It seems likely that the fluorocarbene addition to the cis olefin is also a concerted process. Yields of both cyclopropane isomers are reported in Table I for the ozonolysis of the cis olefin in $CF_3Cl$. While they suggest a preference for the cis,cis isomer, the presence of an unknown compound which could not be completely separated from the cis,cis cyclopropane makes the results less certain. It is clear that more of the cis,trans cyclopropane is produced from the trans olefin than from the cis olefin. Syn stereochemistry has been noted previously in the addition of fluorocarbene to olefins.[27]

**Ozonide Formation.** Orbital symmetry arguments were used in earlier studies to rationalize the low cis/trans ozonide ratio observed in the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene.[7,28] It was pointed out that dipole-dipole interactions may largely determine the transition state leading to final ozonide.[7] This means syn and anti fluorocarbonyl oxides preferentially form trans final ozonide. Hence, experimental conditions which may vary the syn/anti carbonyl oxide ratio will not vary the final ozonide cis/trans ratio.[7] Recent theoretical calculations are in agreement with this reasoning.[29]

Experimentally the cis/trans ozonide ratio is not very solvent dependent.[7] In addition the same ratio is obtained for the ozonolysis of vinyl fluoride where *cis*- and *trans*-1,2-difluoroethylene ozonide are obtained as cross ozonides.[3] Similarly an upper limit of 10/90 is placed upon this ratio in the ozonolysis of trifluoroethylene.[2]

The present work determines the cis/trans ozonide ratio in several new solvents over a wide temperature range and different ozone/olefin concentrations. As shown in Table I, the ratio does not vary much in $CF_3Cl$ at −95 °C and $CF_2ClCFCl_2$ at 0 °C for both the cis and trans olefin isomers. Furthermore, the ratio is not dependent upon different ozone/olefin concentrations for the trans olefin in $CF_2Cl_2$ at −78 °C. These results provide additional support for the orbital symmetry arguments presented previously.

Overall ozonide yields follow earlier reports.[7] The cis olefin produces more ozonide in $CF_3Cl$ and $CF_2ClCFCl_2$ solvents. The higher ozonide yield for the trans olefin in $CF_2Cl_2$ at larger ozone/olefin concentrations is consistent with perfluoroethylene ozonolyses.[6] In that case the highest ozone/olefin concentration (1:1 molar ratio) produced small amounts of perfluoroethylene ozonide.[6]

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(27) Schlosser, M.; Heinz, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 820-821.

(28) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348-358.

(29) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3633-3638.

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# Electron Transfer Induced Reactions. Electrochemically Stimulated Aromatic Nucleophilic Substitution in Organic Solvents

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**Abstract:** The main difference between organic solvents and solvents such as liquid ammonia as far as electrochemically induced aromatic nucleophilic substitution is concerned regards the role of H-atom abstraction from the solvent. This reaction and electron transfer at the electrode and in the solution are major side reactions competing with nucleophilic attack on the aryl radical. The resulting four-cornered competition is analyzed in the context of cyclic voltammetry and preparative scale electrolysis. In most cases, the experimental conditions can be adjusted so that the competition only involves nucleophilic attack, heterogeneous electron transfer, and H-atom abstraction. This allows a quantitative evaluation of the role of the latter reaction. Experimentally, a detailed investigation of the substitution of 9-haloanthracenes by cyanide and thiophenoxide ions has been made. Other systems for which preparative scale results were previously gathered are analyzed in the same context. A general mechanistic picture of the $S_{RN}1$ reaction can thus be drawn which is applicable to the case of electrochemical inducement but also to the other modes of stimulation. In homogeneously induced reactions, the side reactions act as termination steps in the chain mechanism. One consequence of the existence of the competing reactions, particularly H-atom abstraction, is the requirement of a rather high reactivity of the nucleophile toward aryl radicals for a good substitution yield to be reached. The positive counterpart of these negative aspects is that the very existence of side reactions that can be independently characterized allows the mechanism and reactivity patterns of the nucleophilic attack to be investigated. Proofs of the $S_{RN}1$ as opposed to an $S_{RN}2$ mechanism are discussed in this context as well as the nucleophile-aryl radical reactivity data so far obtained by electrochemical means.

Aromatic nucleophilic substitution occurring along an $S_{RN}1$ mechanism[2] can be stimulated in various ways involving all the introduction in the reaction medium or the in-situ generation of one-electron reducing agents: photostimulation,[2] addition of alkali metals dissolved in liquid ammonia,[2] injection of electrons from an electrode,[3] and addition of the anion radical of the substituted product.[4] The electrochemical approach to $S_{RN}1$ aromatic nucleophilic substitution[3] has provided a kinetically based demonstration of the validity of the $S_{RN}1$ mechanism originally proposed on the basis of qualitative arguments.[2] This demonstration con-

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(2) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(3) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

(4) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

0002-7863/82/1504-0817$01.25/0

cerned $S_{RN}1$ reactions occurring in liquid ammonia where the situation is relatively simple due to the fact that $NH_3$ is a poor H-atom donor.[5,6] The only reactions competing with the substitution process are then homogeneous and/or heterogeneous electron transfers to the aryl radical which is the key intermediate of the substitution reaction:

$$ArX + 1e \rightleftarrows ArX^{-}\cdot \qquad (E_0) \tag{0}$$

$$ArX^{-}\cdot \xrightarrow{k_1} Ar\cdot + X^- \tag{1}$$

substitution

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

$$ArNu^{-}\cdot - 1e \rightarrow ArNu \qquad (E^\circ_3) \tag{3}$$

and/or

$$ArNu^{-}\cdot + ArX \rightarrow ArNu + ArX^{-}\cdot \tag{4}$$

electron transfer

$$Ar\cdot + 1e \rightarrow Ar^- \tag{5}$$

$$Ar\cdot + ArX^{-}\cdot \xrightarrow{k_D} Ar^- + ArX \tag{6}$$

$$Ar\cdot + ArNu^{-}\cdot \xrightarrow{k_D} Ar^- + ArNu \tag{6'}$$

$$Ar^- + NH_3 \rightarrow ArH + NH_2^-$$

The demonstration of the mechanism, in the context of cyclic voltammetry[6,9] or preparative scale electrolysis,[6,10] was based on a detailed investigation of the competition between the substitution process leading to ArNu and the homogeneous and heterogeneous electron-transfer reactions leading ultimately to ArH.

Although several examples of electrochemically induced aromatic nucleophilic substitution reactions in organic solvents have been reported,[11,13] no systematic investigation of the reaction mechanism, comparable to what was done in the case of liquid ammonia, has been carried out so far. The situation is indeed more complex since, besides the same electron-transfer reactions as in liquid ammonia, hydrogen-atom transfer from the solvent to the aryl radical is likely to be a major side reaction competing with the substitution process.[3,12] Most of the organic solvents usually employed in organic electrochemistry, such as $CH_3CN$, $Me_2SO$, and DMF, are indeed good H-atom donors and aryl radicals good H-atom acceptors.[14,16] The following reactions are thus anticipated to interfere concurrently with reactions 0–6'. H-atom abstraction by the aryl radical yields in a first stage the same hydrogenolysis product, ArH, as the electron-transfer side reactions together with the radical of the solvent (SH):

$$Ar\cdot + SH \xrightarrow{k_7} ArH + S\cdot \tag{7}$$

The latter radical may undergo several reactions. With solvents such as $CH_3CN$ and $Me_2SO$, where S· is an easily reducible species, the main following steps will be further electron transfer from the electrode and/or from solution species (see ref 17 and references cited therein):

$$S\cdot + 1e \rightarrow S^- \tag{8}$$

$$S\cdot + ArX^{-}\cdot \rightarrow S^- + ArX \tag{9}$$

$$S\cdot + ArNu^{-}\cdot \rightarrow S^- + ArNu \tag{9'}$$

With a sufficient amount of water present, $S^-$ will be protonated by water and thus will not be able to act as a powerful nucleophile leading to another substitution process as already observed in some cases.[18]

In other words, a four-cornered competition—nucleophilic attack, H-atom transfer, and homogeneous and heterogeneous electron transfers—is anticipated to occur at the level of the intermediate aryl radical. The purpose of the present paper is to analyze this rather complex problem. A discussion of its general aspects will first show how it is possible to simplify the competition situation so as to render it more easily amenable to analysis. Several experimental examples will then be discussed on these bases in the context of cyclic voltammetry and preparative scale electrolysis.

## General Aspects of the Competition between Nucleophilic Attack, H-Atom Transfer, and Electron Transfer to the Aryl Radical

As previously discussed,[19] the competition between homogeneous and heterogeneous electron transfers (i.e., competition between "Ece" and "Disp" pathways) in the absence of H-atom transfer and of nucleophilic attack is a function of the parameter $p = (k_D C^0/k_1^{3/2})\theta^{1/2}$, with $\theta = (Fv/RT)$ for cyclic voltammetry and $\theta = (D/\delta^2)$ for preparative scale electrolysis. $k_1$ is the rate constant for the cleavage of the initial anion radical, $ArX^{-}\cdot$, $k_D$ the rate constant for the homogeneous electron transfer (eq 6), usually close to the diffusion limit, $k_{dif}$, $C^0$ the initial concentration of ArX, $v$ the sweep rate in cyclic voltammetry, $\delta$ the diffusion layer thickness in preparative scale electrolysis, and $D$ the diffusion coefficient which is assumed to be approximately the same for all the interfering species. As $p$ increases the Disp pathway tends to prevail over the Ece pathway and vice versa. The dependence of $p$ upon $C^0$ and $v$ (or $\delta$) reflects the fact that the competition occurs between a first order (Ece) and a second order (Disp) process. Of particular importance is the role of $k_1$: the larger $k_1$ the more efficient the Ece pathway and vice versa. The physical reasons for this can be pictured as follows: when $k_1$ is large, Ar· is formed close to the electrode surface to where it can diffuse back and be reduced before having time to react with $ArX^{-}\cdot$ in the solution. The reverse situation is met for small values of $k_1$ leading the Disp pathway to prevail.

