophile and be the product of the reaction of PhS^- with the phenyl radical.

Diphenyl sulfide exhibits an irreversible wave at −2.145 V (at 0.2 V s^{-1}). The peak height varies with the sweep rate as shown in Figure 1. This is consistent with an ECE-type mechanism:[8a]

$$PhSPh + e \rightleftharpoons PhSPh^{-\cdot} \qquad (0)$$

$$PhSPh^{-\cdot} \rightleftharpoons PhS^- + Ph^{\cdot} \qquad (1)$$

$$Ph^{\cdot} + PhSPh^{-\cdot} \rightarrow Ph^- + PhSPh \qquad (4')$$

$$Ph^- + H^+ \text{ (residual water)} \rightarrow PhH$$

in which diffusion begins to compete with the cleavage reaction as the sweep rate is raised. It actually appears[8b] that the second electron transfer instead of taking place at the electrode surface, as in a strictly speaking ECE mechanism, occurs in the solution, the reducing agent being the initial anion radical (eq 4′). The working curve corresponding to the case where the forward cleavage reaction is the rate-determining step(DISP1 mechanism[8a]) shows good agreement with the experimental data (Figure 1). This remains true even if PhS^- anions are added in the solution up to rather high concentrations. PhS^- concentration must reach 0.1 M for a slight deviation to be observed (Figure 1). Fitting of the experimental data obtained without addition of PhS^- with the DISP1 working curve leads to the value of the cleavage rate constant: $k_1 = 10^4\ s^{-1}$.

This rate constant can also be obtained by homogeneous redox catalysis. The principle of the method[9a,b] is to reduce the substrate indirectly, by means of a mediator, giving rise to a reversible electrochemical reduction:

$$P + e \rightleftharpoons Q \qquad (6)$$

$$Q + ArX \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} P + ArX^{-\cdot} \qquad (7)$$

$$ArX^{-\cdot} \overset{k_1}{\rightleftharpoons} Ar^{\cdot} + X^- \qquad (1)$$

$$Q + Ar^{\cdot} \rightarrow P + Ar^- \qquad (8)$$

$$Ar^- + H^+ \rightarrow ArH$$

The addition of the substrate ArX to the solution results in an increase of the P–Q wave, which also looses its reversibility, caused by the regeneration of P via (7) and (8). When using naphthalene

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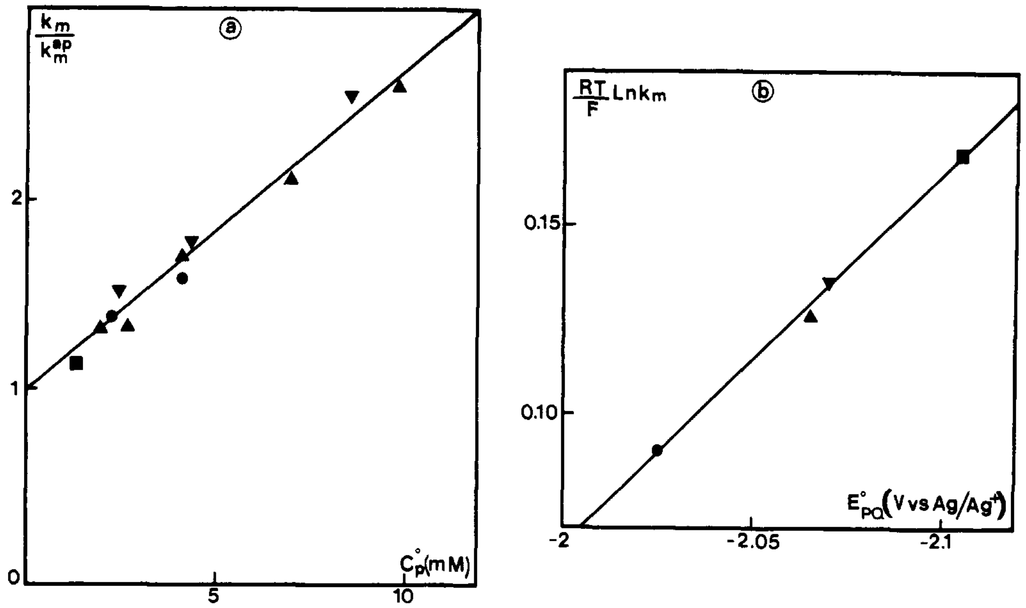

Figure 3. Homogeneous redox catalysis of PhCl in liquid. NH_3 + 0.1 M KBr at −38 °C. (a) Approximate treatment of the data (see text) obtained with four catalysts: naphthalene (●), diethyl phenyl phosphite (▲), 2-methylnaphthalene (▼), 1-methylnaphthalene (□). (b) Variations of the forward electron transfer rate constant between PhCl and the reduced forms of the catalysts as a function of their standard potentials. Same symbolism as in (a).

as the mediator the catalytic efficiency appears independent of the catalyst concentration for a given value of the excess factor (Figure 2). This shows that the rate-determining step in the catalytic process is the cleavage reaction (1), the mediation electron-transfer reaction (7) being at equilibrium. It follows that the kinetic factor $k_m k_1/k_{-m}$ can be derived from the measurement of the catalytic enhancement of the peak current corresponding to the reduction of P using a previously derived working curve.[9b] It was found that:

$$(k_m/k_{-m})k_1 = 1.84$$

On the other hand, variation of the peak potential of the PhSPh irreversible wave with the sweep rate indicates that the electrochemical reduction of this compound is under the kinetic control of the cleavage reaction.[9c–e] The peak potential, E_p, can thus be expressed as:[9e]

$$E_p = E^\circ - 0.78\frac{RT}{F} + \frac{RT}{2F}\ln\left(\frac{RTk_1}{Fv}\right) \qquad \text{(I)}$$

E° being the standard potential of the $ArX/ArX^{-\cdot}$ couple, k_1 the cleavage rate constant, and v the sweep rate. It was found that $E_p = -2.145$ V at 0.2 V s^{-1}.

