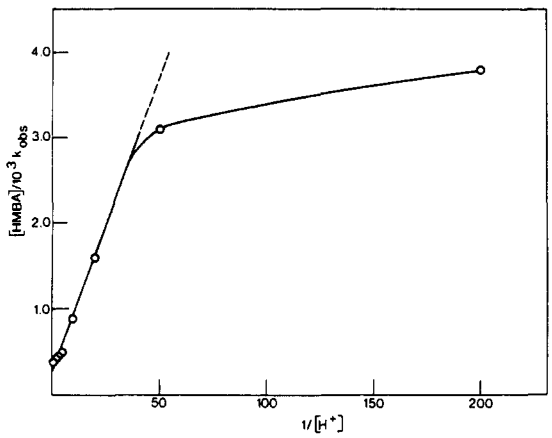

Figure 9. Plot of [HMBA]/k_{obsd} vs. 1/[H^+] for the chromium(V) oxidation. Data from Table VII.

the stability of the reaction product, most likely [$Cr^{III}(HMBA)_2(H_2O)_2]^+$. It is interesting to note that at low concentrations HMBA stabilizes Cr(V).[13] This suggests that chromium(V) achieves maximum stability in a complex with two molecules of HMBA; both the loss of an HMBA ligand as well as the addition of a third HMBA molecule result in destabilization.

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Determination of the Lifetimes of Unstable Ion Radicals by Homogeneous Redox Catalysis of Electrochemical Reactions. Application to the Reduction of Aromatic Halides

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Abstract: Application of the usual electrochemical techniques to the detection and characterization of short-lived ion radicals fails as soon as the lifetimes are shorter than about 0.1 ms. Homogeneous redox catalysis of the electrochemical reaction yielding the ion radical as an intermediate permits the characterization of much more unstable species allowing the determination of lifetimes down to the nanosecond time range. Instead of occurring at the electrode surface the initial electron transfer is carried out by the active form of the catalyst couple. This is produced electrochemically in the context of a standard electrochemical method such as cyclic voltammetry. The kinetics of the overall reaction is derived from the increase of the catalyst wave in the presence of the substrate. According to the relative magnitude of the rate constants of the backward homogeneous electron transfer and of the follow-up decomposition of the initial anion radical, the kinetic control of the catalytic process is either by the latter reaction or by the forward electron transfer step. Mixed kinetic control is obtained for intermediate values of the rate constant ratio. The determination of the lifetime of the ion radical is based upon the shift of the system from one limiting control to mixed kinetic control with a change in the catalyst concentration. Another approach involves the concomitant use of the data featuring the electrode reaction when it is under the kinetic control of the decomposition reaction. The reduction of five aromatic halides (2-chloroquinoline, 9-chloro- and bromoanthracene, and 1-chloro- and bromonaphthalene) in aprotic medium is analyzed to illustrate the practical application of the redox catalytic method to the determination of the lifetimes of frangible ion radicals. The relationships between the lifetimes of the anion radicals, the standard potentials for their formation, and the structure of the parent compound are briefly discussed.

The electrochemical reduction of aromatic halides generally involves the cleavage of the carbon–halogen bond of the initial anion radical followed by further reduction of the resulting neutral aryl radical:

$$ArX + 1e \rightleftarrows ArX^{-}\cdot \qquad (1el)$$

$$ArX^{-}\cdot \xrightarrow{k} Ar\cdot + X^{-} \qquad (2)$$

$$Ar\cdot + 1e \rightarrow Ar^{-} \qquad (3)$$

$$Ar\cdot + ArX^{-}\cdot \xrightarrow{k_4} Ar^{-} + ArX \qquad (4)$$

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$$\mathrm{Ar^-} + \left\{\begin{matrix}\mathrm{SH} \\ \mathrm{H_2O}\end{matrix}\right. \rightarrow \mathrm{ArH} + \left\{\begin{matrix}\mathrm{S^-} \\ \mathrm{OH^-}\end{matrix}\right. \tag{5}$$

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

$$\mathrm{S\cdot} + 1\mathrm{e} \rightarrow \mathrm{S^-} \tag{7}$$

$$\mathrm{S\cdot} + \mathrm{ArX^-\cdot} \xrightarrow{k_8} \mathrm{S^-} + \mathrm{ArX} \tag{8}$$