If now, still in the absence of nucleophilic attack, one considers the interference of the H-atom abstraction reaction, i.e., the conditions prevailing for the reduction of aromatic halides in solvents such as $CH_3CN$ and $Me_2SO$, it has been shown[18,20] that the three-cornered competition between H-atom transfer and heterogeneous and homogeneous electron transfer depends upon two dimensionless parameters: $\sigma_H = k_1/k_7$ and $\rho_H = (k_D/k_1^{1/2}k_7)C^0\theta^{1/2}$, where $k_7$ is the pseudo-first-order rate constant of the H-atom transfer reaction and $\theta$ has the same meaning as above. The number of electron per molecule is the same (i.e, 2) whether electron transfer or H-atom transfer is predominating. Electrochemical techniques such as cyclic voltammetry are therefore of

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(5) (a) Bunnett, J. F.; Gloor, B. F. *J. Org. Chem.* **1974**, *39*, 383. (b) Belloni, J. *Actions Chim. Biol. Radiat.* **1971**, *15*, 47.

(6) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.

(7) Amatore, C.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1979**, *103*, 303.

(8) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1980**, *107*, 59.

(9) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1980**, *107*, 75.

(10) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1981**, *123*, 231.

(11) Pinson, J.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1974**, 934.

(12) Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 1506.

(13) Praefcke, K.; Weichsel, Ch.; Falsig, M.; Lund, H. *Acta Chem. Scand., Ser. B* **1980**, *34*, 403.

(14) Russel, G. In "Free Radicals", Kochi, J., Ed.; John Wiley: New York, 1973; Vol. I, p 275.

(15) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.

(16) Pryor, A.; Echols, J. T.; Smith, K. *J. Am. Chem. Soc.* **1966**, *88*, 1189.

(17) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

(18) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *89*, 347.

(19) (a) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27; (b) **1978**, *86*, 227; (c) **1981**, *123*, 189.

(20) Amatore, C.; M'Halla, F.; Savéant, J. M. *J. Electroanal. Chem.* **1981**, *123*, 219.

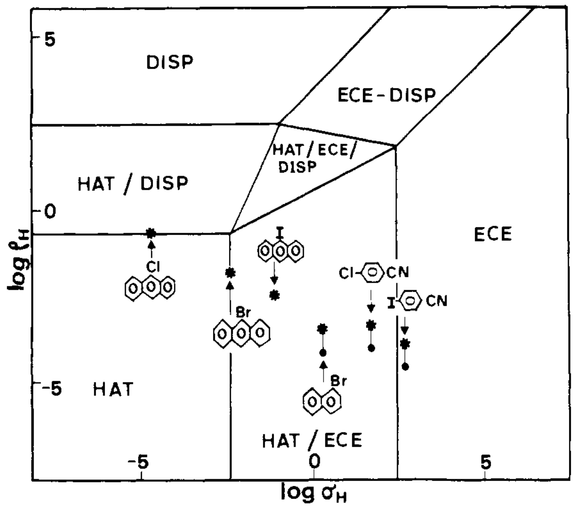

Figure 1. Diagrammatic representation of the amounts of ArH formed in the reduction of ArX in an organic solvent through H-atom (Hat), homogeneous (Disp), and heterogeneous electron transfer (ECE), respectively, as a function of the parameters $\sigma_H = k_1/k_7$ and $\rho_H = (k_D/k_1^{1/2}k_7)C^0\theta^{1/2}$ with $\theta = D/\delta^2$ for preparative scale electrolysis and $\theta = FV/RT$ for cyclic voltammetry: (*) cyclic voltammetry with $C^0 = 10^{-3}$ M, $v = 0.1$ V s$^{-1}$; (●) preparative scale electrolysis with $C^0 = 10^{-2}$ M, $\delta = 3 \times 10^{-3}$ cm, $D = 10^{-5}$ cm$^2$ s$^{-1}$.

no use for distinguishing between these pathways and determining their relative importance. This can be arrived at by analyzing the product distribution after preparative electrolysis with an appropriate labeling of the ArH resulting from electron transfer and the ArH resulting from H-atom transfer. Electrolysis in mixtures of $D_2O$ (10%) with the undeuterated solvent and of $H_2O$ (10%) with the perdeuterated solvent has been used in this connection.[17] The dependence of the yields in ArH arising from H-atom transfer and heterogeneous and homogeneous electron transfer upon the two parameters $\sigma$ and $\rho$ is shown in Figure 1. From an operational viewpoint this diagram represents what product distribution is expected in the above-mentioned deuteration experiments according to the values of the operational ($C^0$, $\delta$) and intrinsic ($k_1$, $k_D$, $k_7$) parameters. It will however also represent the relative importance of the three competing pathways in cyclic voltammetry with $(Fv/RT)^{1/2}$ replacing $(D^{1/2}/\delta)$.

In order to illustrate the above discussion Figure 1 shows on the zone diagram the location of the various experimental systems to be described in the following. The locations of the corresponding points derive from the deuteration data previously obtained[17] adapted to the experimental conditions, i.e., the values of $C^0$, $\delta$, or $v$, of the present study. It is seen that by adjusting the experimental conditions—essentially the substrate concentration—it is possible to render the homogeneous electron-transfer pathway of negligible importance as compared to the H-atom transfer pathway. The latter will either be the predominating route to ArH or compete with the heterogeneous electron-transfer pathway. Under such conditions, the fractions of ArH formed through H-atom transfer and electron transfer respectively are simple functions of the single parameter $\sigma_H$: $\text{Hat(ArH)} = \sigma_H^{1/2}/(1 + \sigma_H^{1/2}) = k_1^{1/2}/(k_1^{1/2} + k_7^{1/2})$, $\text{Ece(ArH)} = 1/(1 + \sigma_H^{1/2}) = k_7^{1/2}/(k_1^{1/2} + k_7^{1/2})$. It is noted that they are independent of both initial concentration and diffusion layer thickness or sweep rate, which reflects the first-order character of the two competing pathways.

The competition between nucleophilic attack and electron transfer to the aryl radical in the absence of H-atom abstraction, as illustrated by what occurs in liquid ammonia, depends similarly upon two dimensionless parameters: $\sigma_{Nu} = k_1/k_2[\text{Nu}^-]$ and $\rho_{Nu} = (k_D/k_1^{1/2}k_2)(C^0/[\text{Nu}^-])\theta^{1/2}$ where $k_2$ is the second-order rate constant of the nucleophilic attack, $[\text{Nu}^-]$ is the concentration of the nucleophile which is assumed to be present in excess so reaction 2 can be pseudofirst order, and $\theta$ has the same meaning as above. The kinetics of the competition is thus of the same type as in the preceding case. There is however a very important difference: increasing efficiency of the substitution process results in a decrease of the number of electrons per molecule, at the level of the ArX reduction wave, from 2 to 1 or 0 while it remained equal to 2 whatever the outcome of the competition in the H-atom abstraction case. This allows techniques such as cyclic voltammetry to be used for investigating the efficiency of the substitution process against the electron-transfer side reactions. Two cases must be distinguished in this connection:

(i) The standard potential of the ArNu/ArNu$^{-\cdot}$ couple, $E_3^0$, must be negative to the reduction potential[21] of the starting material, $E_0$. The number of electrons per molecule would then tend toward zero as the substitution process becomes more and more efficient. This has been referred to as a "catalytic" situation.[3,4,6,7,9] Electrolysis at the ArX reduction wave would indeed yield directly ArNu since it is electrochemically stable at this potential.

(ii) For the opposite order of the potentials, $E_3^0 > E_0$, the number of electrons per molecule would tend toward 1 as the efficiency of the substitution process increases. The substituted product would then be obtained as its anion radical upon electrolysis at the ArX reduction wave. For this reason, the situation has been referred to as "noncatalytic".[3,4,6-8]

The height of the peak current is thus a measure of the degree of competition between the nucleophilic attack in eq 2 and the electron transfers in eq 5 and 6. It depends upon $\rho_{Nu}$ and $\sigma_{Nu}$ as do the yields of ArNu (or ArNu$^{-\cdot}$) and ArH in preparative scale electrolysis.

In the general case where H-atom abstraction as well as homogeneous and heterogeneous electron transfer compete with the nucleophilic attack of the aryl radical, the kinetic situation is too complex to allow a general treatment of the problem in the context of cyclic voltammetry as well as preparative scale electrolysis. However, as noted before, experimental conditions where homogeneous electron transfer can be neglected are not too difficult to achieve. The Hat–Ece–Subst competition then going on is a function of the two parameters $\sigma_H$ and $\sigma_{Nu}$ featuring the competition between H-atom and heterogeneous electron transfer and between the latter and nucleophilic attack, respectively.