On the other hand,

$$\frac{k_m}{k_{-m}} = \exp\left[\frac{F}{RT}(E^\circ - E^\circ_{PQ})\right]$$

where E°_{PQ} is the standard potential of the catalyst couple. Thus

$$\frac{k_m}{k_{-m}}k_1 = k_1\exp\left[\frac{F}{RT}(E^\circ - E^\circ_{PQ})\right] \qquad \text{(II)}$$

k_1 and E° can thus be derived by combination of eq I and II[9a,b] leading to $k_1 = 1.1\ 10^4\ s^{-1}$ and $E^\circ = -2.20$ V. It is seen that there is a good agreement between the values of k_1 derived by two independent methods.

Homogeneous redox catalysis was also used to investigate the characteristics of the reduction of *chlorobenzene*. Four catalysts were employed in this case. The catalysts and their standard potentials are listed in Table I and the experimental results given in Figure 2.[10] It appears, from the observed variations of the catalytic efficiency, $i_p/\gamma i_p^\circ$, with the catalyst concentration, C_p^0 at a given value of the excess factor, γ (Figure 2), that the catalytic process is under mixed control by 7 and 1. The catalytic efficiency is thus a function of two parameters, i.e., $\lambda_m = RTk_mC_P^0/Fv$ and $k_{-m}C_P^0/k_1$. We used here a simplified version of the treatment relative to this case described previously.[9a,b] It indeed appears that, at low catalytic efficiencies and for sufficiently narrow ranges of variations of this quantity and of the excess factor, the following approximate approach can be used with good accuracy. The working curve corresponding to pure control by forward reaction 7 can be used for the general case provided k_m is replaced by k_m^{ap} defined as:

$$\frac{1}{k_m^{ap}} = \frac{1}{k_m} + \epsilon\frac{k_{-m}}{k_m}\frac{C_P^0}{k_1}$$

Fitting the previously derived theoretical results[9a,b] with this approximation in the pertinent ranges of variations shows that $\epsilon = 0.33$. The values of $1/k_m^{ap}$ obtained in this way were plotted as a function of C_P^0 for each catalyst. The intercept of the resulting straight line provided the value of k_m for each catalyst (Table I). Now the results obtained with all four catalysts were replotted in the form:

$$\frac{k_m}{k_m^{ap}} = 1 + \epsilon\frac{k_{-m}C_P^0}{k_1}$$

as shown in Figure 3a. The slope of the resulting straight line provides the ratio

$$k_{-m}/k_1 = 8.2 \times 10^2\ M^{-1}$$

taking $\epsilon = 0.33$. The fact that the same linear k_m/k_m^{ap} vs. C_P^0 is obtained with *all* four catalysts implies that k_{-m} is the same *in* all four cases which indicates that k_{-m} is equal to the diffusion limit, $3 \times 10^{10}\ M^{-1}\ s^{-1}$. It follows that $k_1 = 3.7 \times 10^7\ s^{-1}$. Figure 3b shows the plot of $(RT/F)\ln k_m$ vs. E°_{PQ} obtained with the four catalysts. It is remarkable that the points fall on a straight line of unity slope, confirming that the reverse reaction is under diffusion control.[9f] Extending the straight line up to a value of k_m equal to the diffusion limit gives the value of the standard potential of the $PhCl/PhCl^{-\cdot}$ couple:

$$E^\circ_{PhCl/PhCl^{-\cdot}} = -2.42 \text{ V vs. } Ag/Ag^+$$

Assuming that at a sweep rate of 0.2 V s^{-1} the direct electrochemical reduction of PhCl is under the kinetic control of the

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[10] The results obtained with 1-methylnaphthalene as a catalyst are not represented in Figure 2 since only one (small) concentration could be used owing to partial overlap of the catalyst and the PhCl waves. The data obtained with this catalyst were used in the following treatment (see text and Figure 3).

Table I. Characteristics of the Reduction of PhSPh and PhCl in Liquid NH_3 at −38 °C

substrate	catalyst	$E°_{PQ}$[a]	$(k_m/k_{-m})k_1$ (s^{-1})	k_m (M^{-1} s^{-1})	$E°_{ArX/ArX^{-\cdot}}$[a]	k_1 (s^{-1})
PhSPh	naphthalene	−2.025	1.84		−2.20	1.1×10^4[b] 1.0×10^4[c]
PhCl	naphthalene	−2.025		95	−2.42	
	diethyl phenylphosphite	−2.065		520		4.0×10^7[d]
	2-methylnaphthyl ether	−2.070		815		4.2×10^7[e]
	1-methylnaphthyl ether	−2.105		4550		

[a] In V vs. Ag/Ag^+. [b] From the peak potential and the redox catalysis data. [c] From the variations of the peak height with the sweep rate. [d] From redox catalysis data. [e] From $E°_{ArX/ArX^{-\cdot}}$ determined from redox catalysis data and the peak potential.

cleavage reaction rather than under that of the electrode electron-transfer reaction,[9e] k_1 can be derived from the value of the peak potential, −2.280 V vs. Ag/Ag^+ at this sweep rate. It is found that $k_1 = 4.2 \times 10^7$ s^{-1}, which is in good agreement with the value derived from homogeneous redox catalysis.

The main thermodynamic and kinetic characteristics concerning PhSPh and PhCl are summarized in Table I.

Reactivity of Phenyl Radical toward Nucleophiles. The same compounds, PhSPh and PhCl, the electrochemical behavior of which is described in the preceding section, were used as substrates for determining the absolute reactivity of phenyl radicals toward two nucleophiles: benzenethiolate and diethyl phosphite ions.

