(both 10% v/v), are apparently inconsistent with other evidence that benzene acts as a hydrogen-bond acceptor.[14]

We have therefore measured this shift with both C_6H_6 and c-C_6H_{12} at 1% v/v in a representative series of solvents. The results are recorded in Table IX and show that the benzene signal is downfield shifted relative to that for c-C_6H_{12} in the hydrogen-bond donor solvents $(CF_3)_2CHOH$, CF_3CH_2OH, CF_3CO_2H, and $HCONH_2$ compared to the weak or nonhydrogen-bond donor solvents CCl_4, CH_3OH, $(CH_3)_2CO$, and $CDCl_3$.

The effects of hydrogen-bond donor solvents on the benzene shift may be estimated probably somewhat more reliably from the C_p–SCS values for I and II by taking the difference between the shift calculated by eq 1 and that observed (Table IV). These estimates are also recorded in Table IX. The closer similarity to the structural environment of the benzene carbon with the para carbons of I and II than with the carbon of c-C_6H_{12} probably makes these latter estimates the best measure of the benzene hydrogen-bond acceptor effects.

Electron-Transfer-Induced Reactions. Termination Steps and Efficiency of the Chain Process in $S_{RN}1$ Aromatic Substitutions

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Abstract: An important part of the mechanistic sequence of $S_{RN}1$ aromatic substitution reactions $ArX + Nu^- \rightarrow ArNu + X^-$ is a chain process, the propagation of which involves three intermediate radicals: $ArX^{-}\cdot$, $Ar\cdot$ and $ArNu^{-}\cdot$. A quantitative kinetic model describing the propagation of the chain process is presented and discussed in terms of the time required for reaching a given conversion of the starting ArX. The influence of electron transfer from $ArX^{-}\cdot$ and $ArNu^{-}\cdot$ to $Ar\cdot$ as main termination steps deactivating the chain process in solvents of low H atom donating ability (liquid NH_3) is then investigated. This is a built-in problem in $S_{RN}1$ reactions: the propagation cycle produces the elements of its own destruction. The outcome of this competition is shown to essentially depend upon three parameters, featuring each one of the three steps of the propagation cycle: the rate constant for decomposition of $ArX^{-}\cdot$ into $Ar\cdot$, the rate constant for the addition of the nucleophile on $Ar\cdot$, and the difference of the standard potentials of the $ArX/ArX^{-}\cdot$ and $ArNu/ArNu^{-}\cdot$ redox couples. From previous rate and potential data, a number of systems appear to involve rather unefficient chain processes even though a rather good substitution yield can be obtained. A remarkable exception is the reaction of $(EtO)_2PO^-$ and 4-chlorobenzonitrile where a 100% conversion is obtained in about 10 min by introducing less than 0.01 electron per molecule of the substrate into the solution. It is shown that the main previous observations of homogeneous $S_{RN}1$ processes, particularly the influence of the nature of the leaving group X on reaction times and product distribution, can be interpreted in the framework of the same model which regards electron transfer to $Ar\cdot$, and in some cases to $ArNu^{-}\cdot$, as the essential cause for the deactivation of the chain process. In organic solvents, a significant additional termination step is the abstraction of hydrogen atoms from the solvent by the intermediate aryl radical $Ar\cdot$. A kinetic model is presented for the case where H atom abstraction is the main termination step and used to discuss the experimental results obtained with the reaction of the cyanide ion and 4-bromobenzophenone in acetonitrile.

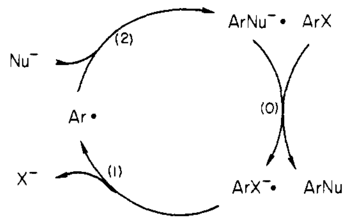
One remarkable feature of $S_{RN}1$ aromatic substitution reactions[2,3]

$$ArX + Nu^- \rightarrow ArNu + X^-$$

is the involvement of a *chain process* that allows the reaction to propagate according to Scheme I.

The *initiation* devices devised so far were essentially of three types: injection of solvated electrons into the solution by addition of alkali metals in liquid ammonia,[2] injection of electrons by means of an electrode set at a suitable potential,[3] and photochemical stimulation.[2,4] In the first two cases the initiation steps involve the formation of the anion radical of the substrate, $ArX^{-}\cdot$, which then enters the propagation cycle. The exact nature of the photoinitiation process giving rise to one of the three species $ArX^{-}\cdot$, $Ar\cdot$, or $ArNu^{-}\cdot$ functioning in the propagation cycle still remains open to question. The initiation mechanism of $S_{RN}1$ reactions occurring in the dark without purposely added electron-donating initiators[5] is even more obscure.

Scheme I



So far, a reasonably complete characterization of the kinetics of $S_{RN}1$ processes was reached only in the case of electrochemical control of the reaction.[3] This provided a rigorous demonstration of the mechanism of $S_{RN}1$ reactions and led to the determination of the rate constants of the key steps for a number of experimental systems.[3,6-10,12] It is noteworthy that the mechanism of elec-

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trochemically initiated $S_{RN}1$ reactions was shown to involve electron-transfer reactions to the Ar· radical

$$\mathrm{Ar}\cdot + 1e^-(\text{electrode}) \rightarrow \mathrm{Ar}^-$$

$$\mathrm{Ar}\cdot + \mathrm{ArNu}^{-}\cdot \rightarrow \mathrm{Ar}^- + \mathrm{ArNu} \tag{3}$$

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

competing with the initiation and propagation of the substitution process. These electron-transfer reactions all ultimately lead to the hydrogenolysis product, ArH, hence contributing to lower the substitution yield.

From this, it is anticipated that, in the context of an homogeneous $S_{RN}1$ process, reactions 3 and 4 are very likely to be efficient *termination steps* of the chain process. These are indeed very fast reactions, with rates probably close to the diffusion limit, since Ar· is much easier to reduce[11] than most of the ArNu and ArX molecules generally involved in $S_{RN}1$ reactions. In other words, deactivation of the process will not only occur by reduction of Ar· by the electron-donating initiator but also by the two species $\mathrm{ArNu}^{-}\cdot$ and $\mathrm{ArX}^{-}\cdot$, leading to deactivation of the propagation cycle itself. The propagation cycle thus produces the elements of its own destruction. This central point was not taken into account in the previous discussion on homogeneous $S_{RN}1$ reactions, the assignment of termination steps remaining rather imprecise.[2]

The main purpose of the work reported hereafter was to investigate the role of electron-transfer reactions 3 and 4 as termination steps of the chain process. A complete kinetic analysis of the problem able to match all the experimental circumstances seems out of reach for the time being due to the following reasons. The nature of the initiation process is unknown for the photoinduced and spontaneous dark reactions. The termination reactions may well not only be electron-transfer reactions 3 and 4. Several other possibilities exist: dimerization of the Ar· radical, H atom transfer from organic solvents to Ar·,[3,12] and fragmentation of the $\mathrm{ArNu}^{-}\cdot$ radical[2,15-21] opening new propagation cycles and termination steps. Even in those cases where the initiation mechanism is known (e.g., addition of an electron source such as alkali metal dissolved in liquid ammonia) and where the electron-transfer termination steps predominate, the kinetic analysis would involve the simultaneous resolution of a large number of equations correspondingly with the large number of simultaneous reactions. The system will then depend on a large number of parameters representing the rates of the various steps, and its resolution would be of little predictive value. This means that the kinetic behavior could be described through a simulation approach for those systems where the characteristic rate constants would be known independently which is generally not the case.

Under these conditions our approach was to simplify the problem as follows. We looked for the conditions to be fulfilled by the characteristic rate constants for obtaining a good efficiency of the chain process (99% conversion of ArX into ArNu) for a small catalytic quantity of the electron source, this being the anion radical $\mathrm{ArNu}^{-}\cdot$ itself. Within this framework the discussion will be restricted to two limiting cases according to the nature of the solvent. The first regards solvents that are poor H atom donors, a typical example of which being liquid ammonia, for which the terminations steps are essentially electron-transfer reactions 3 and 4 and possibly the dimerization of the aryl radicals.

$$2\mathrm{Ar}\cdot \rightarrow \mathrm{Ar{-}Ar} \tag{5}$$

The second situation, which can be obtained in organic solvents, will concern conditions in which H atom transfer from the solvent

$$\mathrm{Ar}\cdot + \mathrm{SH} \xrightarrow{k_6} \mathrm{ArH} + \mathrm{S}\cdot \tag{6}$$

predominates over the other possible termination steps.[46] In both cases $\mathrm{ArNu}^{-}\cdot$ is regarded as chemically stable. Several systems for which rate data are available will be then discussed in this context. The results obtained with the two reactions 4-chlorobenzonitrile + diethyl phosphite anion in liquid ammonia and 4-bromobenzophenone + cyanide anion in acetonitrile will then be presented as tests of the predicted behavior. It will be shown finally that this simplified treatment allows a semiquantitative (determination of reactivity sequences) interpretation of a number of previous experimental data, especially those regarding the effect of the leaving-group ability of X^- on the reaction time and distribution of products.