When $\sigma_H \rightarrow 0$, as can be evaluated using the zone diagram in Figure 1, only the competition between H-atom transfer and substitution remains. The peak current of the ArX wave is then straightforwardly given by[23]

$$i_p/i_p^0 = k_7/(k_7 + k_2[\text{Nu}^-]) \tag{10}$$

in the "catalytic case" and

$$i_p/i_p^0 = (2k_7 + k_2[\text{Nu}^-])/2(k_7 + k_2[\text{Nu}^-]) \tag{11}$$

in the "noncatalytic" case where $i_p^0$ is the peak current of the ArX wave in the absence of nucleophile. Similarly the yields (%) in preparative scale electrolysis will be:

$$\begin{aligned} \text{Ar Nu(or ArNu}^{-\cdot}\text{) \%} &= k_2[\text{Nu}^-]/(k_7 + k_2[\text{Nu}^-]) \\ \text{ArH \%} &= k_7/(k_7 + k_2[\text{Nu}^-]) \end{aligned} \tag{12}$$

In the more general case of a three-cornered Hat–Ece–Subst competition, the peak current is expressed[24] as

$$\begin{aligned} i_p/i_p^0 = {} & \{k_7/(k_7 + k_2[\text{Nu}^-])\} + \\ & \{k_2[\text{Nu}^-]/(k_7 + k_2[\text{Nu}^-])\}k_1^{1/2}/\{k_1^{1/2} + (k_7 + k_2[\text{Nu}^-])^{1/2}\} \end{aligned} \tag{13}$$

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(21) The "reduction potential" of ArX can be taken as the peak or half-peak potential in cyclic voltammetry and as the half-wave potential in polarography and preparative scale electrolysis (potential at which the initial current is half of the maximal current). In all cases it is a function of the standard potential, transfert coefficient, standard rate constant of the initial electron transfer (eq 0), and/or the irreversible reaction 1 together with the parameter featuring the diffusion rate (sweep rate in cyclic voltammetry, diffusion layer thickness in preparative scale electrolysis).[22]

(22) Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113.

(23) Once one molecule of Ar· has been produced from ArX with the consumption of one elctron, $k_7/(k_7 + k_2[\text{Nu}^-])$Ar· are converted into ArH with the consumption of one electron while $k_2(\text{Nu}^-)/(k_7 + k_2[\text{Nu}^-])$ is converted into ArNu$^{-\cdot}$ with no electron consumption in the noncatalytic case and into ArNu with the release of one electron in the catalytic case.

in the “catalytic case” and as

$$i_p/i_p{}^0 = \{(2k_7 + k_2[\mathrm{Nu^-}])/2(k_7 + k_2[\mathrm{Nu^-}])\} + \{k_2[\mathrm{Nu^-}]/2(k_7 + k_2[\mathrm{Nu^-}])\}k_1{}^{1/2}/\{k_1{}^{1/2} + (k_7 + k_2[\mathrm{Nu^-}])^{1/2}\} \quad (14)$$

in the “noncatalytic case”. The yields in preparative scale electrolysis are given by

$$\mathrm{ArNu\ (or\ ArNu^{-}\cdot)\ \%} = k_2[\mathrm{Nu^-}]/(k_7 + k_2[\mathrm{Nu^-}])^{1/2}\{k_1{}^{1/2} + (k_7 + k_2[\mathrm{Nu^-}])^{1/2}\} \quad (15)$$

with ArH % = 1 − ArNu or $\mathrm{ArNu^{-}\cdot}$ %.

In all the above discussion it was implicitely assumed that no chain process leading to substitution occurs in the bulk of the solution. More precisely, it was assumed that all the reactions leading to substitution as well as the side reactions leading to ArH take place in a reaction layer adjacent to the electrode surface, the thickness of which is small as compared to that of the diffusion layer. In this context, the assumption the reaction 4 does not occur outside the reaction layer is particularly important since this is the key step of a chain process leading to substitution.[2,4] Situations may however exist in which this assumption is not valid, i.e., $\mathrm{ArNu^{-}\cdot}$ is able to escape from the reaction layer and thus to trigger the chain process in the diffusion layer or even in the bulk of the solution. For a given system, this is more likely to happen in preparative scale electrolysis than in cyclic voltammetry since much more $\mathrm{ArNu^{-}\cdot}$ is produced during the same time and the electrolysis durations are longer in the first case than in the second. This is the reason why triggering of the chain process in the bulk of the solution during cyclic voltammetric experiments requires that the nucleophilic attack be exceptionally fast. A few systems of that sort have been reported[4] involving the substitution of 2-chloroquinoline by acetonitrile and triphenylmethane conjugated bases and of 1-chloronaphthalene by the lutidine carbanion in liquid ammonia. The diagnosis of such a phenomenon is simple: the waves of the substrate completely disappear after a small number of cycles.

On the other hand, the appearance of trace crossings[8] and dips[9] on time-stable cyclic voltammograms is indicative of the triggering of the chain process in the diffusion layer. It has been shown that these phenomena can be quantitatively modeled.[8,9] Trace crossings appear in “noncatalytic” situations thus corresponding to $\mathrm{ArNu^{-}\cdot}$ being the electrochemically stable form of the substitution product in the potential range of the substrate wave. The $\mathrm{ArNu^{-}\cdot}$ thus formed at the reduction potential of the substrate are then able to trigger the chain process within the time scale of the cyclic voltammetric experiments. Dips may appear in “catalytic” situations involving an Ece type mechanism. They are observed at the foot of the wave of the substituted product, i.e., in a potential region where $\mathrm{ArNu^{-}\cdot}$ is less and less easily reoxidized into ArNu at the electrode. The $\mathrm{ArNu^{-}\cdot}$ thus escaping electrode reoxidation are then able to trigger the chain process in the diffusion layer. If the standard potential of the $\mathrm{ArNu/ArNu^{-}\cdot}$ couple is not too far from the reduction potential of the substrate the dip phenomenon may interfere at the wave of the substrate itself. Such phenomena have been so far observed mainly for reactions occurring in liquid ammonia but they may well appear in organic solvents too as will be shown in the following. Their observation provides an interesting qualitative diagnostic criterion of the occurrence of a chain process going on in the bulk of the solution in preparative scale experiments.

Table I. Characteristic Rate Constants for the Reduction of 9-Haloanthracene in $\mathrm{Me_2SO}$

| halogen | cleavage of the anion radical $k_1$, $\mathrm{s^{-1}}$ | H-atom transfer from $\mathrm{Me_2SO}$ $k_2$, $\mathrm{s^{-1}}$ |
|---|---|---|
| Cl | $(1.5 \pm 0.1) \times 10^{2}$ [a] | $(7.5 \pm 2) \times 10^{6}$ [b] |
| Br | $(9 \pm 4) \times 10^{4}$ [b] | |
| I | $(9 \pm 4) \times 10^{5}$ [b] | |

[a] From cyclic voltammetry.[17] [b] From deuteration experiments,[17] based on $k_{\mathrm{dif}} = 5 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$.

From a strictly electrochemical point of view the “noncatalytic” situation is the most favorable since $\mathrm{ArNu^{-}\cdot}$ produced at the substrate wave cannot be oxidized at the electrode surface. The efficiency of the chain in the solution[4] then depends upon the rates of the steps involved in the propagation cycle: cleavage of $\mathrm{ArX^{-}\cdot}$, nucleophilic attack, forward electron transfer $\mathrm{ArNu^{-}\cdot + ArX \rightarrow ArNu + ArX^{-}\cdot}$, and the rates of the termination step. In this context the “noncatalytic” situation is unfavorable as far as the electron transfer involved in the propagation cycle is concerned. However, the most important factor regards the termination steps: if these are slower than the nucleophilic attack a good efficiency of the chain process will be observed. In the case where H-atom transfer (eq 7) is the predominent termination step, the efficiency of the chain process will mainly depend upon the ratio $k_7/k_2[\mathrm{Nu^-}]$. Under such conditions, considerable trace crossings will be an indication that an efficient chain process is taking place in the solution.

In the “catalytic” case, $\mathrm{ArNu^{-}\cdot}$ produced by nucleophilic attack on Ar· can be reoxidized at the electrode surface, showing that this situation is not favorable to the occurrence of an efficient chain process in the solution from a strictly electrochemical point of view. This unfavorable character will be the more pronounced the more negative the $\mathrm{ArNu/ArNu^{-}\cdot}$ couple is located from the reduction potential of the substrate and the faster the cleavage of $\mathrm{ArX^{-}\cdot}$ which implies a faster reoxidation of $\mathrm{ArNu^{-}\cdot}$ at the electrode surface. On the other hand, these conditions are favorable for a fast rotation of the propagation cycle in the solution.[4] However, the main factor controlling the efficiency of the chain process is again the relative rapidity of the nucleophilic attack as compared to the termination steps, i.e., the ratio $k_7/k_2[\mathrm{Nu^-}]$. It follows that the appearance of a deep dip close to the substrate wave, possibly overlapping the latter wave, will be an indication that an efficient chain process is taking place in the solution and vice versa.

Turning back to the simplified conditions we have selected for the present investigation as illustrated by the systems shown in Figure 1, the same two cases as discussed before can be distinguished:

If H-atom transfer completely predominates not only over homogeneous but also heterogeneous electron transfer, the final yields in ArNu and ArH will not depend upon the occurrence of the chain process in the solution, being given by eq 12 in all cases. What will change is merely the time required for the electrochemical induction of the reaction. This will be shorter in the case where the chain process proceeds efficiently in the solution than in the case where all the process is completed within a thin reaction layer adjacent to the electrode surface.

If H-atom transfer although faster than the homogeneous electron transfer does not necessarily predominate over heterogeneous electron transfer (Hat–Ece–Subst competition), the yields may be quite different for a “catalytic” situation whether the chain process is effectively going on in the solution or not which can be recognized by the location and the deepness of the current dips as discussed above. In the first case the yields will be given by eq 12, while in the second they will be given by eq 15.

## Substitution of 9-Haloanthracenes in $\mathrm{Me_2SO}$

9-Chloro-, 9-bromo-, and 9-iodoanthracenes constitute a suitable series to be investigated in this respect since the competition between electron transfer and H-atom transfer during their reduction in the absence of nucleophile has been thoroughly studied by deuteration experiments.[17,20] The behavior obtained for re-

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(24) Per one molecule of Ar· produced from one ArX with the consumption of one electron, $k_1{}^{1/2}/\{k_1{}^{1/2} + (k + k_2[\mathrm{Nu^-}])^{1/2}\}$ are converted into ArH through the Ece pathway with the consumption of one electron. From what remains a fraction equal to $k_7/(k_7 + k_2[\mathrm{Nu^-}])$ is converted into ArH along the Hat pathway with the consumption of one electron while a fraction equal to $k_2[\mathrm{Nu^-}]/(k_7 + k_2[\mathrm{Nu^-}])$ is converted into $\mathrm{ArNu^{-}\cdot}$ with no electron consumption in the “noncatalytic case” and into ArNu with the release of one electron in the “catalytic case”. The calculation of the fraction of Ar· undergoing a heterogeneous electron transfer as opposed to the fraction corresponding to H-atom transfer and nucleophilic attack as a whole is based on the same reasonings as for the Ece–Hat[17,20] and the Ece–Subst[7,10] competitions.