In the case of chlorobenzene, the direct method,[2d,3a,b,7b] i.e., the observation of the decrease of the reduction wave upon addition of the nucleophile, cannot lead to accurate results because the reduction wave is too close to the discharge of the supporting electrolyte (Figure 4a). Qualititatively, it is seen (Figure 4a), that the reactivity of diethyl phosphite ions toward chlorobenzene is weak as indicated by the fact that the cyclic voltammetric wave corresponding to the reoxidation of the diethyl phenyl phosphite anion radical upon scan reversal is small as compared to the reduction wave of chlorobenzene. The reactivity of benzenethiolate is even weaker: no change of the chlorobenzene cyclic voltammogram is detected upon addition of PhS^- to the solution.

In the case of diphenyl sulfide the reactivity of PhS^- is also weak as seen in Figure 1. On the contrary, the reaction of diethyl phosphite ions with PhSPh is very efficient under electrochemical stimulation as can be seen in Figure 4b which represents the cyclic voltammogram obtained upon addition of 0.11 M $OP(OEt)_2^-$ the reaction is practically total in the time scale of the experiments (0.2 V s^{-1}, i.e., ca. 0.17 s).[11]

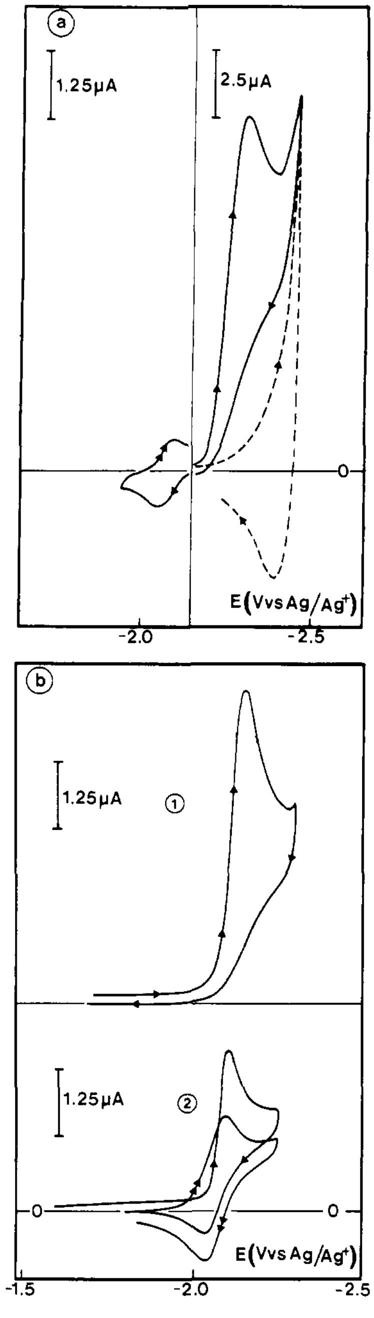

Figure 4. Cyclic voltammetry of chlorobenzene and diphenyl sulfide in liquid NH_3 + 0.1 M KBr at −38 °C, in the presence of potassium diethyl phosphite (0.11 M) at 0.2 V s^{-1}. (a) PhCl (4.6 mM). The dotted line shows the response of the supporting electrolyte, the anodic trace corresponding to the injection of the solvated electrons from the electrode into the solution. (b) PhSPh (2 mM) in the absence (1) and presence (2) of diethyl phosphite ions.

For all these reasons, we preferred to use the homogeneous redox catalytic method rather than the direct method for investigating the reactivity of phenyl radicals toward benzenethiolate and diethyl phosphite ions. The most accurate results were obtained with diphenyl sulfide as the substrate. The catalyst was naphthalene as for the determination of the cleavage rate constant of $PhSPh^{-\cdot}$ described in the preceding section. At a given sweep rate and a given value of the excess factor, i.e., the ratio of the substrate over catalyst concentration, the catalytic current decreases upon addition of the nucleophilic according to the following reaction sequence:[2g,7b]

$$P + e \rightleftharpoons Q \qquad (6)$$

$$Q + ArX \underset{k_{-m}}{\overset{k_m}{\rightleftharpoons}} P + ArX^{-\cdot} \qquad (7)$$

$$ArX^{-\cdot} \overset{k_1}{\rightleftharpoons} Ar^{\cdot} + X^- \qquad (1)$$

$$Ar^{\cdot} + Q \overset{k_d}{\rightleftharpoons} Ar^- + P \qquad (8)$$

$$Ar^{\cdot} + Nu^- \overset{k_2}{\rightleftharpoons} ArNu^{-\cdot} \qquad (2)$$

$$ArNu^{-\cdot} + P \xrightarrow{k_d} ArNu + Q \qquad (9)$$

in which the rate constants of (8) and (9) are both equal to the diffusion limit, k_d.

As shown in the preceding section, the catalytic process is under the kinetic control of forward reaction 1, eq 7 remaining at

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[11] The reaction could in principle be investigated directly by cyclic voltammetry at higher sweep rate. As made clear in the Discussion and in Figure 5, sweep rates in the 10–100 V s^{-1} range would then be required. These figures are too high for good accuracy to be obtained when using a solid electrode as was the case here (gold).