Efficiency of the Chain Process

Let us first establish the time characteristics of the chain process in the absence of any termination reactions as a basis for the further discussion of the effect of these reactions. The reaction scheme is then

$$\mathrm{ArX} + \mathrm{ArNu}^{-}\cdot \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \mathrm{ArX}^{-}\cdot + \mathrm{ArNu} \tag{0}$$

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

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

In such conditions, the sum of the concentrations of the three species $\mathrm{ArNu}^{-}\cdot$, $\mathrm{ArX}^{-}\cdot$, and Ar· functioning in the propagation cycle remains constant and equal to the $\mathrm{ArNu}^{-}\cdot$ concentration $[\mathrm{ArNu}^{-}\cdot]^0$ introduced at $t = 0$. After a short transient behavior these three concentrations are such that the rates of the three steps are equal. The decay of the ArX concentration is then given by eq 7,[22] where $[\mathrm{ArX}]^0$ is the initial concentration of ArX and χ_1

$$([\mathrm{ArX}]/[\mathrm{ArX}]^0) - 1 - \chi_1 \ln([\mathrm{ArX}]/[\mathrm{ArX}]^0) = \chi_2 [\mathrm{ArNu}^{-}\cdot]^0 t \tag{7}$$

and χ_2 are constants depending upon the rate constants k_0, k_{-0}, k_1, and k_2 and upon $[\mathrm{ArX}]^0$ and the nucleophile concentration $[\mathrm{Nu}^-]$ which is assumed to be in excess.

$$\chi_1 = (k_{-0} + k_1/[\mathrm{ArX}]^0)/\{k_{-0} - k_0(1 + k_1/k_2[\mathrm{Nu}^-])\} \tag{8}$$

$$\chi_2 = k_0(k_1/[\mathrm{ArX}]^0)/\{k_{-0} - k_0(1 + k_1/k_2[\mathrm{Nu}^-])\} \tag{9}$$

The increase of the ArNu concentration with time will then be given by

$$[\mathrm{ArNu}] = [\mathrm{ArX}]^0 - [\mathrm{ArX}]$$

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(22) Writing that the three steps have the same rate and that $[\mathrm{ArNu}^{-}\cdot] + [\mathrm{ArX}^{-}\cdot] + [\mathrm{Ar}\cdot] = [\mathrm{ArNu}^{-}\cdot]^0$ gives $[\mathrm{ArNu}^{-}\cdot] = [\mathrm{ArNu}^{-}\cdot]^0/\{1 + k_0[\mathrm{ArX}](1 + k_1/k_2[\mathrm{Nu}^-])/(k_1 + k_{-0}[\mathrm{ArX}]^0 - k_{-0}[\mathrm{ArX}])\}$, the rate of decay of ArX being $\mathrm{d}[\mathrm{ArX}]/\mathrm{d}t = -k_1k_0[\mathrm{ArX}][\mathrm{ArNu}^{-}\cdot]/\{k_1 + k_{-0}([\mathrm{ArX}]^0 - [\mathrm{ArX}])\}$ the integration of which leads to eq 7.

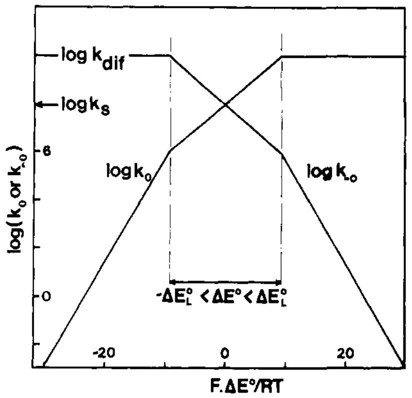

Figure 1. Schematic representation of the variations of the rate constants for the $ArNu^{-}\cdot + ArX \rightleftarrows ArNu + ArX^{-}\cdot$ electron transfer as a function of the standard potential difference $\Delta E° = E°_{ArX/ArX^{-}\cdot} - E°_{ArNu/ArNu^{-}\cdot}$ (transfer coefficient $\alpha = 0.5$; standard rate constant $k_s = 10^8$ M^{-1} s^{-1}; diffusion limit $k_{dif} = 10^{10}$ M^{-1} s^{-1}; $\Delta E_1° = (2RT/F) \ln (k_{dif}/k_s) \simeq 0.2$ V at 25 °C).

It follows that the time $t_\gamma{}^0$, required for a γ (%) conversion of the starting ArX into ArNu is such that

$$t_\gamma{}^0[ArNu^{-}\cdot]^0 = \theta_\gamma{}^0 = [-0.01\gamma - \chi_1 \ln (1 - 0.01\gamma)]/\chi_2$$

i.e., for a 99% conversion

$$t_{99}{}^0[ArNu^{-}\cdot]^0 = \theta_{99}{}^0 = (4.6\chi_1 - 0.99)/\chi_2 \simeq (4.6\chi_1 - 1)/\chi_2 \qquad (10)$$

where $\theta_{99}{}^0$ is a function of the parameters of the system through χ_1 and χ_2. When these have given values, $t_{99}{}^0$ is inversely proportional to the starting concentration of $ArNu^{-}\cdot$. Evaluation of $\theta_{99}{}^0$ thus allows the determination of the 99% conversion time for a given value of $[ArNu^{-}\cdot]^0$ or conversely of the value of $[ArNu^{-}\cdot]^0$ for a given 99% conversion time. When the standard potential difference is introduced between the ArX and the ArNu redox couple $\Delta E° = E°_{ArX/ArX^{-}\cdot} - E°_{ArNu/ArNu^{-}\cdot}$, the expression of $\theta_{99}{}^0$ appears as the sum of three terms

$$\theta_{99}{}^0 = 4.6/k_0 + [1 + 3.6 \exp(-F\Delta E°/RT)][ArX]^0/k_1 + [ArX]^0/(k_2[Nu^-]) \qquad (11)$$

featuring successively the three steps of the propagation cycle.

In order to simplify the evaluation of $\theta_{99}{}^0$, let us make the following assumptions regarding electron-transfer reaction 0. For most of the reactants used in the $S_{RN}1$ reactions, this can be regarded as an outer-sphere electron transfer.[23,24] The variations of the rate constants k_0 and k_{-0} with the standard potential difference $\Delta E°$ are approximate as shown in Figure 1, where the variations of the transfer coefficient α with the potential were neglected and its value was assumed to be equal to 0.5.[23,25] These variations show three regions, two corresponding to diffusion control with k_0 and k_{-0} being respectively equal to the diffusion limit value k_{dif} and one corresponding to activation control with k_0 and k_{-0} being then proportional to the standard activation rate constant k_s (activation rate constant for $\Delta E° = 0$). k_0 and k_{-0} are thus expressed as follows: for $\Delta E° > \Delta E_1°$ ($\Delta E_1° = (2RT/F) \ln (k_{dif}/k_s)$), $k_0 = k_{dif}$ and $k_{-0} = k_{dif} \exp(-F\Delta E°/RT)$; for $-\Delta E_1° < \Delta E° < \Delta E_1°$, $k_0 = k_s \exp(F\Delta E°/2RT)$ and $k_{-0} = k_s \exp(-F\Delta E°/2RT)$; for $\Delta E° < -\Delta E_1°$, $k_0 = k_{dif} \exp(F\Delta E°/RT)$ and $k_{-0} = k_{dif}$. Current values of k_{dif} are on the order of 10^{10} M^{-1} s^{-1} ($k_{dif} = 3 \times 10^{10}$ M^{-1} s^{-1} in liquid NH_3 at −40 °C;[6] $k_{dif} = 5 \times 10^9$ M^{-1} s^{-1} in Me_2SO at room temperature[24]). A reasonable value of k_s for a number of reactants currently used in $S_{RN}1$ reactions is 10^8 M^{-1} s^{-1}.[23,24,26] With these values and thus $\Delta E_1° \simeq 0.2$ V at 25 °C, Figure 2 shows a set of working curves allowing for the determination of $\theta_{99}{}^0$ and thus of the 99% conversion time, once $\Delta E°$, k_1, and k_2 are known. If one had, for example, $\Delta E° = -0.2$ V, $k_1 = 10^3$ s^{-1}, $k_2[Nu^-] = 10^2$ s^{-1}, and $[ArX]^0 = 10^{-2}$ M, at 25 °C, $F\Delta E°/RT \simeq -7.8$, thus $\theta_{99}{}^0$ would be equal to 0.1; i.e., for $[ArNu^{-}\cdot]^0 = 10^{-4}$ M, $t_{99}{}^0 \simeq 17$ min. This underscores the remarkable efficiency of the chain process: a rather short conversion time is obtained even though $\Delta E°$ has an unfavorable value and k_1 and k_2 are much less than those obtained in a number of actual experimental situations. It is, however, emphasized that these evaluations do not take the termination steps into account.