The reduction of the Ar· radical may occur through electron transfer at the electrode (3) or in the solution (4) and, competitively, through H-atom transfer in the case of an organic solvent, SH (see ref 1 and references cited therein). The interference of the latter reaction is negligible when poor H-atom donors such as liquid ammonia are used as solvents.[2,3]

Electrochemical techniques such as cyclic voltammetry and potential step chronoamperometry have been employed for estimating the lifetime of the initial $\mathrm{ArX^-\cdot}$ anion radical.[2-9] However, as soon as the lifetime is shorter than about 10^{-4} s its determination becomes impossible by the standard use of these techniques as well as of the other existing electrochemical methods. In, e.g., cyclic voltammetry, an irreversible wave will thus be obtained in the whole range of accessible sweep rates. The voltammetric process is then kinetically controlled either by the charge-transfer step (1el) or by the cleavage reaction (2) or by both steps concomitantly. In the first case, the only derivable quantitative data are the transfer coefficient, α, of the electron-transfer reaction and its forward apparent rate constant $k_f^{\mathrm{el,ap}}$, i.e., a combination of the standard potential $E°$ and the apparent standard rate constant $k_S^{\mathrm{el,ap}}$:

$$\ln k_f^{\mathrm{el,ap}} = \ln k_S^{\mathrm{el,ap}} + (\alpha F/RT)E°$$

In the second case the analysis of the wave provides a combination of the standard potential and the rate constant, k, of the cleavage reaction:

$$E° + (RT/2F)\ln k$$

while in the third, $E°$, $k_S^{\mathrm{el,ap}}$, and k cannot be separated one from the other. In all cases the intrinsic value of k cannot be determined. This is a quite general problem that will arise in any electrochemical process where the initial charge-transfer step is followed by a chemical reaction which is so fast that the maximal diffusion rates accessible with the usual electrochemical techniques cannot compete successfully with it. A severe limitation is then encountered in determining correlations between each of the electrochemical parameters and the structure of the starting compound. The determination of $E°$, k_S^{el}, and k by electrochemical means will indeed be often restricted to a series of compounds in which the structure variation is too narrow to allow the derivation of sound correlations. This is the case with the aromatic halides, a large number of which fall into the category defined above. So far, the only haloaromatics for which the determination of the standard potential and of the dissociation rate constant of the anion radical has been possible by electrochemical means are the following: chloro- and bromobenzophenones[2,5] and fluorenones,[5,8] halonitrobenzenes,[4,6] fluorobenzonitriles,[7] and *m*-chloroacetophenone.[9] This should also be possible for 4-(chlorostyryl)pyridines[10] and in the series of haloquinoxalines and phenazines.[11] It appears therefore desirable to devise other kinetic approaches able to overcome the limitations encountered in the standard application of the usual electrochemical techniques, i.e., to provide an access to each of the three main constants, $E°$, k_S^{el}, and k, for systems in which the lifetime of the first intermediate is less than 10^{-4} s. From homogeneous redox catalysis[12] of the considered electrochemical reaction it is possible to derive a method offering such capabilities. Instead of occurring at the electrode surface, the electron exchange reaction is carried out in the solution by means of a redox catalyst couple P/Q. The concentrations of P and Q are monitored electrochemically, which allows both the controlled-potential production of the active form of the catalyst, Q, and the determination of the kinetics of its reaction with the substrate. The method has already been applied to the determination of the standard potentials and standard rate constants of the electron transfer to several aromatic halides in the benzene and pyridine series.[13-15] It is the purpose of the present report to show how homogeneous redox catalysis can be used to determine the lifetimes of unstable ion radicals within the range 1 ns–10 μs. The method will be experimentally illustrated by the reduction of several aromatic and heteroaromatic halides in aprotic media.