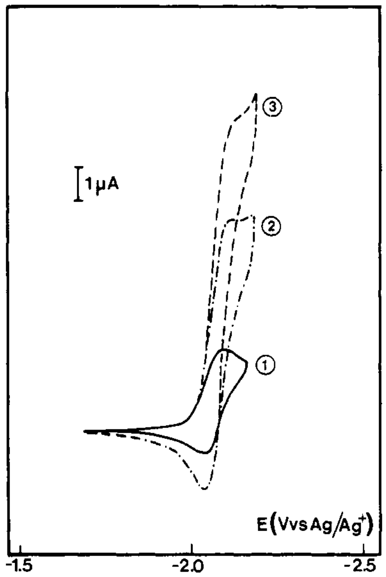

Figure 5. Cyclic voltammetry of diethyl phenyl phosphite (2 mM) in liquid NH_3 + 0.1 M KBr at −38 °C in the presence of 0.275 M $(EtO)_2POK$ in the absence (—) and presence of 9.3 mM (–•–) and 17.5 mM (---) PhCl: Sweep rate, 0.2 V s^{-1}.

equilibrium. Thus in the diffusion equation pertaining to PhX the kinetic term is:

$$-\frac{k_{\mathrm{m}}}{k_{-\mathrm{m}}}k_1\frac{[\mathrm{PhX}][\mathrm{X}]}{[\mathrm{P}]}$$

and in that pertaining to P, it is:

$$2\frac{k_{\mathrm{m}}}{k_{-\mathrm{m}}}k_1\frac{[\mathrm{PhX}][\mathrm{Q}]}{[\mathrm{P}]\,(1+(k_2[\mathrm{Nu}^-]/k_{\mathrm{d}}[\mathrm{Q}]))}$$

Instead of using the rigorous treatment developed previously[2g,7b], we use in the following the same approximation as in the analysis of the catalytic process in the absence of nucleophile (see the preceding section). This amounts to considering that the concentration of Q in the diffusion-reaction layer is approximately constant: $[\mathrm{Q}]_{\mathrm{av}} = (1-\epsilon_0)C_{\mathrm{P}}^0 = 0.67C_{\mathrm{P}}^0$. It follows that, under these conditions, the kinetics can be viewed as formally equivalent to that of an "EC" catalytic process[9b] in which the excess factor, γ, would be replaced by an apparent excess factor γ^{ap} defined as:

$$\gamma^{\mathrm{ap}} = \frac{2\gamma}{1+(k_2[\mathrm{Nu}^-]/0.67k_{\mathrm{d}}C_{\mathrm{P}}^0)}$$

We then used the working curves previously computed for an "EC mechanism",[9b] knowing $k_{\mathrm{m}}k_1/k_{-\mathrm{m}}$ to determine γ^{ap}. The value of k_2 ensues:

$$k_2 = \frac{0.67k_{\mathrm{d}}C_{\mathrm{P}}^0}{[\mathrm{Nu}^-]}\left(\frac{2\gamma}{\gamma^{\mathrm{ap}}}-1\right)$$

The results obtained with $OP(OEt)_2^-$ and PhS^- are listed in Table II. The error introduced by the above approximation is negligible vis-â-vis the experimental uncertainty as shown by comparison of the approximation to the rigorous treatment developed previously.[2g,7b]

Another estimation of the reactivity of phenyl radicals toward $OP(OEt)_2^-$ ions was obtained as follows. Diethyl phenylphosphonate, the substitution product, is taken as the catalyst and the potential is scanned repetitively on its wave in the presence of diethyl phosphite ions, leading to a steady-state current–potential pattern. As shown in Figure 5, the reduction wave of diethyl phenylphosphonate very significantly increases upon addition of PhCl to the solution. This corresponds to the following reaction sequence:

Table II. Catalytic Reduction of PhSPh by Naphthalene in the Presence of Nucleophiles[a]

PhS^- (0.53 M)

C_{P} (mM)	γ	v (V s^{-1})	$i_{\mathrm{p}}/i_{\mathrm{p}}^{0}$ [b]	$10^{-7}k_2$ (M^{-1} s^{-1})
0.92	1.09	0.115	2.19	1.1
		0.200	2.07	0.06
	0.537	0.115	1.55	2.9
		0.200	1.47	2.0
1.86	1.08	0.115	2.12	2.7
		0.200	2.00	1.6
		0.380	1.65	3.1
	1.60	0.115	2.68	2.2
		0.200	2.37	2.1
		0.380	2.03	2.7
2.75	1.08	0.115	2.15	3.4
		0.200	1.96	3.0
		0.380	1.72	3.3
3.74	0.80	0.115	1.90	3.8
		0.200	1.69	4.4
		0.380	1.49	5.0
				av 2.6 ± 0.9

$OP(OEt)_2^-$ (0.103 M)

C_{P} (mM)	γ	v (V s^{-1})	$i_{\mathrm{p}}/i_{\mathrm{p}}^{0}$ [b]	$10^{-8}k_2$ (M^{-1} s^{-1})
1.92	0.54	0.115	1.35	4.7
		0.200	1.30	4.0
		0.380	1.18	5.5
	1.06	0.115	1.72	4.4
		0.200	1.63	3.5
		0.380	1.52	2.8
	2.11	0.115	2.5	3.6
		0.200	2.7	1.3
3.96	2.07	0.115	1.42	3.5
		0.200	1.66	1.9
6.5	1.26	0.115	2.17	6.6
		0.200	2.07	4.5
		0.380	1.9	3.3
	2.05	0.115	3.02	4.7
		0.200	2.9	2.1
				av 3.8 ± 1

[a] In liquid NH_3 + 0.1 M KBr at −38 °C. [b] i_{p}: observed peak current; i_{p}^0: peak current for a 1e reversible wave.

$$\mathrm{ArNu} + e \rightleftarrows \mathrm{ArNu}^{-}\cdot \tag{6}$$

$$\mathrm{ArNu}^{-}\cdot + \mathrm{ArX} \rightleftarrows \mathrm{ArNu} + \mathrm{ArX}^{-}\cdot \tag{7}$$

$$\mathrm{ArX}^{-}\cdot \rightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \tag{1}$$

$$\mathrm{Ar}\cdot + \mathrm{Nu}^- \xrightarrow{k_2} \mathrm{ArNu}^{-}\cdot \tag{2}$$

$$\mathrm{Ar}\cdot + \mathrm{ArNu}^{-}\cdot \xrightarrow{k_{\mathrm{d}}} \mathrm{Ar}^- + \mathrm{ArNu} \tag{8}$$

$$\mathrm{Ar}^- + \mathrm{H}^+ \rightarrow \mathrm{ArH} \tag{10}$$

The increase of the reduction current of ArNu results from the fact that the phenyl radicals generated from the homogeneous redox catalysis of the reduction of chlorobenzene (eq 6 and 7) react, at least partially, with diethyl phosphite ions leading to the production of $ArNu^-\cdot$ and then ArNu through eq 7 and 9.