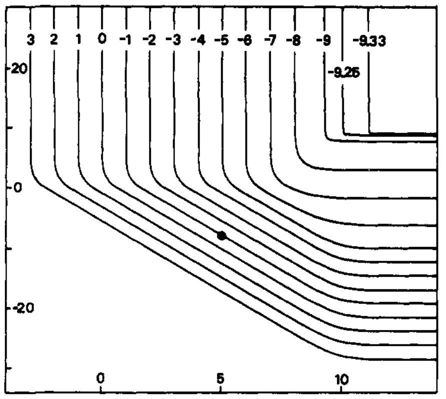

Figure 2. Variations of the time required for a 99% conversion, $\theta_{99}{}^0 = t_{99}{}^0[ArNu^{-}\cdot]^0$, with $\Delta E°$, k_1, and $k_2[Nu^-]$ for a chain process with no termination steps. The numbers on the curves are the values of $\log (\theta_{99}{}^0 - [ArX]^0/k_2[Nu^-])$.

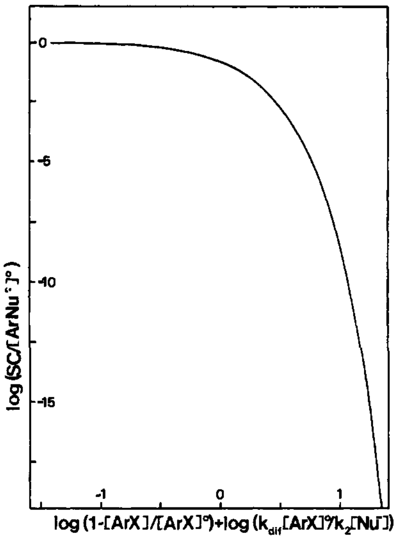

Figure 3. Variations of the total concentration of the catalytic species with the conversion ratio featuring the effect of the terminations reactions 3, 4, and 5. ($SC = [ArNu^{-}\cdot] + [ArX^{-}\cdot] + [Ar\cdot]$).

The effect of the termination steps amounts to eliminating a fraction of $ArNu^{-}\cdot$ during each successive cycle. We consider first the simultaneous occurrence of three termination steps electron-transfer reactions 3 and 4 and dimerization 5 and assume that each of these reactions is at the diffusion limit, which corresponds to the use of a *poor H atom donating solvent* such as liquid ammonia.

Looking for the conditions required for an efficient chain process, it can be assumed that the kinetic effect of the termination steps is small within each cycle and that it results in an overall decay of the sum, SC of the concentrations of the catalytic species ($ArNu^{-}\cdot$, $ArX^{-}\cdot$, $Ar\cdot$), with the conversion ratio, according to[27]

$$SC = [ArNu^{-}\cdot]^0 \exp\{-2(k_{dif}[ArX]^0/k_2[Nu^-])(1 - [ArX]/[ArX]^0)\} \qquad (12)$$

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Figure 3 shows how the total concentration of the catalytic species varies with the conversion ratio. It is seen that the parameter $k_{\mathrm{dif}}[\mathrm{ArX}]^0/k_2[\mathrm{Nu}^-]$ plays an essential role in determining the time required for a good conversion of the starting ArX, through the decay of the catalytic species. If, e.g., this parameter is equal to 10, the total concentration of the catalytic intermediates passes from $[\mathrm{ArNu}^-\cdot]^0$ to $4 \times 10^{-5}[\mathrm{ArNu}^-\cdot]^0$ during the conversion of the first 50% of the starting material and from $4 \times 10^{-5}[\mathrm{ArNu}^-\cdot]^0$ to $2 \times 10^{-9}[\mathrm{ArNu}^-\cdot]^0$ during the conversion of the last 50%. If this parameter is now equal to 20, i.e., for the same system but with a nucleophile concentration divided by 2, we obtain a decay from $[\mathrm{ArNu}^-\cdot]^0$ to $2 \times 10^{-9}[\mathrm{ArNu}^-\cdot]^0$ during the first 50% conversion and from $2 \times 10^{-9}[\mathrm{ArNu}^-\cdot]^0$ to $2 \times 10^{-18}[\mathrm{ArNu}^-\cdot]^0$ during the last 50%, corresponding to a total conversion time about 2×10^8 times longer than that obtained in the preceding case. For the chain process without termination steps the same variation of $[\mathrm{Nu}^-]/C^0$ would have resulted in an increase by a factor smaller than 2 of the conversion time. This example emphasizes the dramatic effect of a slight variation of the excess factor $[\mathrm{Nu}^-]/C^0$ as soon as the termination steps interfere significantly.

In practice, this means that if the parameter $k_{\mathrm{dif}}[\mathrm{ArX}]^0/k_2[\mathrm{Nu}^-]$ is larger than a few units, the chain process will stop before the complete conversion of the starting material ArX into the product ArNu. It follows that the time required for converting 99% of the starting ArX can be estimated as[28]

$$t_{99}\,[\mathrm{ArNu}^-\cdot]^0 = \theta_{99} \simeq \theta_{99}{}^0\,[(\exp\Lambda - 1)/\Lambda] \qquad (13)$$

where $\theta_{99}{}^0$ is the value of θ_{99} in the absence of termination reactions (eq 10) and $\Lambda = 2k_{\mathrm{dif}}[\mathrm{ArX}]^0/k_2[\mathrm{Nu}^-]$. In the example discussed above corresponding to $[\mathrm{ArX}]^0 = 10^{-2}$ M, $k_1 = 10^3$ s^{-1}, $k_2[\mathrm{Nu}^-] = 10^2$ s^{-1}, and $\Delta E° = -0.2$ V, at room temperature, and $\Lambda = 10^6$, thus $\theta_{99} \simeq 10^{400000}$ M s, which means that appreciable conversion of ArX into ArNu is not feasible within a reasonable time, the catalyst being destroyed in the very first cycles of the chain process. This illustrates the central role of reaction 2 in the propagation of the chain process due to the fact that the termination steps involve the species Ar·. Although important, the role of reactions 0 and 1 appears less critical. It is reflected by the dependence of $\theta_{99}{}^0$ upon the values of $F\Delta E°/RT$ and $k_1/[\mathrm{ArX}]^0$ as shown in eq 10 and Figure 2.

For those systems in which θ_{99} goes to very large values, only a small conversion of ArX into ArNu will be reached within a reasonable time, say a few hours. Since Λ takes rather high values in these cases, the above approximation neglecting the effect of the termination steps within each cycle may well be no longer quite as valid.[27,28]

In *organic solvents*, abstraction of H atoms from the solvent by the aryl radicals cannot any longer be neglected as a termination step. A complete study of the problem would then require the analysis of the kinetics for the reaction scheme involving reactions 0–6. Then the sum, *SC*, of the concentrations of the intermediates Ar·, $\mathrm{ArX}^-\cdot$, and $\mathrm{ArNu}^-\cdot$ obeys the equation

$$\mathrm{d}SC/\mathrm{d}t = -(k_6 + 2k_{\mathrm{dif}}SC)[\mathrm{Ar}\cdot]$$

When $k_6 << 2k_{\mathrm{dif}}SC$, H atom abstraction can be ignored as termination step. Conversely, when $k_6 >> 2k_{\mathrm{dif}}SC$, reaction 6 prevails over all the other termination steps. This situation is a fortiori reached if $k_6 >> 2k_{\mathrm{dif}}[\mathrm{ArNu}^-\cdot]^0$ since $SC \leq [\mathrm{ArNu}^-\cdot]^0$. Let us focus our attention on this case.