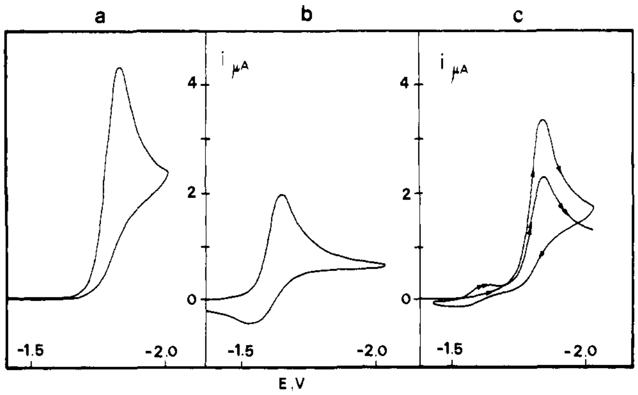

**Figure 2.** Cyclic voltammetry in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$ of: (a) 9-bromoanthracene ($10^{-3}$ M); (b) 9-cyanoanthracene ($10^{-3}$ M); (c) 9-bromoanthracene ($10^{-3}$ M) + $CN^-$ (0.08 M). (→) first scan, (→•→) second scan, sweep rate 0.25 V $s^{-1}$, reference electrode Ag|0.01 M $Ag^+$.

ductions in $Me_2SO$ in the presence of 10% $H_2O$ follows satisfactorily the above analysis summarized by the diagram in Figure 1. The values of $k_1$ have been determined by cyclic voltammetry or homogeneous redox catalysis leading to the derivation of $k_7$ from the deuteration experiments as reported in Table I.[25] The cyclic voltammetric experiments described below were carried out in the same experimental conditions.[25] Two nucleophiles were investigated, the cyanide ion and the thiophenoxide ion, corresponding to a "noncatalytic" and a "catalytic" situation, respectively.

**Cyanide Ion as the Nucleophile.** Figure 2 shows a typical example of what happens in cyclic voltammetry when cyanide ions ($8 \times 10^{-2}$ M) are added to a solution of *9-bromoanthracene* ($10^{-3}$ M) in $Me_2SO$. A similar behavior is observed with *9-chloroanthracene*. A significant decrease of the haloanthracene wave is observed during the first cathodic sweep while an anodic wave corresponding to the anion radical of 9-cyanoanthracene appears upon reoxidation. The redox couple of the 9-cyanoanthracene builds up upon repetitive cycling while the substrate wave goes on decreasing. This behavior is typical of a "noncatalytic" substitution process,[6,8,12] the strong mesomeric electron withdrawing character of the cyano substituent resulting in a standard potential of the substituted product positive to the reduction potential of the halo derivative. It is however noted that the 9-cyanoanthracene wave remains smaller than what is expected from the decrease of the substrate wave. This is due to the instability of the 9-cyanoanthracene anion radical toward dimerization.[26,27] At the substrate wave, this reaction does not play any role in the overall kinetics since it takes place after the rate-determining steps and does not change the number of electrons exchanged.

For both the chloro and the bromo derivatives H-atom transfer largely predominates over homogeneous and heterogeneous electron transfer (Figure 1). In the presence of cyanide ions a Hat–Subst competition is thus anticipated. The peak current of the substrate wave should then vary with the cyanide ion concentration according to eq 11. This is indeed what is experimentally observed as shown in Figure 3 since the quantity $(i_p^0 - i_p)/(2i_p - i_p^0)$ appears to be proportional to $[CN^-]$. It is noteworthy that the chloro and the bromo derivative give rise to the same straight line, the slope of which provides the ratio of the rate constants of H-atom transfer and nucleophilic attack: $k_7/k_2$ = 0.12 M. Using the value of $k_7$ previously determined[17] (Table I) it is found that $k_2 = 6.5 \times 10^7$ $M^{-1}$ $s^{-1}$.

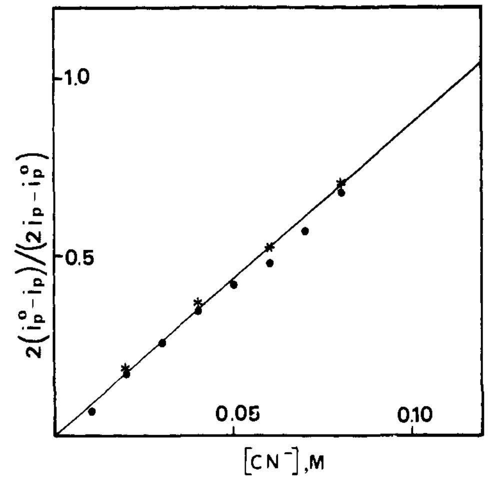

**Figure 3.** Variations of the peak height ($i_p$) of 9-chloro (*) and 9-bromoanthracene (●) with the concentration of $CN^-$ in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$ as analyzed according to eq 11. Sweep rate 0.25 V $s^{-1}$, $i_p^0$ = peak height in the absence of $CN^-$.

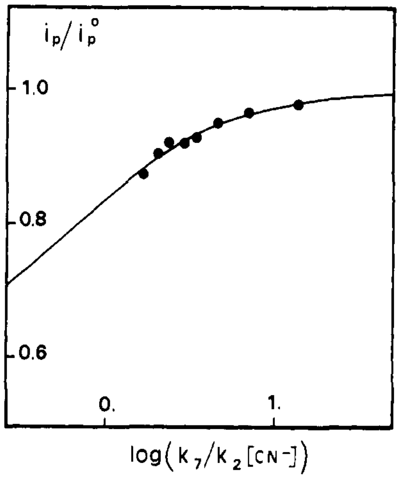

**Figure 4.** Variations of the peak height ($i_p$) of 9-iodoanthracene with the concentration of $CN^-$ in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$ as analyzed according to eq 13. Sweep rate 0.25 V $s^{-1}$, $i_p^0$ = peak height in the absence of $CN^-$.

It is difficult to carry out a meaningful investigation of the same reaction at the preparative level. Indeed while cyclic voltammetry of 9-cyanoanthracene indicates the formation of a dimer,[26,27] preparative scale reduction leads to quite different products after workup, mainly anthaquinone and the starting compound. It is however noted that the yield in anthracene (80%) obtained upon reduction of 9-bromoanthracene ($10^{-3}$ M) in the presence of $CN^-$ ($8 \times 10^{-2}$ M) is on the same order of magnitude as the yield calculated from eq 12 (60%).

In the case of *9-iodoanthracene*, the cyclic voltammograms recorded in the presence of $CN^-$ are qualitatively similar to those obtained with the chloro and bromo derivatives. Quantitatively, however, the situation is different insofar as the competition with heterogeneous electron transfer can no longer be neglected as compared to H-atom transfer and nucleophilic attack as is clearly seen in the zone diagram in Figure 1. It is thus predicted that the variations of the $i_p/i_p^0$ ratio with $[CN^-]$ should follow eq 14. This is what is observed experimentally (Figure 4), the best fitting, starting from $k_1 = 5 \times 10^5$ $s^{-1}$ (Table I) being obtained for $k_7/k_2$ = 0.13 M, in close agreement with what was found for the chloro and bromo derivatives.

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(25) The data in Table I pertain to experiments carried out in 10% $H_2O$–$Me_2SO$ mixtures with 0.1 M $LiClO_4$ as supporting electrolyte.[17] Such a high concentration of water was necessary both to lower the error due to residual water and to protonate the $^-CH_2$–$SOCH_3$ anion which could react on the anthryl radical similarly to what was observed in the case of 4-bromobenzophenone.[18] The use of tetraalkylammonium salts as supporting electrolyte was avoided since they may give rise themselves to H-atom transfer. In the present cyclic voltammetric experiments carried out with the same composition of the solution on a mercury working electrode, it was observed that the use of a lithium salt leads to a slow passivation of the electrode surface at negative potentials presumably due to the formation of lithium hydroxide at the electrode surface. This is the reason why a dropping mercury electrode was used instead of a hanging mercury drop electrode.

(26) Yildiz, A.; Baumgärtel, H. *Ber. Bunsenges. Gesel.* **1977**, *81*, 1177.

(27) Amatore, C.; Pinson, J.; Savéant, J. M., submitted.

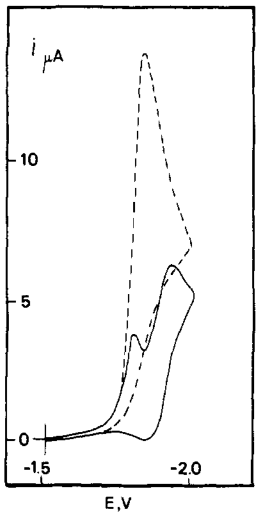

**Figure 5.** Cyclic voltammetry of 9-bromoanthracene ($10^{-3}$ M) in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$ in the absence (- - -) and in the presence (—) of lithium thiophenoxide (0.06 M). Sweep rate 0.25 V $s^{-1}$, reference electrode Ag|0.01 M $Ag^+$.