In the steady state, the average concentrations of ArNu, $ArNu^-\cdot$, and ArX are constant, the first two concentrations being equal. Thus the quantity of ArNu generated from the reduction of ArX can be expressed as:

$$[\overline{\mathrm{ArNu}}] - [\mathrm{ArNu}]^0 = ([\mathrm{ArX}]^0 - [\overline{\mathrm{ArX}}])\frac{k_2[\mathrm{Nu}^-]}{k_2[\mathrm{Nu}^-] + k_{\mathrm{d}}[\mathrm{ArNu}]}$$

where $[\mathrm{ArNu}]^0$ and $[\mathrm{ArX}]^0$ are the starting concentrations of the

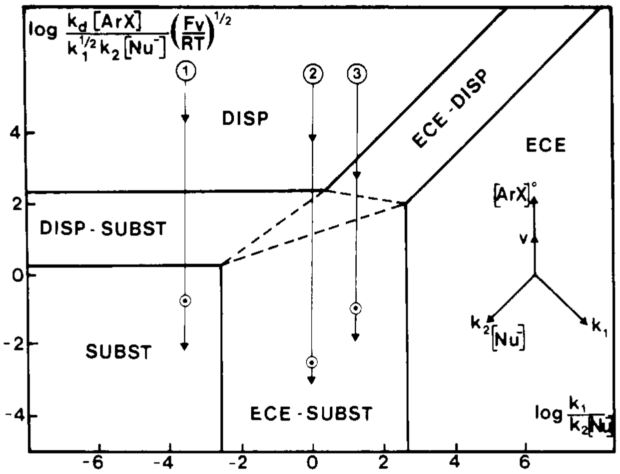

Figure 6. Zone diagram representing the competition between the various reactions involving the aryl radical: DISP (homogeneous electron transfer), ECE (heterogeneous electron transfer), SUBST (attack by the nucleophile). The boundary lines correspond to a 5% accuracy on the peak height of ArX. The shifts (in direction, sign, and magnitude) of the representative point with the various experimental parameters are shown by the set of arrows in the right-hand side of the diagram: (1) PhSPh + $(EtO)_2PO^-$, (2) PhCl + $(EtO)_2PO^-$, (3) PhCl + PhS^-. In all three cases ⊙ corresponds to $[ArX]^0 = 10^{-2}$ M, $[Nu^-] = 0.1$ M, $v = 0.115$ V s^{-1}.

two species and $[\overline{\mathrm{ArNu}}]$ and $[\overline{\mathrm{ArX}}]$ are their average concentrations at steady state. The remainder of the reduced ArX is converted into ArH through (8) and (10). On the other hand,

$$[\overline{\mathrm{ArNu}}]/[\mathrm{ArNu}]^0 = i_p/i_p^0$$

where i_p and i_p^0 are the heights of the ArNu reduction peak in the presence and absence of ArX, respectively. It follows that the rate constant k_2 can be obtained from:

$$\frac{k_2[\mathrm{Nu}^-]}{k_d[\mathrm{ArNu}]^0} = \frac{\frac{i_p}{i_p^0}\left(\frac{i_p}{i_p^0} - 1\right)}{1 + \frac{[\mathrm{ArX}]^0}{[\mathrm{ArNu}]^0} - \frac{i_p}{i_p^0} - \frac{[\overline{\mathrm{ArX}}]}{[\mathrm{ArNu}]^0}}$$

$[\overline{\mathrm{ArX}}]$ is derived from the height of the ArX wave at steady state. In our case this was close to zero and therefore neglected in the estimation. The results obtained at a sweep rate of 0.2 V s^{-1} for a series of values of $[Nu^-]$, $[ArNu]^0$, and $[ArX]^0$ are given in Table III. It is found that $k_2 = (3 \pm 1)\ 10^8$ M^{-1} s^{-1}. This value is likely to be less accurate than that obtained by the other method described above. One difficulty is the estimation of $[\overline{\mathrm{ArX}}]$ from the steady-state wave of PhCl since this is overlapping with the discharge current of the supporting electrolyte. This is probably not completely negligible as assumed above. It follows that k_2 is likely to be somewhat higher that the value we derived. Taking this into account, the agreement between the values found with the two methods is quite satisfactory.

Another way of estimating the reactivity of phenyl radicals toward benzothiolate ions is to use the variations of the peak height of the reduction wave of PhSPh observed upon addition of PhS^- (Figure 1). The electrochemical reaction involves the following sequence:

$$\mathrm{PhSPh} + e \rightleftarrows \mathrm{PhSPh}^{-\cdot} \qquad (0)$$

$$\mathrm{PhSPh}^{-\cdot} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{Ph}\cdot + \mathrm{PhS}^- \qquad (1)$$

$$\mathrm{Ph}^\cdot + \mathrm{PhSPh}^{-\cdot} \xrightarrow{k_d} \mathrm{Ph}^- + \mathrm{PhSPh} \qquad (4')$$

$$\mathrm{Ph}^- + \mathrm{H}^+ \rightarrow \mathrm{PhH} \qquad (10)$$

Table III. Reduction of PhCl by the $PhP(O)(OEt)_2/PhP(O)(OEt)_2^{-\cdot}$ Couple in the Presence of $(EtO)_2PO^-$ in Liquid NH_3 at -38 °C[a]

$[(EtO)_2PO^-]$ (M)	$[PhP(O)(OEt)_2]^0$ (mM)	$[PhCl]^0$ (mM)	$10^{-8}k_2$[b] (M^{-1} s^{-1})
0.150	2.3	4.2	2.1
		8.7	2.7
		13.1	3.3
	5.0	13.0	2.2
	7.3	13.0	4.6
0.275	2.0	3.6	1.2
		9.3	3.2
		13.5	3.0
		17.5	3.9
	4.1	17.5	4.7
	6.4	17.5	4.2
	8.7	17.5	4.7
		21.3	4.0
		33.6	4.6
0.370	1.5	6.2	1.2
		9.1	1.6
	3.1	9.1	1.5
		20.0	2.0
			av 3 ± 1

[a] From steady-state repetitive cyclic voltammetric data (sweep rate: $v = 0.2$ V s^{-1}). [b] For the derivation of k_2, see text.