It can then be shown[29] that the conversion of ArX into ArNu may remain smaller than 100% even if the reaction were allowed to proceed indefinitely. This maximal conversion percentage $\gamma_{\mathrm{m}}{}^{\mathrm{ArX}}$ is defined as follows.[29] If $\Gamma = (1 + k_2[\mathrm{Nu}^-]/k_6)([\mathrm{ArNu}^-\cdot]^0/[\mathrm{ArX}]^0) < 1$

$$\gamma_{\mathrm{m}}{}^{\mathrm{ArX}} = 100\Gamma \qquad (14)$$

Then the yield in substituted product is

$$\gamma_{\mathrm{m}}{}^{\mathrm{ArNu}} = \gamma_{\mathrm{m}}{}^{\mathrm{ArX}}/(1 + k_6/k_2[\mathrm{Nu}^-]) \qquad (15)$$

and the yield in ArH

$$\gamma_{\mathrm{m}}{}^{\mathrm{ArH}} = \gamma_{\mathrm{m}}{}^{\mathrm{ArX}}/(1 + k_2[\mathrm{Nu}^-]/k_6) \qquad (16)$$

The time required for 99% of the maximal conversion to be reached is then given by[30]

$$t_{99}[\mathrm{ArNu}^-\cdot]^0 = \theta_{99}{}^{\mathrm{H}} = [\Gamma/(1 - \Gamma)][4.6(\chi_1' - 1 + \Gamma) + \chi_1' \ln (1 - 0.99\Gamma)]/\chi_2' \qquad (17)$$

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[27] *SC* is a solution of $\mathrm{d}SC/\mathrm{d}t = -2k_{\mathrm{dif}}SC[\mathrm{Ar}\cdot]$. On the other hand, $d([\mathrm{ArNu}] + [\mathrm{ArNu}^-\cdot])/\mathrm{d}t = k_2[\mathrm{Nu}^-][\mathrm{Ar}\cdot]$. Dividing the first by the second equation and integrating leads to $SC = [\mathrm{ArNu}^-\cdot]^0 \exp\{-2(k_{\mathrm{dif}}/k_2[\mathrm{Nu}^-])\text{-}([\mathrm{ArNu}] + [\mathrm{ArNu}^-\cdot])\}$. Since we are looking for the conditions leading to a quasi-complete conversion of ArX into ArNu by using a catalytic amount of $\mathrm{ArNu}^-\cdot$ very rapidly, $[\mathrm{ArNu}] = [\mathrm{ArX}]^0 - [\mathrm{ArX}] \gg [\mathrm{ArNu}^-\cdot]$ and thus the above equation is equivalent to the simplified expression given by eq 12.

[28] It is seen on eq 12 and Figure 3 that when $\Lambda = 2k_{\mathrm{dif}}[\mathrm{ArX}]^0/k_2[\mathrm{Nu}^-]$ is larger than a few units, *SC* rapidly becomes negligible. It follows that for the systems in which a good conversion is reached within a reasonable time by using a catalytic amount of $[\mathrm{ArNu}^-\cdot]$, $\Lambda[\mathrm{ArNu}^-\cdot]^0/[\mathrm{ArX}]^0 \ll 1$. It follows that the differential equation pertaining to $[\mathrm{Ar}\cdot]$ is $\mathrm{d}[\mathrm{Ar}\cdot]/\mathrm{d}t = k_1[\mathrm{ArX}^-\cdot] - k_2(1 + \epsilon)[\mathrm{Ar}\cdot]$, where $\epsilon = (\Lambda[\mathrm{ArNu}^-\cdot]^0/[\mathrm{ArX}]^0)(SC + [\mathrm{Ar}\cdot]/2[\mathrm{ArNu}^-\cdot]^0)$ is much smaller than unity. The differential equation for $[\mathrm{Ar}\cdot]$ is thus practically the same as for the chain process without termination steps. Within the same approximation, this is also true for ArX, $\mathrm{ArX}^-\cdot$, and $\mathrm{ArNu}^-\cdot$. In other words, the effect of the termination steps is small within each cycle. The differential equation describing the decay of ArX is practically the same as that for the process without termination steps, replacing $[\mathrm{ArNu}^-\cdot]^0$ by *SC* (from eq 12). Integration of this equation leads to the following expression of the time required of a 99% conversion of ArX into ArNu

$$t_{99}[\mathrm{ArNu}^-\cdot]^0 = \theta_{99} = [(\exp\Lambda - 1)/\Lambda][J(\Lambda)\chi_1 - 1]/\chi_2 \qquad (13\mathrm{a})$$

with

$$J(\Lambda) = [\Lambda/(\exp\Lambda - 1)] \int_{0.01}^{1} \exp[\Lambda(1 - u)]\mathrm{d}u/u \qquad (13\mathrm{b})$$

χ_1 and χ_2 being as defined by eq 8 and 9. The variations of $J(\Lambda)$ and $[(\exp\Lambda - 1)/\Lambda]$ with Λ are shown on Figure 4. Equation 13a can be rewritten as

$$\theta_{99} = \theta_{99}{}^0[(\exp\Lambda - 1)/\Lambda]\{[J(\Lambda)\chi_1 - 1]/[J(0)\chi_1 - 1]\}$$

with

$$1 < [J(\Lambda)\chi_1 - 1]/[J(0)\chi_1 - 1] < [J(\Lambda) - 1]/[J(0) - 1]$$

where the last term varies much less than that of $(\exp(\Lambda - 1))/\Lambda$ as long as Λ is not larger than a few units. Its maximal value (Figure 4) is 7.3 whereas for the corresponding value of Λ (40), $(\exp\Lambda - 1)/\Lambda$ is about $6 \times 10.^{15}$ Equation 13 which is the simplified form of eq 13a, taking the above discussion into account, thus provides a correct order of magnitude for θ_{99}. As soon as a better accuracy on θ_{99} is required eq 13a,b should be used instead.

[29] *SC* is a solution of $\mathrm{d}SC/\mathrm{d}t = -\mathrm{k}_6[\mathrm{Ar}\cdot]$. With the assumption that the stationary-state approximation to be valid for Ar· and $\mathrm{ArX}^-\cdot$, the time-dependence of [ArX] is given by $\mathrm{d}[\mathrm{ArX}]/\mathrm{d}t = -(k_6 + k_2[\mathrm{Nu}^-])[\mathrm{Ar}\cdot]$. Integration of the ratio of these two differential equations provides the dependence of *SC* upon the conversion ratio, γ (expressed in percent)

$$SC = [\mathrm{ArNu}^-\cdot]^0\{1 - 10^{-2}\gamma([\mathrm{ArX}]^0/[\mathrm{ArNu}^-\cdot]^0)/(1 + k_2[\mathrm{Nu}^-]/k_6)\}$$

Since $SC \geq 0$, $\gamma = 100(1 - [\mathrm{ArX}]/[\mathrm{ArX}]^0)$ is such as

$$10^{-2}\gamma \leq \Gamma = (1 + k_2[\mathrm{Nu}^-]/k_6)[\mathrm{ArNu}^-\cdot]^0/[\mathrm{ArX}]^0$$

If $\Gamma \leq 1$, the chain process stops because of the complete disappearance of the catalytic species and thus the maximal conversion ratio is $\gamma_{\mathrm{m}}{}^{\mathrm{ArX}} = 100\Gamma$. If $\Gamma \geq 1$ all the starting ArX is converted into ArNu ($\gamma_{\mathrm{m}}{}^{\mathrm{ArX}} = 100$). In all cases the balance equation of the overall process is

$$\mathrm{ArNu}^-\cdot + (1 + k_2[\mathrm{Nu}^-]/k_6)\mathrm{ArX} \rightarrow \mathrm{ArH} + (1 + k_2[\mathrm{Nu}^-]/k_6)\mathrm{ArNu}$$