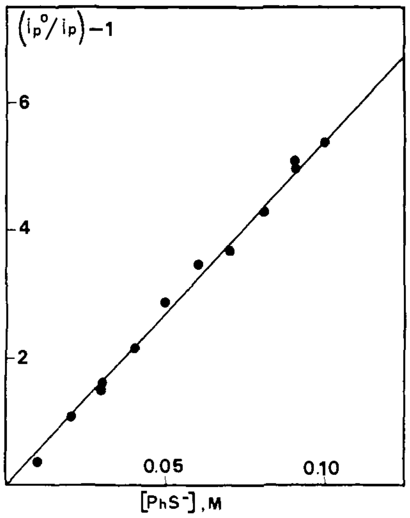

**Figure 6.** Variations of the peak height ($i_p$) of 9-bromoanthracene ($10^{-3}$ M) with the concentration of $PhS^-$ in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$ as analyzed according to eq 10. Sweep rate 0.25 V $s^{-1}$, $i_p^0$ = peak height in the absence of $PhS^-$.

**Thiophenoxide Ion as the Nucleophile.** The reaction with $PhS^-$ was investigated with *9-bromoanthracene* as the substrate giving rise to a "catalytic" situation since, due to the electron-donating character of the PhS substituent, the $E^0$ of the substituted product is negative to the reduction potential of the substrate as seen in Figure 5 where the addition of $PhS^-$ is shown to decrease the wave of 9-bromoanthracene and, accordingly, to make the reversible wave of 9-thiophenoxyanthracene appear. It is thus expected that the variation of the peak height with the concentration of $PhS^-$ follow the behavior depicted by eq 10 since H-atom transfer is the only reaction competing with nucleophilic attack (Figure 1). This is indeed what is experimentally found as shown on Figure 6. From the slope of the straight line thus obtained the ratio between the rate constants for H-atom transfer and nucleophilic attack is found to be: $k_7/k_2 = 1.8 \times 10^{-2}$ M, and therefore $k_2 = 4.5 \times 10^8$ $M^{-1}$ $s^{-1}$.

An electrolysis of 9-bromoanthracene ($10^{-3}$ M) in $Me_2SO$ + 10% $H_2O$ + 0.1 M $LiClO_4$, in the presence of PhSLi leads to about 80% of 9-anthrylphenyl sulfide[28] as determined by polarography of the electrolyzed solution and 20% of anthracene which compares satisfactorily with the yields predicted on the basis of the above determined rate constant ratio, 83% and 17%, respectively.

## Other Systems

The following discussion is devoted to substrate–nucleophile systems for which preparative scale electrolysis data have been previously gathered.[11,12] Cyclic voltammetric data pertaining to these systems are described and used to evaluate the characteristic rate constant ratios. The electrolysis yields predicted on this basis are then compared with the observed yields. It should be emphasized in this respect that the determination of the latter suffer from rather larger uncertainties due to various causes: further reaction in the injector of uncompletely reacted systems when gas chromatography of the electrolyzed solution is directly used as an analytical tool and chemical reactivity of the nucleophile toward other reactants than the starting halide. The latter is observed for tetraalkylammonium thiophenoxide which slowly decomposes presumably by reaction of $PhS^-$ with $NR_4^+$. $PhS^-$ is also very sensitive to oxygen leading to the formation of the diphenyldisulfide. While the ratio between the rate constants for nucleophilic attack and H-atom abstraction can be derived from cyclic voltammetry, the absolute value of the former cannot be obtained in the absence of data about the latter. Rate constants of H-atom abstraction derived from deuteration experiments carried out in $LiClO_4$ solutions with 10% $H_2O$[17] cannot be soundly used for treating the data obtained with solutions containing tetraalkylammonium salts as supporting electrolyte and low water concentrations. One reason for this is the possible interference of the ammonium cations as H-atom donor particularly in regions where they are highly concentrated as is the case in the double layer. This phenomenon, if interfering, may also lead to some difference between what happens in cyclic voltammetry and in preparative scale electrolysis, being another source of inaccuracy in the comparison between the data obtained by each type of experiment. What follows thus just aims at a semiquantitative description of the course of the substitution in terms of its competition with H-atom abstraction revealing the trends of main chemical significance when varying the nucleophile, the substrate, and the solvent.

**Substitution of 4-bromobenzophenone by thiolates and cyanide ions** provides an example of a situation where H-atom abstraction is practically the only side reaction competiting with nuleophilic attack of the aryl radical. This is clearly shown by the results of deuteration experiments carried out in $Me_2SO$ and $CH_3CN$ in the presence of a quaternary ammonium salt as supporting electrolyte (Table 3 in ref 18).

The height of the reduction peak of 4-bromobenzophenone decreases upon addition of $PhS^-$, $t\text{-}C_4H_9S^-$, or $CH_3S^-$ with concomitant appearance of a wave of increasing height corresponding to the reduction of the substituted product. The latter, due again to the electron-donating character of the thiolate group, is located at potential negative to the substrate wave. The kinetic situation is thus of the "catalytic" type. No dips are observed at the foot of the wave of the substituted product. This is related to the fact that the cleavage of the 4-bromobenzophenone anion radical being relatively slow,[29] the reoxidation of $C_6H_5COC_6H_4SC_6H_5^{-}\cdot$ essentially occurs by electron transfer to the substrate rather than at the electrode surface. The height of the substrate wave is thus anticipated to vary with the thiolate concentration according to eq 10. This is indeed what is experimentally observed as shown in Figure 7 where it is seen that $(i_p/i_p^0) - 1$ is proportional to the thiolate concentration. The rate ratio $k_2/k_7$ is derived from the slope of the corresponding straight line leading to the values listed in Table III. It is noted that the reactivities of the three thiolates on the 4-benzoylphenyl radical lie in the order $PhS^- > t\text{-}C_4H_9S^- > CH_3S^-$. The values thus found for $k_2/k_7$ can then be used to calculate the predicted yields in preparative scale electrolysis. It is seen that the predicted yields roughly parallel the observed yields. In the case of $CH_3S^-$ and $t\text{-}C_4H_9S^-$, the $C_6H_5\text{–}CO\text{–}C_6H_4SR^{-}\cdot$ radicals could cleave into $C_6H_5\text{–}CO\text{–}C_6H_4S^-$ and R· as observed in the case of Ph–S–Et.[30] However, this is very unlikely to occur

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[28] Beckwith, A. L. J.; Low, Beng See. *J. Chem. Soc.* **1961**, 1304.

[29] Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1971**, *30*, 41.

[30] Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740.

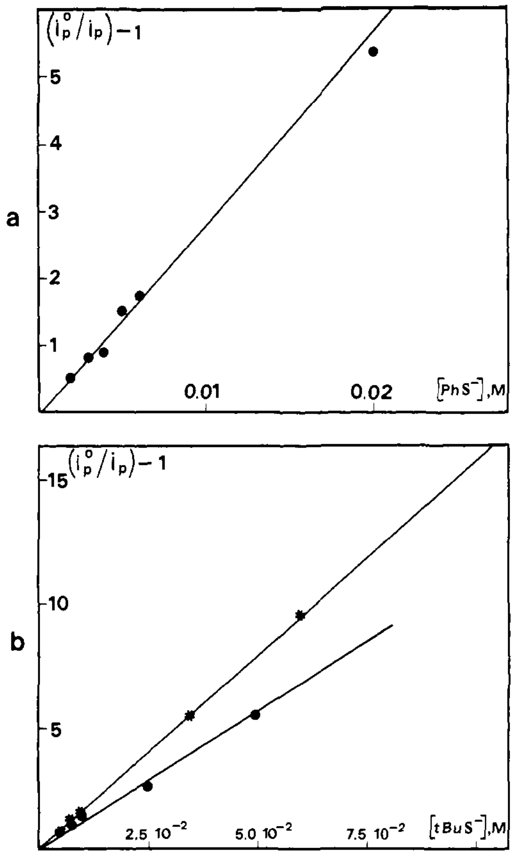

**Figure 7.** Variations of the peak height ($i_p$) of 4-bromobenzophenone ($10^{-3}$ M) with the concentration of (a) $PhS^-$ in $CH_3CN$ + 0.1 M $NEt_4ClO_4$ and of (b) $t$-$C_4H_9S^-$ in $CH_3CN$ + 0.1 M $NEt_4ClO_4$ (●) and in $Me_2SO$ + 0.1 M $NEt_4ClO_4$ (*). $i_p^0$ = peak height in the absence of thiolate, sweep rate 0.2 V $s^{-1}$.

within the time scale of cyclic voltammetry since the $C_6H_5COC_6H_4SR$ wave appears reversible even at low sweep rates. The cleavage reaction thus appears unable to compete with the reoxidation of the anion radical by the substrate.

The reaction of 4-bromobenzophenone with cyanide ions offers an example of a "noncatalytic" situation as clearly seen in Figure 3 in ref 12. Again this is due to the strong mesomeric electron-withdrawing character of the CN substituent which is responsible for the wave of the cyano compound being more positive than that of the bromo compound. If the possible occurrence of a chain process in the diffusion layer were to be ignored the height of the substrate peak in the presence of cyanide ions would be given by eq 11. Since $i_p/i_p^0$ is found equal to 0.85 for $[CN^-]$ = 0.1 M it is then deduced that $k_2/k_7$ = 4.5 $M^{-1}$. There is actually some interference of the chain process in the diffusion layer as revealed by the observation of a trace crossing phenomenon in cyclic voltammetry (Figure 3 in ref 12). The value of $k_2/k_7$ = 3 $M^{-1}$ found in a series of homogeneous experiments where the substitution was triggered by addition of $(p\text{-}CN\text{-}C_6H_4\text{-}CO\text{-}C_6H_5)^{-\cdot}$ thus appears as more reliable. The preparative scale yield predicted on this basis from eq 12 is compared with the experimental yield in Table II.