As already discussed, the reduction of Ph$^\cdot$ involves the homogeneous electron-transfer reaction (4′) rather than the heterogeneous electron-transfer reaction 4. We thus deal with a "DISP" rather than an ECE mechanism.[8a] In this context, forward reaction 1 is the rate-determining step when no PhS^- ions are added to the solution ("DISP1" reaction scheme[8a]). Upon addition of PhS^-, backward reaction 1 tend to interfere; i.e., the system tends to shift toward a "DISP2"[8a] situation where (4′) is the rate-determining step while (1) remains at equilibrium. An approximate treatment of the data is as follows. The master diffusion equation describing the kinetic of the system can be written:[8]

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - \frac{2\lambda_1 b}{1 + (\lambda_2/\lambda_d b)}$$

where $b = [\mathrm{PhSPh}]/[\mathrm{PhSPh}]^0$, $\tau = Fvt/RT$, $y = x(Fv/RTD)^{1/2}$, $\lambda_1 = RTk_1/Fv$, $\lambda_2 = RTk_2[\mathrm{PhS}^-]/Fv$, and $\lambda_d = RTk_d \cdot [\mathrm{PhSPh}]^0/Fv$, the current being given by $\Psi = -(\partial b/\partial y)_{x=0} = i/FS[\mathrm{PhSPh}]^0 D^{1/2} (Fv/RT)^{1/2}$. In the sweep rate range where the peak current height varies between 1 and 2 electrons per molecule, $b = {}^1/_2$. Thus the above differential equation is:

$$\frac{\partial b}{\partial \tau} = \frac{\partial^2 b}{\partial y^2} - 2\lambda^{\mathrm{ap}} b$$

where

$$\lambda^{\mathrm{ap}} \simeq \frac{\lambda_1}{1 + (2\lambda_1/\lambda_d)}$$

We can thus use the working curve relating Ψ to λ_{-1} in the framework of the DISP1 mechanism[8a] simply replacing λ_1 by λ^{ap}. Using then the data shown in Figure 1, we find $k_2 = 2.5 \times 10^7$ M^{-1} s^{-1}. This is certainly not an accurate value since the experimental points obtained upon addition of PhS^- to the solution are not very different from those obtained before the addition (Figure 1). The fact that the value of k_2 thus found is in good agreement with the value derived from homogeneous redox catalysis demonstrates the consistency of the two series of experiments.

Discussion

It is noticed that the cleavage rate constants of $PhSPh^{-\cdot}$ and $PhCl^{-\cdot}$ in liquid NH_3 at -38 °C are both significantly lower, by two to three orders of magnitude, than in dimethylformamide a room temperature.[12] A large part of this difference in reactivity can be attributed to the difference in temperature. However, differences in solvation, and possibly ion pairing, may also interfer. NH_3 is expected to solvate, because of its acidic properties, the anions better than DMF (ion pairing with the alkali metal ions of the supporting electrolyte are expected to act in the same direction). In this connection, it is interesting to note that the cleavage rate constant of $PhCl^-$ is only slightly larger than that of the 1-chloronaphthalene[7b] and significantly smaller that those of 2- and 4-chlorobenzonitrile anion radicals.[7b] The rough correlation, observed in DMF, between the cleavage rate constants and the $ArX/ArX^{-\cdot}$ standard potential (the more difficult the reduction, the faster the cleavage)[13] would have predicted the opposite. A possible explanation can be derived from solvation effects. The negative charge is more concentrated in the cleavage transition state than in the starting anion radical. Solvation is thus expected to increase the cleavage rate (both on enthalpic and entropic grounds). This effect would be larger the better the delocalization of the negative charge in the anion radical and should thus be more important for the benzonitrile and naphthalene derivatives than for the chlorobenzene anion radical.

The preceding analysis of the experimental data showed that $k_2 = (2.6 \pm 0.9)10^7$ and $(3.8 \pm 1)10^8$ M^{-1} s^{-1} can be considered as reliable values of the rate constant of the reaction of phenyl radicals with benzenethiolate and diethyl phosphite ions, respectively. It is interesting to note that their ratio, 0.07, is in excellent agreement with the ratio, 0.06, found by an independent determination of the relative reactivities of the two nucleophiles.[7a]

Using these values and those of the rate constants of the cleavage of $PhSPh^{-\cdot}$ and $PhCl^{-\cdot}$ (Table I), we can now interprete several qualitative observations we have described at the beginning of the preceding section. This is best done by using a kinetic zone diagram summarizing the effect of the competition between the three concurrent pathways involving the aryl radical: attack by the nucleophile (SUBST), homogeneous electron transfer (DISP), and heterogeneous electron transfer (ECE). With the PhSPh + $(EtO)_2PO^-$ system it appears that it suffices that the concentration of the nucleophile exceed that of the substrate for total substitution to be reached as observed experimentally. Conversely, with the PhCl + PhS^- system one understands why the PhCl reduction wave is hardly affected by the addition of PhS^- even at a 0.1 M concentrations. Under these conditions it is indeed predicted that the decrease of the peak current should be less than 10%. It is also understood why only partial substitution is observed in the case of the PhCl + $(EtO)_2PO^-$ system.