The overall maximal yield in ArNu, which may require oxidation of the solution to be reached, is thus in each case

$$\gamma_{\mathrm{m}}{}^{\mathrm{ArNu}} = \gamma_{\mathrm{m}}{}^{\mathrm{ArX}}/(1 + k_6/k_2[\mathrm{Nu}^-])$$

while the corresponding yield in ArH is

$$\gamma_{\mathrm{m}}{}^{\mathrm{ArH}} = \gamma_{\mathrm{m}}{}^{\mathrm{ArX}}/(1 + k_2[\mathrm{Nu}^-]/k_6)$$

[30] The time dependence of [ArX] is given by

$$\mathrm{d}[\mathrm{ArX}]/\mathrm{d}t = -\chi_2'[\mathrm{ArNu}^-\cdot]^0\{1 - (1 - [\mathrm{ArX}]/[\mathrm{ArX}]^0)10^2/\Gamma\}/\{(\chi_1'/[\mathrm{ArX}]) - (1/[\mathrm{ArX}]^0)\}$$

where $\chi_2' = 1/\{([\mathrm{ArX}]^0/k_1)(1 - k_{-0}/k_0) + [\mathrm{ArX}]^0/(k_6 + k_2[\mathrm{Nu}^-])\}$ and $\chi_1'/\chi_2' = \chi_1/\chi_2$ (see eq 8 and 9). Integration of this differential equation gives to the variations of [ArX] with time. If $\Gamma \neq 1$

$$t[\mathrm{ArNu}^-\cdot]^0\chi_2' = \{\Gamma/(1 - \Gamma)\} \times \{\chi_1' \ln ([\mathrm{ArX}]/[\mathrm{ArX}]^0) + (1 - \chi_1' - \Gamma) \ln [1 - (1 - [\mathrm{ArX}]/[\mathrm{ArX}]^0)/\Gamma]\}$$

If $\Gamma = 1$

$$t[\mathrm{ArNu}^-\cdot]^0\chi_2' = \chi_1'([\mathrm{ArX}]^0/[\mathrm{ArX}] - 1) + \ln ([\mathrm{ArX}]/[\mathrm{ArX}]^0)$$

which leads to eq 17–19.

Table I. Efficiency of the Chain Process for Some Systems in Liquid Ammonia at −40 °C

system		kinetic parameters				time required for a 99% conversion,[c] h	
ArX	Nu^-	k_1, s^{-1}	k_2, M^{-1} s^{-1}	$F\Delta E°/RT$	ref	$[Nu^-]/[ArX]^0 = 10^2$	$[Nu^-]/[ArX]^0 = 10^3$
4-chlorobenzonitrile[a]	$(EtO)_2PO^-$	9×10^8	1.5×10^9	−18.5	9	0.11 (3)	0.09 (3)
2-chloroquinoline[b]	PhS^-	1.7×10^4	1.4×10^7	0.9	7	10^{13} ((4) > (3))	10^4 ((4) > (3))
–	4-ClPhS^-	–	6×10^6	−1.6	7	2×10^{37} ((4) > (3))	8×10^{15} ((4) > (3))
–	$(EtO)_2PO^-$	–	1.8×10^7	−10.6	7	2×10^{12} (3)	2×10^5 (3)
2-bromoquinoline[b]	PhS^-	1.3×10^5	1.4×10^7	5.0	7	10^{11} ((4) > (3) ≃ (5))	10^2 ((4) > (3))
2-iodoquinoline[b]	PhS^-	3×10^6	1.4×10^7	17.5	7	5×10^9 ((5) > (4) > (3))	5 ((4) > (5) > (3))
1-chloronaphthalene[b]	PhS^-	1.5×10^4	2.3×10^7	−3	7	10^6 ((3) > (4))	5 ((3) > (4))

[a] $[ArX]^0 = 1.55 \times 10^{-2}$ M. [b] $[ArX]^0 = 10^{-3}$ M. [c] Estimated from eq 13 with $[ArNu^{-}\cdot]^0/[ArX]^0 = 10^{-2}$; numbers between parentheses are the most efficient termination steps.

where χ_1' and χ_2' have the same expressions as χ_1 and χ_2 (eq 8 and 9), $k_2[Nu^-]$ being replaced by $(k_6 + k_2[Nu^-])$.[30] If $\Gamma \geq 1$ $\gamma_m^{ArX} = 100$, and the yields are still given by eq 15 and 16. The times required for 99% conversion are then for $\Gamma = 1$

$$t_{99}[ArNu^{-}\cdot]^0 = \theta_{99}^{H} = (99\chi_1' - 4.6)/\chi_2' \qquad (18)$$

and for $\Gamma > 1$

$$t_{99}[ArNu^{-}\cdot]^0 = \theta_{99}^{H} = [\Gamma/(\Gamma - 1)][4.6\chi_1' + (\chi_1' - 1 + \Gamma)\ln(1 - 0.99\Gamma)]/\chi_2' \qquad (19)$$

Experimental Illustration

In Table I are listed several ArX–nucleophile systems in liquid ammonia for which the rate constants k_1 and k_2 are known from electrochemical determinations, and $\Delta E°$ can be derived from the corresponding cyclic voltammetric data.[7,9,31] The time required for 99% conversion was estimated for each of these systems according to the above kinetic analysis. This estimate was carried out for two values of the excess factor $[Nu^-]/[ArX]^0$, 10^2 and 10^3. It is indeed seen that this parameter has a considerable influence on the conversion times for the systems in which the efficiency of the chain process is relatively low; i.e., the termination steps have a strong influence.

The system involving *4-chlorobenzonitrile* as the substrate and *potassium diethyl phosphite* as the nucleophile in liquid ammonia at −40 °C appears as particularly remarkable since it shows a 99% conversion particularly rapid as compared to that most of the other systems on the list. In order to experimentally test these predictions, we carried out the following experiment. Starting with a solution of 1.55×10^{-2} M 4-chlorobenzonitrile and 0.663 M potassium diethyl phosphite in liquid NH_3 at −40 °C, in a preparative electrochemical cell, the potential of the working electrode was held at a value corresponding to the $ArNu/ArNu^{-}\cdot$ wave for a short period (~2 min) so as to consume 10^{-2} electron per molecule of ArX.[9] The circuit was then opened and the reaction allowed to proceed for 10 min. Analysis of the reaction mixture[9] revealed the formation of 4-cyanophenyl diethyl phosphonate in practically 100% yield. This experiment closely corresponds to the conditions of the above kinetic analysis, since the injection of 0.01 electron per mole of ArX into the solution amounts to introducing 1.55×10^{-4} M of $ArNu^{-}\cdot$ which is then allowed to catalyze the conversion of ArX into ArNu after the circuit has been opened. Since the excess factor $[Nu^-]/[ArX]^0$ is 43, the predicted time for 99% conversion is 9 min. There is thus a good fit between the theoretical predictions and the experimental results.

Most of the other systems listed in Table I correspond to rather low efficiencies of the chain process. Again this does not mean that good substitution yields cannot be reached. It was indeed shown that in the case of 2-chloroquinoline + benzenethiolate 80–90% substitution yields can be obtained by means of electrochemical stimulation with a corresponding consumption of electricity of 0.40–0.20 F/mol.[10] The low efficiency of the chain process for these systems also matches the fact that their cyclic voltammetric and preparative scale investigation could be correctly analyzed in the framework of a kinetic model in which reactions 3 and 4 were considered to occur within a thin reaction layer close to the electrode with negligible propagation of the chain process outside this layer and a fortiori outside the diffusion layer.[3,6,7,10]

Table II. Reaction of the Cyanide Ion with 4-Bromobenzophenone in Acetonitrile at 20 °C, Triggered by the Injection of the 4-Cyanobenzophenone Anion Radical[a]

$[ArNu^{-}\cdot]^0$ M	$[CN^-]$, M	γ_m^{ArX}, %		γ_m^{ArNu}, %		time required for $0.99\gamma_m^{ArX}$ conversion (from eq 17), s
		exptl	from eq 14	exptl	from eq 15	
1.45×10^{-3}	0.85	55	60.5	45	43.5	60
1.35×10^{-3}	0.20	22	25.5	10	9.5	17
3.4×10^{-4}	0.31	6.5	7.5	4	3.5	17

[a] $[ArX]^0 = 8.5 \times 10^{-2}$ M in each case.