**Substitution of 4-Iodo- and 4-Bromobenzonitrile by Thiophenoxide in Acetonitrile.** Previous preparative scale electrolysis data show a sharp difference between the behavior of the bromo and the iodo derivative.[12] The former is characterized by a good substitution yield, a small yield of ArH, and low consumption of electricity while the latter shows the opposite characteristics. This has been interpreted[3,12] as resulting from the heterogeneous electron transfer to Ar· being more efficient for the iodo than for the bromo compounds due to the better leaving group character of $I^-$ as compared to $Br^-$ at the level of the substrate anion radical:

Table II. Electrochemically Induced Substitution of 4-Bromobenzophenone by Thiolates and Cyanide Ions. Rate Constant Ratio between Nucleophilic Attack and H-Atom Transfer to the 4-Benzoylphenyl Radical

| | nucleophile | | | |
|---|---|---|---|---|
| | $PhS^-$ | $t$-$C_4H_9S^-$ | $CH_3S^-$ | $CN^-$ |
| $k_2/k_7$, $M^{-1}$ | 290[a] | 110[a] | 2[a] | 3[a] |
| substitution yield, % | | | | |
| predicted | 97[a] | 94[b] | 17[a] | 75[a] |
| observed | 95[a] | 60[b] | 5[a] | 95[a] |
| nucleophile concn, M | 0.1 | 0.1 | 0.1 | 1 |

[a] In $CH_3CN$ + $10^{-1}$ M $NEt_4^+ClO_4^-$. [b] In $Me_2SO$ + $10^{-1}$ M $NEt_4^+ClO_4^-$.

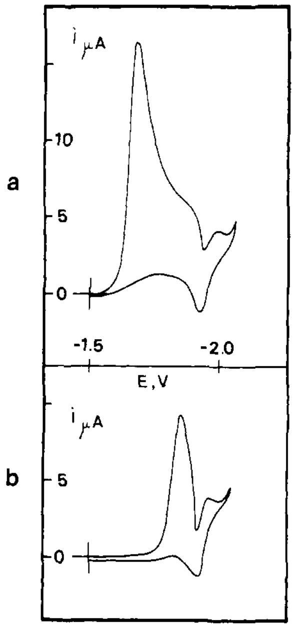

**Figure 8.** Cyclic voltammetry of 4-iodobenzonitrile (a) and 4-bromobenzonitrile (b) in acetonitrile + 0.1 M $NBu_4NClO_4$ in the presence of 0.1 M $PhS^-$. Substrate concentration $10^{-3}$ M, sweep rate 0.25 V $s^{-1}$, reference electrode Ag|0.01 M $Ag^+$.

the 4-cyanophenyl radical would be formed closer to the electrode surface and thus be more easily reduced by the electrode in the first case than in the second. The rate constant for the cleavage of the anion radical, $ArX^{-\cdot}$, has indeed been found to be larger in the first (8 × $10^{10}$ $s^{-1}$) than in the second (1.5 × $10^{10}$ $s^{-1}$) case.[17] The difference is however small and the question may therefore be raised whether it can explain quantitatively the large difference of yields and electricity consumption found experimentally.

The cyclic voltammetry of 4-iodobenzonitrile in the presence of $PhS^-$ (Figure 8a) is typical of a "catalytic" situation. There is a significant dip at the foot of the 4-thiophenoxybenzonitrile wave but there is no overlap with the substrate wave due to the large difference between the reduction potential of the iodo and the thiophenoxy derivatives. As shown in Figure 1, the heterogeneous electron transfer to Ar· largely predominates over homogeneous electron transfer and H-atom abstraction in acetonitrile with $LiClO_4$ as supporting electrolyte. The situation might be somewhat different with a quaternary ammonium but presumably not to a large extent. In the presence of $PhS^-$ the competition thus essentially involves heterogeneous electron transfer and nucleophilic attack, i.e., $i_p/i_p^0 = k_1^{1/2}/\{k_1^{1/2} + (k_2[PhS^-])^{1/2}\}$. It is indeed found experimentally (Figure 9) that $[(i_p^0 - i_p)/i_p]^2$ is proportional to $[PhS^-]$. From the slope of the straight line $k_1/k_2$ = 3.7 M and thus $k_2 \sim 2 \times 10^{10}$ $M^{-1}$ $s^{-1}$, i.e., close to the diffusion limit in acetonitrile. On this basis, the yields in a preparative scale experiment carried out with $[PhS^-]$ = 0.1 M are predicted to be ArH % = $100k_1^{1/2}/\{k_1^{1/2} + (k_2[PhS^-])^{1/2}\}$ = 85, ArNu % = 15, and the electricity consumtpion = 1.7 faraday/mol. These figures compare satisfactorily with what is found experimentally: 80, 20,

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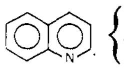
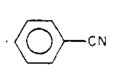
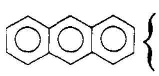
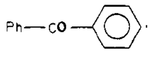
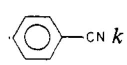
(31) Helgee, B.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *34*, 129.

Table III. Reactivity of Nucleophiles on Aryl Radicals

| solvent (temp) | aryl radical | | nucleophiles | | | |
|---|---|---|---|---|---|---|
| liquid $NH_3$ (−40 °C) | | | | 4-ClPhS$^-$ | PhS$^-$ | |
| |  | rel reactivity<br>$k_2/k_{dif}$<br>$k_2$,$^a$ $M^{-1}$ $s^{-1}$ | | 1<br>$(2.0 \pm 0.15) \times 10^{-4}$<br>$(6 \pm 0.5) \times 10^6$ | $2.3 \pm 0.1$<br>$(4.7 \pm 0.3) \times 10^{-4}$<br>$(1.4 \pm 0.1) \times 10^7$ | |
| | | | | $(EtO)_2PO^-$ | | |
| |  | $k_2/k_{dif}$<br>$k_2$,$^a$ $M^{-1}$ $s^{-1}$ | | $(4.7 \pm 0.2) \times 10^{-2}$<br>$(1.4 \pm 0.07) \times 10^9$ | | |
| $Me_2SO$ (20 °C) | | | | PhS$^-$ | CN$^-$ | |
| |  | $k_2/k_H{}^{Me_2SO}$,$^b$ $M^{-1}$<br>$k_2/k_{dif}$<br>$k_2$,$^c$ $M^{-1}$ $s^{-1}$ | | $5.5 \pm 6$<br>$(9 \pm 4) \times 10^{-2}$<br>$(4.5 \pm 2) \times 10^8$ | $8.7 \pm 0.4$<br>$(1.3 \pm 0.5) \times 10^{-2}$<br>$(6.5 \pm 2.5) \times 10^7$ | |
| $CH_3CN$ (20 °C) | | | PhS$^-$ | $t$-$C_4H_9S^-$ | $CH_3S^-$ | CN$^-$ |
| |  | $k_2/k_H{}^{CH_3CN}$,$^b$ $M^{-1}$ | $290 \pm 15$ | $110 \pm 8$ | $2 \pm 0.6$ | $3 \pm 1$ |
| | | | PhS$^-$ | | | |
| |  | $k_2$, $M^{-1}$ $s^{-1}$ | $\sim 2 \times 10^{10}$ | | | |

$^a$ Based on $k_{dif} = 3 \times 10^{10}$ $M^{-1}$ $s^{-1}$. $^b$ $k_H{}^{Me_2SO}$ and $k_H{}^{CH_3CN}$, first order rate constants for H-atom abstraction from $Me_2SO$ and $CH_3CN$, respectively. $^c$ Based on $k_{dif} = 5 \times 10^9$ $M^{-1}$ $s^{-1}$.

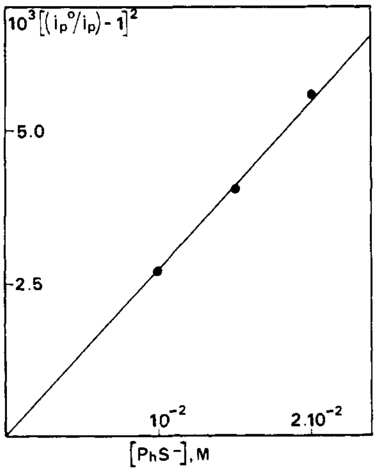


Figure 9. Cyclic voltammetry of 4-iodobenzonitrile ($10^{-3}$ M) in acetonitrile + 0.1 M $C_4H_9NClO_4$ in the presence of PhS$^-$. Variation of the peak height with PhS$^-$ concentration. Sweep rate 0.25 V $s^{-1}$.

and 1.5, respectively. It is emphasized that an important point in the preceding analysis in the assumption that practically no chain process occurs in the solution which is due to the large potential difference between the reactant and the product wave and the very fast cleavage of the 4-iodobenzonitrile anion radical: $ArNu^{-}\cdot$ is formed very close to the electrode surface at a potential which is very favorable for its oxidation.

The situation is quite different for 4-bromobenzonitrile as seen in Figure 8b. The dip at the foot of the product wave now clearly overlaps the substrate peak. The height of the latter is smaller than predicted for an Ece–Subst situation corresponding to $i_p/i_p{}^0 = k_1{}^{1/2}/\{k_1{}^{1/2} + (k_2[PhS^-])^{1/2}\}$. Preparative scale electrolysis carried out beyond the peak will then involve the triggering of the chain process in the solution. Oxidation of $ArNu^{-}\cdot$ at the electrode is indeed much less effective than with the iodo derivative. On the other hand the propagation of the chain process on the solution is itself very efficient since the nucleophilic attack on Ar·, having a second-order rate constant close to the diffusion limit, is fast as compared to H-atom and homogeneous electron transfers which can act as termination steps.[4]

It can thus be concluded that the sharp difference observed in the behaviors of 4-iodo- and 4-bromobenzonitrile is partly due to the difference in rates for the cleavage of the reactant anion radical but that this effect is greatly enhanced by the chain process occurring much more efficiently in the second case than in the first, the latter effect being mainly caused by a more favorable spacing of the reduction potentials of reactant and product.