From the values of the rate constants of the reaction of $Ph^\cdot$ with PhS^- and $(EtO)_2PO^-$ determined in this work, and the relative reactivities of $Ph^\cdot$ with a series of other nucleophiles reported previously,[7a] the following series of absolute rate constants (k_2, M^{-1} s^{-1}) was determined: PhS^-, 2.6×10^7; $Me_3CCOCH_2^-$, 2.7×10^8; $(EtO)_2PO^-$, 3.8×10^8; Ph_2PO^-, 7.3×10^8; Ph_2P^-, 1.6×10^9.

Two mains facts are worth emphasizing. (i) All rate constants are clearly below the diffusion limit.[14] (ii) Benzenethiolate is much less reactive than most of the other nucleophiles.

(i) It has been previously shown that, in a series of nine other aryl radicals, the rate constants are all practically at the diffusion limit with the two exceptions of the 2-quinolyl and 2-pyridyl radicals for which special ortho effects have been shown to interfere.[7b] The question thus arises as to why the phenyl radicals exhibit such a particularly low reactivity. Comparison can be made, for example, with the 1-naphthyl radical which is not activated by the presence of an electron-withdrawing group. In the latter case, the reactions with PhS^-, $(OEt)_2PO^-$, and $CH_3COCH_2^-$ are all at the diffusion limit, while in the present case the reactions with the five nucleophiles listed above are 20 to 10^3 times below the diffusion limit.

As discussed previously,[2c,7,13] the formation of the $ArNu^{-\cdot}$ anion radical as a result of the reaction of $Ar^\cdot$ with Nu^- can be viewed as a process in which the unpaired electron first occupies the σ^* C–Nu orbital and is then transferred into the π^* orbital of the aromatic system. The state in which the unpaired electron lies in the σ^* C–Nu orbital thus appears as a likely picture of the transition state for both the addition and the cleavage reactions. The following relationships apply:

$$\Delta G_f^{\ddagger} - \Delta G_c^{\ddagger} = \Delta G^\circ_{ArNu^{-\cdot}}$$

$$\Delta G^\circ_{ArNu^{-\cdot}} = \Delta G^\circ_{ArNu} - FE^\circ_{ArNu/ArNu^{-\cdot}} + FE^\circ_{Nu\cdot/Nu^-}$$

where $\Delta G_f^{\ddagger}$ and $\Delta G_c^{\ddagger}$ are the addition and cleavage activation free energies, respectively; $\Delta G^\circ_{ArNu^{-\cdot}}$ is the standard free energy of the addition reaction, ΔG°_{ArNu} is the bond strength of the C–Nu bond in ArNu, and the two E°'s are the standard potentials of the subscript redox couples. On the other hand, in the context of a Brønsted-type free-energy relationship:

$$\Delta G_f^{\ddagger} = \Delta G_s^{\ddagger} + \alpha \Delta G^\circ_{ArNu^{-\cdot}}$$

$$\Delta G_c^{\ddagger} = \Delta G_s^{\ddagger} - (1 - \alpha) \Delta G^\circ_{ArNu^{-\cdot}}$$

where $\Delta G_s^{\ddagger}$ stands for the standard activation free energy, i.e., corresponding to a unity equilibrium constant of the addition/cleavage equilibrium, and α the Brønsted transmission coefficient. It is thus expected, when comparing two Ar's with the same Nu^-, that the more negative the $ArNu/ArNu^{-\cdot}$ standard potential, the smaller the driving force, $\Delta G^\circ_{ArNu^{-\cdot}}$, of the addition reaction and therefore the slower the addition reaction. This matches what is observed when passing from the 1-naphthyl to the phenyl radical in the case of $(EtO)_2PO^-$: $\Delta E^\circ_{ArNu/ArNu^{-\cdot}} = -0.445$ V,[7b] $\Delta \log k_2 \leq -1.9$,[7b] implying that $\alpha \geq 0.2$. The same is true in the case of PhS^-: $\Delta E^\circ_{ArNu/ArNu^{-\cdot}} = -0.460$ V,[7b] $\Delta \log k_2 \leq -2.9$,[7b] corresponding to $\alpha \geq 0.29$.

In other words, when passing from naphthyl to phenyl, the energy of the σ^* orbital is likely to be approximately the same while the π^* orbital energy increases, paralleling the variations of the $ArNu/ArNu^{-\cdot}$ standard potential. The same has been demonstrated on theoretical and experimental grounds for the cleavage of aryl halides.[13,15]

The solvatation (and ion-pairing) effects evoked in the discussion of the cleavage rate constant data should also be taken into account in the present case. They are, however, expected to be less important since the concentration of negative charge when passing from $Ar^\cdot$, Nu^-, to $ArNu^{-\cdot}$ is likely to be small.

(ii) The fact that benzenethiolate is significantly less reactive than the other four nucleophiles can be simply rationalized by noting that the driving force of the addition reaction, $\Delta G^\circ_{ArNu^{-\cdot}}$, is also significantly less in the former case than with the other nucleophiles. The equilibrium constant of the addition reaction is only $2.6\ 10^3$ M^{-1} with PhS^- whereas there is no indication of reversibility of the reaction with the other nucleophiles. The decrease of the rate constant thus parallels the decrease of the driving force.