On the other hand, we found that the systems involving 2-chloroquinoline as the substrate and the carbanions of acetonitrile and triphenylmethane as the nucleophiles in liquid ammonia or 1-chloronaphthalene and the carbanion of lutidine in the same solvents give rise to very efficient propagation of the chain process: the recording of a single voltammogram is sufficient to trigger the substitution. This very fact precludes the determination of the rate constants k_1 and k_2 by cyclic voltammetry. These systems, which corresponds to favorable values of $\Delta E°$ ($\Delta E° > 0$), thus involve high values of the rate constant k_2 ($k_2 > 5.10^8$ M^{-1} s^{-1}).

For illustrating the effect of the termination steps in an *organic solvent*, we investigated the reaction of 4-bromobenzophenone with the cyanide ion in acetonitrile. A procedure which adheres even more strictly to the conditions of the above kinetic analysis was followed in that case: the anion radical of 4-cyanobenzophenone was generated electrochemically in acetonitrile from the parent compound and then rapidly introduced into a vigorously agitated solution of 4-bromobenzophenone and cyanide ions in acetonitrile. The dark blue color of the 4-cyanobenzophenone anion radical disappeared within a few tenths of a second. Sampling 1 min after mixing and then every 10 min during 1 h followed by HPLC analysis did not show any significant variations of the solution composition. The results are given in Table II for three typical experiments. The yields obtained are in good agreement with those predicted by eq 14 and 15[32] taking $k_2/k_6 = 3$ M^{-1}. This figure is in good agreement with that found by cyclic voltammetry.[14] Table II also gives the times required for 99% of the maximal conversion to be reached (eq 16) by using the following values: $k_1 = 10^4$ s^{-1}; $2.5 \times 10^8 < k_2 < 8.10^8$ M^{-1} s^{-1}; $2.10^7 < k < 7 \times 10^7$ s^{-1}; $k_0 \simeq 9 \times 10^5$ M^{-1} s^{-1}; $F\Delta E°/RT = -10$ (as estimated from cyclic voltammetry).[14] The times thus obtained as on the order of a few tenths of a second which is compatible with the experimental observations.

These results show that the induction of the substitution reaction while possible according to the procedure employed leads to rather modest substitution yields. This does not imply that a good conversion of 4-bromo- into 4-cyanobenzophenone is impossible by other means. This would, however, require the consumption of a definitely larger amount of an electron-donating inductor.

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

(32) For the three experiments in Table II, $k_{dif}SC \leq 3 \times 10^7$ $s^{-1} \leq k_6$,[14] taking $k_{dif} = 2 \times 10^{10}$ M^{-1} s^{-1} in acetonitrile.[24] Deactivation of the chain process is thus predominantly caused by H atom abstraction from the solvent.

This is what was indeed found in the context of electrochemical stimulation of the reaction:[31] setting the electrode potential at the level of the ArX wave, i.e., negative to the $ArNu/ArNu^{-}\cdot$ standard potential in the present case, resulted in the formation of 95% 4-cyanobenzophenone after air oxidation of the solution. This required the consumption of 0.25 F/mol, showing that the chain process although not very efficient is by no means negligible since in the absence of any chain process the electricity consumption would have been 1.10 F/mol for a 95% yield.

Discussion

What preceeds has shown how the efficiency of the chain process hinges upon the termination steps, these being essentially electron transfers from $ArX^{-}\cdot$ and $ArNu^{-}\cdot$ to $Ar\cdot$ in solvents of low hydrogen atom donating ability. Several experimental examples have illustrated the validity of this approach. It is now possible to discuss, in this context, previous findings by other authors regarding the kinetics and the reactivity patterns of $S_{RN}1$ aromatic substitution.

A first general observation concerns the important role played by the ratio of the nucleophile to the substrate concentration. Inspection of Table I reveals that this factor has a particularly strong influence for the very numerous systems involving a chain process of rather low efficiency. This offers an explanation why, for these systems, the yields are so much dependent upon the exact experimental conditions leading to some irreproducibility while reproductibility is better for efficient systems.[2,5]

It is also interesting to roughly estimate the relative importance of the three termination steps (3), (4), and (5). This can be done by computing the ratio of the concentrations in $ArX^{-}\cdot$, $ArNu^{-}\cdot$, and $Ar\cdot$ since these three species react with the same diffusion-limited rate on $Ar\cdot$. The results of such an estimation are given in Table I. The quantitative estimation of these concentration ratios are strictly valid only for rather efficient processes (Λ not larger than a few units). However the trends they reveal will be the same for less efficients processes: the larger $k_2[Nu^-]$ as compared to k_1, the less efficient the dimerization reaction 5 will be in front of the electron-transfer reaction 3; the larger $k_2[Nu^-]$ as compared to k_0, the less efficient the dimerization reaction 5 in front of the electron-transfer reaction 4; the larger k_1 as compared to $k_0[ArX]^0$, the less efficient electron-transfer reaction 3 in front of electron-transfer reacton 4. It is noted from Table I that the dimerization reaction 5 is seldom the dominant termination step which agrees with the previous experimental observation that only small amounts of Ar–Ar, if any, are generally found among the reaction products.[2,4]

Another question of interest regards the influence of the leaving group ability of X^- on the reactivity patterns of the $S_{RN}1$ reaction. Three series of experiments are of particular relevance to this point: photostimulated reaction of aliphatic ketone enolates with heteroaromatic halides in the quinoline and pyridine series,[33] photostimulated reaction of halobenzenes and other substituted benzenes with diethyl phosphite and pinacolone enolate ions,[34] and solvated electron-stimulated reaction of the same type of substrates with acetone enolate ion.[35] All these experiments having been carried out in liquid ammonia; H atom transfer from the solvent to the $Ar\cdot$ radical can be excluded, the main termination steps being thus the electron-transfer reactions 3 and 4 and possibly the dimerization reaction 5.

It was found in the first series of experiments that the reactivities of the halides on potassium acetone enolate lie in the order 2-chloroquinoline > 2-bromopyridine > bromobenzene and 2-bromopyridine > 2-chloropyridine > 2-fluoropyridine.[33] As can be estimated from cyclic voltammetry the 2-chloroquinoline + acetone enolate system is not expected to give rise to very efficient chain process. This will thus be a fortiori true for the 2-bromo-, chloro-, and fluoropyridine. Since, with the exception of iodobenzene, all the members of the benzene series are less reactive on the same acetone enolate than bromobenzene,[34,35] the same conclusion will also hold for the benzene series with the possible exception of iodobenzene. Sustained stimulation is thus required in order to reach a good conversion of the starting compound. This is particularly clear in the case of solvated electron stimulation where dissolved potassium/ArX molar ratios ranging from 0.73–1.83 were found necessary in order to convert most of the starting material ArX.[35] This shows that even in the case of PhI the efficiency of the chain process is rather low.

The conditions in which these reactions were carried out thus do not exactly conform under those for which the above quantitative analysis was derived: conversion of most of the ArX in a reasonable time by means of a catalytic amount of $ArNu^{-}\cdot$. However, the general trends revealed by this analysis will nevertheless be followed: when two systems are compared, the less efficient the chain process, i.e., the longer the time required for 99% conversion under the conditions of the preceding analysis, the longer the time required for reaching a given conversion ratio under the conditions of the quoted experiments, also the larger the amount of alkali metal needed for obtaining this conversion, and also the higher the formation of the hydrogenolysis product ArH. The latter indeed stems directly from the electron-transfer termination steps 3 and 4. In the case of solvated electron stimulation part of the ArH formed can also derive from the direct reduction of $Ar\cdot$ by the initiator. Overall, however, the more rapid the rotation of the propagation cycle, the less ArH will be formed. It is noteworthy in this connection that the way in which the addition of the solvated electrons is performed does not affect critically the final distribution of products.[35a]