**Substitution of 1-Bromonaphthalene by Thiophenoxide in Acetonitrile and Dimethyl Sulfoxide.** It has been previously noted[12] that the substitution of 1-bromonaphthalene by thiophenoxide is more efficient in $Me_2SO$ than in acetonitrile. This was tentatively related[12] to the fact that acetonitrile is a better H-atom donor than $Me_2SO$[15] in the context of a competition between nucleophilic attack and H-atom transfer to the naphthyl radical. As seen in Figure 1 the reduction of 1-bromonaphthalene in $Me_2SO$ with 0.1 M $LiClO_4$ as supporting electrolyte involves a balanced competition between heterogeneous electron transfer and H-atom transfer to the naphthyl radical, homogeneous electron transfer being practically negligible. The same is very likely to be true also in the presence of a quaternary ammonium salt. The cyclic voltammetry of 1-bromonaphthalene in $Me_2SO$ (which is very similar to Figure 2 in ref 12 recorded in acetonitrile) corresponds to a "catalytic" situation in which the peak height of the first wave should be derived by eq 13. Application of eq 13 requires that the ratio $k_1/k_7$ be known in order to determine $k_2/k_7$. $k_1/k_7 = 2$ has been measured in $Me_2SO + 10\%\ H_2O + LiClO_4$.[17] This leads to $k_2/k_7 = 40$ $M^{-1}$ in $Me_2SO$. Using $k_7 = 10^8$ $s^{-1}$[17] one finds $k_2 = 4$ $10^9$ $M^{-1}$ $s^{-1}$. The same value of $k_2/k_7$ (40 $M^{-1}$) has been obtained by homogeneous competition experiments.[31]

In acetonitrile, $k_1/k_7$ is not known. However, it can be estimated in the following manner: it is a reasonable assumption to use the same value of $k_1$ both for $Me_2SO$ and ACN and $k_7(CH_3CN)$ can be taken as $2.3k_7(Me_2SO)$.[32] Using these two approximated values, one finds $k_2/k_7 = 15$ $M^{-1}$ in ACN, leading to $k_2$ of the order of $4 \times 10^9$ $M^{-1}$ $s^{-1}$.

The occurrence of a dip very close from the peak of 1-bromonaphthalene (Figure 2, ref 12) indicates than a chain process is certainly occurring during the preparative electrolysis where the potential is set somewhat behind the peak. These conditions are similar to those already discussed for 4-bromobenzonitrile and thiophenoxide where chain propagation occurs in the bulk of the solution. The expected yields are 80% in $Me_2SO$ and 60% in ACN. It is difficult to compare this last value to the experimental data as the overall yield measured in ACN corresponds only to 72% of the starting compound (ref 12, Table II). However, in $Me_2SO$ a yield of 80% is found by polarographic titration in good

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(32) For the phenyl[15] and 9-anthryl[17] radicals $k_7(ACN)/k_7(Me_2SO)$ was found equal to 2.3. It is a reasonable assumption to use the same value for the 1-naphthyl radical.

agreement with the kinetic data but somewhat lower than the yields previously measured by gas chromatography.[12]

Although the value obtained for $k_2/k_7$ in ACN is only estimated it clearly appears that the difference of reactivity in acetonitrile and $Me_2SO$ is related to the higher hydrogen atom donor ability of acetonitrile since the two constants of nucleophilic attack ($k_2$) are almost identical.

## Discussion

The preceding results and interpretations show that besides the homogeneous and heterogeneous electron transfer prevailing in solvents such as liquid ammonia, H-atom transfer is a major reaction competing with nucleophilic attack of the aryl radical in organic solvents. This completes the mechanistic picture of electrochemically induced aromatic substitution previously based on investigations carried out in non-H-atom-donating media.[3,6,10] The determination of the nature and exact role of the reactions competing with the substitution process has a twofold mechanistic implication. This is first a necessary part of the general description of the mechanism of the whole process. It can then be used as a base for devising a strategy for optimizing the yield of the target product, here the substitution product, by a proper selection of the substrate nucleophile couple, reaction medium, concentrations, and electrode potential programming. In addition, the intimate course of the substitution process itself is revealed by the characteristics of the competition with the independently known competing reactions. This concerns the description of both the nature and the reactivity of the key intermediates. It is very often considered that the only "direct" evidence for a given mechanism is the physical, essentially spectral, characterization of the transient intermediates. One has then the impression of actually "seeing" the intermediate. Note however that the "seeable" intermediate is not necessarily the most chemically important intermediate and therefore that the characterization of the later requires a kinetic description of its fate matching the kinetic characteristics of the overall process. On the other hand, to "see" an intermediate does not necessarily require its spectral characterization. Its electrochemical or even chemical characteristics can be used instead. In the present case the three essential intermediates are $ArX^{-}\cdot$, $Ar\cdot$, and $ArNu^{-}\cdot$. There is little doubt about the intermediacy of $ArX^{-}\cdot$ radicals in processes triggered by setting up of the electrode potential at the reduction wave of ArX: $ArX^{-}\cdot$ radicals having a lifetime larger than about $10^{-4}$ s can be "seen" by means of their reoxidation wave in organic solvents as well as in liquid ammonia (see ref 6, 17, 18, and 33 and references cited therein); for shorter lifetimes a more "indirect" method, redox catalysis, can be used involving the reoxidation of $ArX^{-}\cdot$ by a reversible redox couple in solution.[34] $ArNu^{-}\cdot$ radicals appear also be means of their reoxidation wave on the cyclic voltammograms of a number of substrate nucleophile systems giving rise to electrochemically induced aromatic substitution (see ref 3, 6, 8, 9, 11, and 12 and Figures 2, 5, and 8). $ArNu^{-}\cdot$ radicals are usually easier to detect electrochemically than $ArX^{-}\cdot$ radicals being more stable in most systems giving rise to aromatic nucleophilic substitution. In some instances[12,35] $ArNu^{-}\cdot$ radical anions have been characterized by ESR spectroscopy. In the context of the $S_{RN}1$ mechanism, the aryl radical is both the most important intermediate and the most difficult to detect being present at a very small stationnary state concentration level. The principle of the characterization of this intermediate under electrochemical control was based on its independently known reducibility and H-atom abstraction properties[14,17] being involved during the substitution process. Let us, in this context, discuss some more specific mechanistic and reactivity features of the $S_{RN}1$ reaction as revealed by the present results and those previously obtained in liquid ammonia.[3,6-10] It is emphasized that the conclusions thus reached are also valid for $S_{RN}1$ reactions initiated by other means than an electrode, i.e, by other one-electron reductants such as solvated electrons[2] and $ArNu^{-}\cdot$,[4] or photochemically.[2]

**Mechanism.** As discussed earlier,[3,12] a mechanism involving a radical coupling between the aryl radical, $Ar\cdot$, and the radical of the nucleophile $Nu\cdot$ can be excluded on the basis of the electrochemical observations. Let us now envisage the possibility of an $S_{RN}2$ mechanism in which the substitution step would involve the attack of the $ArX^{-}\cdot$ radical by $Nu^{-}$ with simultaneous expulsion of $X^{-}$ instead of a prior dissociation followed by nucleophilic attack. Reaction 2 would then be replaced by:

$$ArX^{-}\cdot + Nu^{-} \xrightarrow{k_2'} ArNu^{-}\cdot + X^{-} \qquad (2')$$

For a charged nucleophile, Coulombic repulsion works against this possibility and bond formation occurs most probably under less favorable conditions at $ArX^{-}\cdot$ than at ArX itself. Bond breaking could however be favored which might compensate the above unfavorable effects. Within such a mechanistic framework, the cleavage reaction 1 would appear as the initiation of a series of reactions competing with the substitution process involving electron and H-atom transfers as in the $S_{RN}1$ case.

Two series of electrochemical experiments are particularly suited for discriminating the $S_{RN}1$ and $S_{RN}2$ mechanisms. The first involves the substitution processes electrochemically induced in liquid ammonia under homogeneous electron-transfer conditions. A typical example of this situation is the substitution of 2-chloroquinoline by thiophenoxide or 4-chlorothiophenoxide ions.[6,7] While in the $S_{RN}1$ case the relative height of the substrate wave, $i_p/i_p^0$, is a function of the parameter $\rho = (k_D/k_1^{1/2}k_2[Nu^-])\cdot(Fv/RT)^{1/2}$, in the $S_{RN}2$ case $i_p/i_p^0 = k_1/(k_1 + k_2'[Nu^-])$ and is thus independent of both initial concentration and sweep rate. This simply reflects the fact that the competition is between a first-order and a second-order reaction at the level of $Ar\cdot$ in the first case and between two first-order reactions at the level of $ArX^{-}\cdot$ in the second case. Systematic investigations of the effect of initial concentration and sweep rate with the experimental systems just mentioned showed without ambiguity that $i_p/i_p^0$ does vary with these two parameters according to the behavior predicted for an $S_{RN}1$ mechanism which thus rules out the occurrence of an $S_{RN}2$ mechanism.

Another series of interest in this connection involves the substitution of 9-haloanthracenes by $CN^-$ in $Me_2SO$ as discussed in the second section of the present paper. For the chloro and bromo derivatives the only reaction competiting with substitution is H-atom transfer which predominates over homogeneous and heterogeneous electron transfers. In the framework of the $S_{RN}2$ mechanism, $i_p/i_p^0$ would be expressed by an equation similar to eq 11 in which the rate ratio would be $k_2'/k_1$ instead of $k_2/k_7$ in the $S_{RN}1$ case. The competition indeed occurs at the level of $ArX^{-}\cdot$ in the first case instead of $Ar\cdot$ in the second. While $k_2/k_7$ remains constant when passing from Cl to Br, $k_2'/k_1$ has no reason to remain constant. $k_1$ increases by about 1000 from Cl to Br. Since the bond formation is likely to be the most important rate-determining factor in the $S_{RN}2$ reaction, $k_2'$ should decrease from Cl to Br. The $k_2'/k_1$ ratio should then decrease as opposed to what is observed experimentally. In this context, the experimental observations summarized in Figure 3 clearly rule out the $S_{RN}2$ mechansim confirming the occurrence of the $S_{RN}1$ mechanism. In the case of 9-iodoanthracene, heterogeneous electron transfer should be taken into account besides H-atom transfer. In the framework of an $S_{RN}2$ mechanism the $i_p/i_p^0$ ratio would be expressed by an equation similar to eq 14 in which $k_7$ would be replaced by $k_1$, all other terms remaining the same. There would then be no reason why the application of such an equation to the experimental results should lead to the same value as for the Cl or Br derivatives as it does in the context of an $S_{RN}1$ mechanism.