Experimental Section

The instrumentation, cell, auxilliary and reference electrodes, solvent, and supporting electrolyte characteristics were the same as have already

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(12) (a) The rate constant for the cleavage of $PhSPh^{-\cdot}$ in DMF at 25 °C was found to be 6×10^6 s^{-1}[12b] based on the combination of homogeneous redox catalysis and direct electrochemistry data according to a procedure previously used for other systems.[9a] The value 5×10^9 M^{-1} s^{-1} was used for the diffusion limit in DMF; 10^{10} M^{-1} s^{-1} actually appears as a better value as discussed earlier.[9a] Thus the $PhSPh^{-\cdot}$ cleavage rate constant can be considered as equal to 2×10^7 s^{-1}. (b) Griggio, L. *J. Electroanal. Chem.* **1982**, *140*, 155. (c) In an early publication on the homogeneous redox catalysis method, the cleavage rate constant of $PhCl^{-\cdot}$ in DMF at 22 °C was erroneously reported to be 10^7 s^{-1} because of unsufficient accuracy of the available working curves.[12d] It later appeared[9f] that the rate constant is too high to be actually determined, i.e., falls above 10^9 s^{-1}. (d) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *88*, 43.

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(14) Which does not agree with what has been previously hypothesized for all the considered nucleophiles with the exception of PhS^-.[7a]

(15) An investigation of the cleavage rate constants of a series of aryl halides in organic aprotic solvents showed a rough correlation with the standard potentials corresponding to a transmission coefficient, α, close to 0.5 There is however, no reason why α should be the same in the present case.

described.[7b] The working electrode was a gold disk (0.5-mm diameter). PhCl, PphSPh, and the various catalysts were from commercial origin with the exception of diethyl phenyl phosphite which was synthesized according to the literature.[16] The solution of benzenethiolate and diethyl phosphite ions were prepared by reduction of the conjugated acids by potassium.

Registry No. PhSPh, 139-66-2; PhCl, 108-90-7; naphthalene, 91-20-3; diethyl phenyl phosphite, 4894-60-4; 2-methylnaphthyl ether, 93-04-9; 1-methylnaphthyl ether, 2216-69-5; phenyl radical, 2396-01-2; benzenethiolate ion, 13133-62-5; diethyl phosphite ion, 62305-77-5.

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Mixed-Ligand Poly(pyridine) Complexes of Ruthenium(II). Resonance Raman Spectroscopic Evidence for Selective Population of Ligand-Localized ^{3}MLCT Excited States

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Abstract: The resonance Raman spectra of the series of mixed-ligand complexes, $Ru(bpy)_{3-N}(DMB)_N^{2+}$ (where N = 0–3 and bpy and DMB are 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine, respectively), are reported for both the ground and excited metal-to-ligand charge-transfer (MLCT) electronic states. In both sets of spectra, vibrational bands associated with the unsubstituted ligand in the mixed-ligand complexes (N = 1 and 2) are more intense than the corresponding bands from 2:1 and 1:2 mixtures of $Ru(bpy)_3^{2+}$ and $Ru(DMB)_3^{2+}$. Conversely, those bands associated with DMB ligand in the N = 1 and 2 mixed-ligand complexes are less intense than those from the 2:1 and 1:2 mixtures of the N = 0 and 3 complexes. These results are discussed in terms of localized excited states (both ^{1}MLCT and ^{3}MLCT) and indicate that, in the ^{3}MLCT state, the optical electron preferentially resides on a bpy ligand rather than on a DMB ligand, on the viabrational time scale. In addition to the Raman spectra, excited-state decay times, quantum yields, and emission energies are given. These data allow estimation of the summed nonradiative decay rate constants for the series of complexes from which a modified energy gap law plot is constructed. For complexes containing a bpy ligand, linear behavior is observed. These results imply that a substantial degree of selectivity can be induced into the charge-transfer excited states by a relatively mild chemical modification.

The metal-to-ligand charge-transfer (MLCT) excited states of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) continue to attract wide interest. A number of recent studies have suggested that these largely triplet[1] MLCT excited states are ligand-localized; that is, they are properly formulated as $[Ru^{3+}(bpy)_2(bpy^{-}\cdot)]^{2+}$. A summary of these studies includes the following.

(1) The temperature dependence of the ESR spectrum of $Ru(bpy)_3^{1+}$, where the redox orbital involved in the 2+/1+ reduction is thought to be similar to the optical orbital involved in the MLCT excited state, has been interpreted in terms of ligand-to-ligand intramolecular electron transfer, implying localized orbitals.[2,3]

(2) The absorption spectrum of $Ru(bpy)_3^{m}$, where m = 1+, 0, or 1−, contains features associated with both the (Ru–bpy) and the $bpy^{-}\cdot$ chromophores.[4]

(3) The absorption spectrum of $^*Ru(bpy)_3^{2+}$ (* indicates the ^{3}MLCT excited state) has similarities to $Na^+(bpy^{-}\cdot)$.[5]

(4) Carlin and DeArmond have employed photoselection data to present a strong case that excitation is localized in a single-ligand ring.[6]

(5) The time-resolved resonance Raman (TR^3) spectrum of the excited state is characterized by two sets of bands, one associated with the fully reduced coordinated ligand and the other corresponding to the Ru^{III}–bpy fragment.[7,8] In fact, the same frequency shifts observed in proceeding from the neutral to the anion radical form of bpy in the MLCT excited state of $Ru(bpy)_3^{2+}$ are seen in the resonance Raman (RR) spectrum of the MLCT excited state of a Re(I) compound that contains only one bipyridine, *fac*-$ClRe(CO)_3(bpy)$.[9]

(6) Finally, Angel et al. have recently shown that the RR spectrum of $[Ru^{II}(bpy)_2(bpy^{-})]^{1+}$ is a composite of the spectra of the n = 1− and 2+ spectra.[10]

Inasmuch as the localized formulation of the excited state seems now firmly estabished, it is of interest to investigate the effects of subtle modifications of the parent structure on the stability of the electronic states and pertinent photophysical processes. A few recent studies are relevant to this issue. For a series of "mixed-ligand" complexes of this type, $(RuL_{3-N}L'_N)^{2+}$, where L and L′ are distinct diimine ligands and N = 0, 1, 2, and 3, it has been generally observed that emission occurs only from the lowest ^{3}MLCT state.[11-14] In addition, Ferguson et al.[15] and Ford et al.[16]

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