In each series, i.e., for the same $Ar\cdot$ and the same Nu^-, k_2 is the same while k_1 and $\Delta E°$ vary when passing from one X to the other. In the halogen series, the orders for $E°$ and k_1 are the same as for the leaving group ability: $E°_1 > E°_{Br} > E°_{Cl} > E°_F$; $k_{1,1} > k_{1,Br} > k_{1,Cl} > k_{1,F}$.[37] Since an increase of both $E°$ and k_1 has a favorable effect on the efficiency of the chain process as depicted in Figure 2, this exactly matches the order of reactivity found in the halopyridine[33] and in the halobenzene[34] series for the photostimulated reaction with potassium acetone enolate. The same is true for the formation of ArH in the benzene series under solvated electron stimulation which is roughly paralleled by the values of the dissolved K/ArX ratio.[35a] The yield in ArH increases when passing from I to Br, Cl, and F as anticipated from the fact that $E°$ and k_1 decrease in the same order. Comparing Ph–S–Ph to Ph–O–Ph the sulfur atom is expected to accommodate an electron more easily than the oxygen atom which would result in both $E°$ and k_1 being larger in the first case than in the second.[24,38] This again matches, in the framework of our interpretation, the fact that a larger amount of ArH was found to be formed in the first case than in the second.[35] There is no available data concerning the $E°$ and k_1 values for $PhN^+(CH_3)_3$, Ph–S–Ph, and Ph–O–Ph relative to those of the halides. However the fact that the reduction potentials in liquid NH_3 are in the order PhI > PhBr > $PhN^+(CH_3)_3$ > PhSPh > PhCl > PhF > PhOPh[39] is not incompatible with the order found for the half-reaction time under photostimulation[34] or for the ArH formation under stimulation by the solvated electron since $E°$ and k_1 are likely to vary in the same direction.[24,38] With Ar = Ph, the effect of $E°$ is most probably much more important than that of k_1. For benzene derivatives, k_1 values are indeed likely to be very large so that

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(33) Komin, A. P.; Wolfe, J. F. *J. Org. Chem.* **1977**, *42*, 2481.

(34) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6137.

(35) (a) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2852. (b) Tremelling, M. J.; Bunnett, J. F. *Ibid.* **1980**, *102*, 7375.

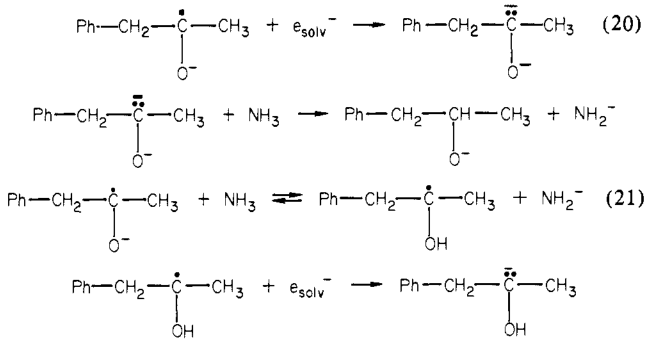
(36) It is in fact likely to be less reactive since the imine-like character of the pyridine ring should increase the electrophilic character of the radical in the 2-position as compared to the phenyl.

(37) See ref 21 and 24 and references therein.

(38) Falsig, M.; Lund, H.; Nadjo, L.; Savéant, J. M. *Nouv. J. Chim.* **1980**, *4*, 445.

(39) The cyclic voltammetric peak potentials (±0.02 V) for the corresponding irreversible waves at $v = 0.2$ V s^{-1} were found to be the following: PhI, –1.05; PhBr, –1.50; $PhN^+(CH_3)_3$, –2.24; PhSPh, –2.30; PhCl, –2.34; PhF, –2.40 V vs. Ag/Ag^+ (0.01 M). The wave for PhF is almost merged with the discharge of the supporting electrolyte while no wave can be detected for PhOPh (Amatore, C.; Savéant, J. M.; Thiébault, A., unpublished results).

Scheme II



$$Ph{-}CH_2{-}\dot{C}(O^-){-}CH_3 + e_{solv}^- \rightarrow Ph{-}CH_2{-}\ddot{C}^-(O^-){-}CH_3 \quad (20)$$

$$Ph{-}CH_2{-}\ddot{C}(O^-){-}CH_3 + NH_3 \rightarrow Ph{-}CH_2{-}CH(O^-){-}CH_3 + NH_2^-$$

$$Ph{-}CH_2{-}\dot{C}(O^-){-}CH_3 + NH_3 \rightleftharpoons Ph{-}CH_2{-}\dot{C}(OH){-}CH_3 + NH_2^- \quad (21)$$

$$Ph{-}CH_2{-}\dot{C}(OH){-}CH_3 + e_{solv}^- \rightarrow Ph{-}CH_2{-}\ddot{C}^-(OH){-}CH_3$$

in eq 11, the second term will be much smaller than the first. The effect of the leaving group thus mainly depends upon ΔE°, through k_0, electron transfer between $ArNu^{-}\cdot$ and ArX being indeed likely to be under activation control,[23] and to a much lesser extent upon the rate of $ArX^{-}\cdot$ cleavage contrary to what has been hypothesized previously.[35b]

In the solvated-electron-stimulated reaction of phenyl halides and related substrates with potassium acetone enolate, it was noted that the ketone resulting from the substitution process, $PhCH_2COCH_3$, is partially reduced into the corresponding alcohol, $PhCH_2{-}CHOH{-}CH_3$, during the course of the reaction.[35] An interesting observation in this connection is that the ketone/alcohol ratio roughly parallels the amount of ArH formed: the less ArH, the higher the ketone/alcohol ratio. This can be interpreted as follows. The formation of the alcohol reveals the existence of additional termination steps, involving the reduction of $ArNu^{-}\cdot$ in addition to that of Ar·. The reduction of $ArNu^{-}\cdot$ may occur by electron transfer from the solvated electrons followed by protonation or, alternatively, by protonation followed by electron transfer (Scheme II). Passing from Ph–O–Ph and PhF to PhI the rotation of the propagation cycle is faster and faster, giving less and less opportunity for reactions 20 and/or 21 to occur and thus resulting in the formation of smaller and smaller amounts of alcohol from the reduction of the ketone. Specifically the rate of reaction 0 increases from Ph–O–Ph and PhF to PhI which renders reactions 20 and/or 21 less and less efficient. This falls on line with the observation that the ketone/alcohol ratio is an increasing function of the rate of attachment of hydrated electrons to ArX.[40] This rate is indeed related to E°, k^0, and k_1 in a way similar to that of the cyclic voltammetric peak potential. Our explanation of these observations thus resembles that originally offered by Bunnett et al.[40] and further abandoned in favor of an interpretation based on the rate of cleavage of $ArX^{-}\cdot$[35b] which seems unlikely for the same reasons as discussed above when rationalizing the leaving-group effect on ArH formation. The key importance of the reaction of $ArNu^{-}\cdot$ with ArX (eq 0) as ensuring the propagation of the chain against the electron-transfer termination steps 3 and 20 is that the leaving group is still present in one reacting species at the points where product selection occurs. It still acts as a leaving group rather than as a "left"[35b] group. Actually the leaving-group effect observed in the phenyl series is mainly indirect: it stems from the fact that the better the leaving groups, the more rapidly ArX can be reduced by $ArNu^{-}\cdot$, thus lowering the efficiency of reactions 3 and 20 or 21.

With regard still to the further reduction of the ketone into the corresponding alcohol, interesting experiments were carried out involving the simultaneous reduction of two substrates, e.g., PhI and C_6D_5Cl with the same nucleophile, the acetone enolate ion.[35a] It was noted that ratio of ketone over alcohol formed is within the experimental uncertainty of the yield determinations on the same order of magnitude as when the two substrates are separately reacted with the same nucleophile. This can be explained by taking into account that the reaction with PhI is faster than the reaction with C_6D_5Cl (or PhCl): PhI first reacts practically as if it were alone and C_6D_5Cl begins to react appreciably after PhI has disappeared. This would result in a product distribution being the sum of those observed in each separate experiment. The results obtained by reacting simultaneously PhI and 3-methoxychlorobenzene or PhCl and 3-methoxyiodobenzene with the acetone enolate ion[35a] can be interpreted along the same lines.