These two examples clearly show the validity of the $S_{RN}1$ mechanism as opposed to the $S_{RN}2$ mechanism. This conclusion is obviously not dependent upon the mode of inducement of the substitution reaction and is thus of general validity. Another mechanistic point of importance brought about by the electrochemical approach to $S_{RN}1$ aromatic nucleophilic substitution

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(33) Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1978**, *89*, 335.

(34) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806.

(35) Ciminale, F.; Bruno, G.; Testaferri, L.; Tiecco, M.; Martelli, G. *J. Org. Chem.* **1978**, *43*, 4509.

concerns the nature of the termination steps in homogeneous chain processes. It is indeed clearly apparent from what preceeds that the main termination steps in such processes are the electron and H-atom transfers to the aryl radical. This point is fully developed elsewhere.[4]

**Reactivities.** Several absolute or relative rate constants characterizing the nucleophilic attack of the aryl radicals have been determined by electrochemical means as done in the present paper for organic solvents or done previously in liquid ammonia.[6-8,10] They are summarized in Table III. Before discussing the dependence of the reactivity upon the nature of the substrate and nucleophile it is useful to estimate the reliability and accuracy of these determinations.

Among the systems investigated in liquid ammonia[6,8,10] only those involving 2-chloroquinoline with $PhS^-$ or $4\text{-}ClPhS^-$ and 4-chlorobenzonitrile with $(EtO)_2PO^-$ gave reliable rate-constant data. With the other nucleophiles $CH_3COCH_2^-$, $PhCOCH_2^-$, and $(EtO)_2PO^-$ with 2-chloroquinoline or 2-iodoquinoline as substrates only very rough estimates of the reactivity were obtained, the rate constants being probably undervalued. This results from an insufficient mastering of effects of the high basicity generated at the electrode surface as already noted[6] and from an underestimation of the Ece character of the process. The latter point could be solved by a systematic investigation of the effect of sweep rate and initial concentration which has not been carried out so far. This is presently underway and the results will be published elsewhere. In the case of $PhS^-$ and $4ClPhS^-$ with 2-chloroquinoline as substrate such a detailed analysis was carried out[6,8] allowing the determination of $k_D/k_1^{1/2}k_2$ with $k_D$ being equal to the diffusion limit. This rate ratio was obtained with good accuracy (±2%). The error on $k_1$ determination must then be taken into account for deriving $k_2/k_{dif}$. This is on the order of ±10%[6,33] thus introducing an uncertainty of ±5% on the determination of $k_2/k_{dif}$. The reactivity of $(EtO)_2PO^-$ on the 4-cyanophenyl radical was determined using 4-chlorobenzonitrile as the substrate corresponding to a "noncatalytic" Ece–Subst situation and giving rise to trace crossings.[7] The uncertainty on $k_2/k_1$ was on the order of ±5% and that on $k_1/k_{dif}$ was negligible, the determination resulting from curve fitting for several values of the experimental parameters. The absolute values of $k_2$ hinge upon the value selected for $k_{dif}$. A reasonable estimate for this is $3 \times 10^{10}\ M^{-1}\ s^{-1}$.[16] This is however not known with certainty. A sounder approach would then be to view the reactivity of the nucleophiles on the aryl radicals in terms of the diffusion limit value taken as the unit of second-order rate constants.

The reactivity of the 9-anthryl radical with $PhS^-$ and $CN^-$ and that of the 4-benzoylphenyl radical with $PhS^-$, $t\text{-}C_4H_9S^-$, $CH_3S^-$, and $CN^-$ were determined in conditions where the only competition reaction is H-atom transfer from the solvent. What is thus derived from the experiments are the values of the ratio $k_2/k_7$ in each case with an accuracy ranging from ±5 to ±10%. The relative reactivities of the nucleophiles with each of these two radicals are thus known within ±10 to ±20%. Absolute values of $k_2$ have been determined for the anthryl radical where $k_7$ was obtained from deuteration experiments. Reproducibility of the deuteration ratios is on the order of ±5% resulting in an average error or $k_{dif}/k_1^{1/2}k_7$ equal to ±25%. $k_1$ being itself known with an uncertainty of ±10%, the error on $k_7/k_{dif}$ is ±30%. It follows that the value of $k_2/k_{dif}$ is known with an uncertainty ranging from ±35 to ±40%. The value of $k_{dif}$ in $Me_2SO$ is estimated as $5 \times 10^9\ M^{-1}\ s^{-1}$,[31] leading to the absolute values shown in Table III. However, the $k_2$ values are again more soundly expressed as fractions of the diffusion limit.

The determination of $k_2$ of the 4-cyanophenyl,$PhS^-$ system derives from an Ece–Subst situation involving the extremely fast cleaving 4-iodobenzonitrile anion radical. It requires the knowledge of the cleavage rate $k_1$ which was determined with a rather poor accuracy due to the very fact that it is very large. In addition double-layer effects are likely to interfere since the reaction layer is very small. For all these reasons the figure given for $k_2$ is not more than a rough order of magnitude.

As noted before,[6] the reactivities of nucleophiles on the 2-quinolyl radical as determined in liquid ammonia all lie in a rather narrow range, less than a factor of 10. They are however far from the diffusion limit. Accordingly the existence of more reactive nucleophiles is shown by the fact that the reaction of $^-CH_2CN$, $Ph_3C^-$ on 2-chloroquinoline and of the carbanion of lutidine on 1-chloronaphthalene can be induced to occur in the solution simply by the recording of a few voltammograms at a microelectrode.[4,6] The results obtained with the 4-benzoylphenyl radical now show that the range of reactivities can be expanded up to a factor of about 150. The relative narrowness of the range of reactivities of nucleophiles with aryl radicals is fundamentally related to the fact that the nucleophilic attack always occurs in parralel with other reactions of the aryl radical—electron and/or H-atom transfers, the latter reactions acting as termination steps in homogeneously induced chain processes. This results in a lower limit of effectness for the reactivity of the nucleophile—its concentration cannot be raised to a very large extent due to solubility limitations—from a synthetic viewpoint and also for the determination of the rate constant by cyclic voltammetry. Conversely, fast-reacting systems will lead to undectectably small cyclic voltammetric peaks and to a substitution yield close to 100% preventing the quantitative determination of the reactivity. This higher limit could be raised by using smaller and smaller concentrations of the nucleophile which would require an extension of the theory so far confined to conditions in which the nucleophile is in excess as compared to the substrate in order to make sure that pseudo-first-order kinetics are followed.

It is noted that the 4-cyanophenylradical is about 100 times more reactive toward $(EtO)_2PO^-$ than the 2-quinolyl radical in liquid ammonia. The high reactivity of the 4-cyanophenyl radical also appears as compared to the 9-anthryl radical in their reactions with $PhS^-$ in organic solvents at room temperature. On the other hand, as discussed elsewhere,[4] the reactivity of the phenyl radical is likely to be lower than that of the 2-quinolyl radical toward the same nucleophile. It can thus be concluded that the electron-withdrawing character of the cyano group has a pronounced effect on the reactivity despite the $\sigma$ character of the aryl radical.

A last remark concerns the reactivity of cyanide ions. Although not at the top of the reactivity range, it is seen that $CN^-$ is able to react on 9-anthryl and 4-benzoylphenyl radicals, confirming that the absence of reaction observed in liquid ammonia is related to insolubility rather than to intrinsic inactivity.

## Experimental Section

**Chemicals.** The solvents, supporting electrolytes, substrates, and nucleophiles were from commercial origin or prepared as described in ref 12 with the exception of 9-iodoanthracene which was kindly provided to us by Dr. O. Hammerich (Oersted Institute, Copenhaghen). Acetonitrile was distilled over calcium hydride before use. The 9-anthrylphenyl sulfide[28] prepared by electrochemically induced reaction of $PhS^-$ with 9-bromoanthracene as described in the text was recovered by preparative gas chromatography and identified by its mass spectrum: 286 (100), 218 (45), 209 (64), 180 (48), 160 (40), 147 (50), 109 (54).

**Instrumentation and procedures** were similar to those previously described.[12] The reference electrode was an $Ag|Ag^+$ 0.01 M electrode in $Me_2SO$ and in acetonitrile. The working electrode for the cyclic voltammetric study of the 9-haloanthracenes in $Me_2SO$ + 0.1 M $LiClO_4$ was a long droping time mercury electrode. The drop was mechanically renewed every 20 s, the recording of the voltammogram starting 15 s after the fall of the preceding drop.

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**Registry No.** 9-Chloroanthracene, 716-53-0; 9-bromoanthracene, 1564-64-3; 9-iodoanthracene, 22362-86-3; 4-bromobenzophenone, 90-90-4; 2-quinolinyl, 54978-39-1; 4-cyanophenyl, 56263-67-3; 9-anthryl, 27735-77-9; 4-benzoylphenyl, 59922-54-2; DMSO, 67-68-5; $PhS^-$, 13133-62-5; $t\text{-}C_4HgS^-$, 20733-19-1; $CH_3S^-$, 17302-63-5; $CN^-$, 57-12-5; $4\text{-}ClPhS^-$, 35337-68-9; $(EtO)_2PO^-$, 29800-93-9.