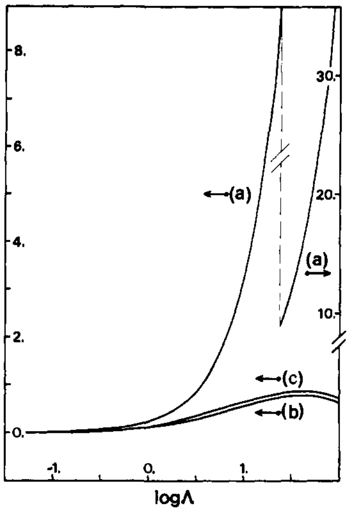


Figure 4. Variations of the functions log [(expΛ − 1)/Λ] (a), log [$J(\Lambda)/J(0)$] (b) ($J(0)$ = 4.6), and log {[$J(\Lambda)$ − 1]/[$J(0)$ − 1]} (c). For definition of symbols see text and ref 28.

The above rationalizations of the effect of the leaving group on substitution efficiency, ArH formation, amount of initiator required, and ketone/alcohol ratio for substitutions by ketone enolate ions do not appear to critically depend upon whether the reaction occurs during or after the reactants are mixed with the solvated-electron solution when potassium dissolved in liquid NH_3 is used as the initiation. Competition between the rotation of the propagation cycle and termination steps would indeed essentially follow the same trends in both cases. It is noteworthy in this connection that similar leaving-group effects are found in photostimulated reactions.[33,34] Note that if the initiation reaction involving solvated electrons was shown to have a marked heterogeneous character, the situation would be similar to what occurs with stimulation by an electrode.[3] Then, besides the competition between the chain process and the homogeneous termination step, the reduction of Ar· at the electrode–solution interface or here, at the interface between the "electron-rich" and "electron-less" zones,[35] acts as a side reaction, raising ArH formation at the expense of substitution.[3] For what regards this additional side reaction there should be a leaving-group effect working in the opposite direction as that experimentally found: for faster and faster $ArX^{-}\cdot$ cleavage, Ar· is formed closer and closer to the electrode, or to the electron-rich zone, and has thus more and more opportunity to diffuse back and be converted into Ar^- before reacting with Nu^- in the solution.[3] This is one reason why 2-iodoquinoline gives rise to less efficient substitution by PhS^- in liquid NH_3 than 2-chloroquinoline,[3,7] and the same effect is found when comparing 4-iodo- to 4-bromobenzonitrile as reacted with the same nucleophile in acetonitrile.[3,31] This has already been noted and rationalized.[3,7,31] The question of the interplay between the surface reaction and the homogeneous chain process and termination steps is fully discussed in a forthcoming publication.[14] It can thus be concluded that the heterogeneous character of the reaction during mixing of the reactants with solvated electrons does not play a major role in controlling the product distribution.

We can thus conclude that our kinetic model for the propagation and deactivation of the chain process explains the main experimental observations made in the study of homogeneous $S_{RN}1$ aromatic substitution processes. It should be emphasized again that the cruxial point in this interpretation is the important role played by the electron-transfer reactions to Ar·, and eventually to $ArNu^{-}\cdot$, as termination steps, in solvents of low H atom donating ability such as liquid ammonia while H atom transfer to Ar· plays a major role in organic solvents.

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J. Am. Chem. Soc. **1981**, *103*, 6937–6947

Experimental Section

Chemicals. Starting Materials. They were of commercial origin except for 2-bromoquinoline,[41] 2-iodoquinoline,[42] and 4-cyanobenzophenone.[31] 4-Cyanophenyl diethyl phosphonate was synthetized by the reaction of 4-chlorobenzonitrile with potassium diethyl phosphite in the presence of nickel chloride:[43] mp 31–33 °C; NMR ($CDCl_3$, Me_4Si reference) δ 1.33 (CH_3, t), 2.51 (CH_2, 2 q, $J_{CH_2-CH_3} = 7$ Hz, $J_{P-CH_2} = 9$ Hz), 7.7–8.2 (C_6H_4, m); mass spectrum, *m/e* 239 (33), 212 (27), 185 (100), 166 (93), 130 (43), 119 (37), 110 (33), 103–102 (60), 77 (15), 76 (22); IR ($CHCl_3$) 2220 (CN), 1120 (P=O), 1030 cm^{-1} ($P(OEt)_2$).

Nucleophiles. They were prepared in a manner similar to that in ref 7 for experiments in liquid ammonia. Tetraethylammonium cyanide (Fluka) was used in acetonitrile.

Solvents. Liquid ammonia was purified as previously described.[44,45] The supporting electrolyte was potassium bromide in 0.1 M concentration. Acetonitrile was distilled on calcium hydride before use. In acetonitrile the supporting electrolyte was tetrabutylammonium fluoborate (0.1 M).

Electrochemical Instrumentation. It was the same as those previously described in ref 7 for liquid ammonia and in ref 31 for acetonitrile.

Procedures. Induction of the reaction of 4-chlorobenzonitrile (1.55×10^{-2} M) with diethylphosphite (0.663 M) in liquid ammonia was performed in an electrolysis cell (50 mL); the working electrode was a platinum grid (15-cm^2 surface area) and the counterelectrode a platinum wire separated by a no. 4 glass frit. The temperature was −40 °C. The potential was set at −1.35 V for 2 min until 10^{-2} F were passed. The cell was then disconnected and the reaction was allowed to run for 10 min. The resulting product was extracted with ether after evaporation of liquid ammonia and identified by comparison (VPC, mass spectrometry) with an authentic sample prepared as described above. The yield was determined by gas chromatography (3% OV17, 1.5 m) and was found to be 100%.

Induction of the reaction of the cyanide ion (M) with 4-bromobenzophenone (10^{-2} M) was carried out in a three-necked flask containing 50 mL of deoxygenated acetonitrile kept under a nitrogen atmosphere. The flask was connected with an electrolysis cell containing 2×10^{-3} M of 4-cyanobenzophenone and 10^{-1} M tetrabutylammonium fluoborate in 10 mL of acetonitrile. This last solution was electrolyzed (−1.8 V vs. Ag/Ag^+ (0.01 M)) exhaustively and poured while being stirred into the flask with careful exclusion of oxygen. Samples were withdrawn through a septum at regular intervals (10 min), quenched by air, and titrated by liquid chromatography (RP18 column, elution with 50–50 acetonitrile–methanol, UV detection at 254 nm).

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(46) Possible occurrence of another type of termination steps involving the disproportionation of $ArX^{-}\cdot$: $2ArX^{-}\cdot \rightarrow ArX + ArX^{2-}$ with the latter fragmenting to Ar^- and X^- as suggested by a reviewer is extremely unlikely as results from the electrochemistry of aryl halides. In most cases the cleavage of $ArX^{-}\cdot$ is fast enough not to allow the disproportionation to proceed. When not the case, the distance between the waves featuring the successive reduction of ArX into $ArX^{-}\cdot$ and ArX^{2-} is such[47] as to imply that the coproportionation is much largely favored thermodynamically as compared to disproportionation. The latter reaction as pulled by the further cleavage of ArX^{2-} is thus likely to be slow. Note in this respect that the other termination steps are either second-order reactions close to the diffusion limit or very fast pseudo-first-order reactions.

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Low-Temperature Fluorination of Aerosol Suspensions of Hydrocarbons Utilizing Elemental Fluorine

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Abstract: This work describes a new concept in direct fluorination methodology and an apparatus designed to achieve conditions necessary for the rapid, continuous partial or complete fluorination of hydrocarbon molecules under controlled conditions of temperature and concentration. Results from the fluorination of neopentane are presented which indicate that although the degree of fluorination for a given set of conditions indicates a Gaussian distribution, investigation of specific isomers indicates significant deviations from statistical isomer distributions in fluorinated neopentanes. Photochemical assisted fluorinations of neopentane, 1,4-dioxane, cyclohexane, and 2,2-dimethyl-1,3-dioxolane are described which produce the perfluorinated analogues directly in good purity and in high yields.

The fluorination of hydrocarbon molecules by present technology is limited to a few distinct methodologies. In most cases the most appealing methods from the standpoint of reaction rate and scale-up operate in anhydrous hydrogen fluoride which reacts with many organic moieties (Swart's halogen-exchange reaction and Simon's electrochemical process),[1-5] utilize metal fluoride reagents which are expensive (AgF_2, HgF_2), give incomplete fluorination with increasing complexity of the structure of the molecule to be fluorinated (CoF_3, $KCoF_4$)[6,7] or operate at elevated temperatures, and produce generally lower yields of more complex molecules (Bigelow's "jet fluorination").[8-10] The "LaMar"

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