Principle of the Method

Let us first consider the EC mechanism, which is the simplest of the reaction schemes where follow-up chemical steps are associated with electron-transfer reactions:

$$\begin{array}{lll} \text{electrode process} & \text{catalytic process} & \\ & \mathrm{P} + 1\mathrm{e} \rightleftarrows \mathrm{Q} & (0) \\ \mathrm{A} + 1\mathrm{e} \rightleftarrows \mathrm{B}\ (1\mathrm{el}) & \mathrm{Q} + \mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{P} + \mathrm{B} & (1\ \mathrm{sol}) \\ \end{array}$$

$$\mathrm{B} \xrightarrow{k} \mathrm{C} \qquad (2)$$

The analysis will be carried out for a reduction process, transposition to oxidation being immediate. Although EC mechanisms are seldom encountered in current practice of organic electrochemistry, the analysis of their redox catalytic behavior provides a correct qualitative prediction of what will be observed for a large variety of other mechanisms. Quantitative relationships between the redox catalytic behavior of EC mechanisms and that of two-electron processes will be given in the following. The whole discussion will be carried out mainly in the context of cyclic voltammetry. Extension to other transient or stationary techniques does not involve particular difficulties, being essentially obtained by a modification of the relationships between the dimensionless kinetic parameters and the rate constants.

The catalyst redox couples P/Q are selected so as to fulfill the following conditions: the standard potential $E°_{\mathrm{PQ}}$ is positive to the reduction potential of the substrate A; electron transfer between the electrode and P or Q is fast; both P and Q are chemically stable toward the species present in the reaction medium as well as toward A and B (except for the outer-sphere electron transfer $\mathrm{A} + \mathrm{Q} \rightleftarrows \mathrm{B} + \mathrm{P}$) and the products and intermediates of the reduction process. Under such conditions, starting from the reversible wave of P, addition of A will result in an increase of the peak current featuring the regeneration of P through reaction (1 sol) (Figure 1). The kinetics of this regeneration is controlled by the forward and backward reaction (1 sol) and by reaction 2. The principle of the application of redox catalysis to the determination of equilibrium and rate constants of irreversible systems is based upon the experimental observation of these kinetics as a function of operational parameters such as catalyst and substrate concentrations and diffusion rate which is governed in the context of cyclic voltammetry by the sweep rate.

Quantitatively, the kinetics of P regeneration is conveniently expressed as the ratio $i_p/\gamma i_{pd}$, where i_p is the catalytic peak current, i_{pd} is the peak current of the reversible P wave in the absence of A, and γ is the excess factor, i.e., the ratio between the substrate and catalyst concentrations ($\gamma = C_A^0/C_P^0$). On the other hand, the effect of the rate constants, concentration, and sweep rate on the kinetics of the catalyst can be analyzed rigorously by introducing the following dimensionless kinetics parameters:

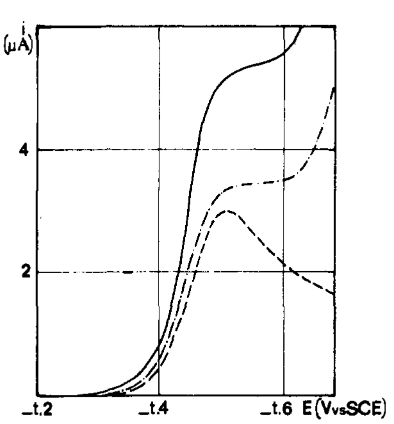

Figure 1. An example of the increase of the catalyst cyclic voltammetric peak upon addition of the substrate. Catalyst: benzo[*c*]cinnoline (2×10^{-3} M). Substrate: 2-chloroquinoline (concn: - - -, 0; -·-·-, 4×10^{-3} M; —, 10^{-2} M) in DMF + 0.1 M Et_4NClO_4, $v = 0.033$ V s^{-1}.

$$\lambda_1 = (k_1 C_P{}^0/v)(RT/F),\ \lambda_2 = k_2 C_P{}^0/v)(RT/F),$$
$$\lambda = (k/v)(RT/F)$$

which represent forward reaction (1 sol), backward reaction (1 sol), and reaction 2, respectively. The form given to each of these parameters reflects the first-order character of reaction 2 and the second-order character of reaction (1 sol) in both directions.

The overall kinetics of the catalytic system, i.e., the ratio $i_p/\gamma i_{pd}$, depends in general upon four parameters (λ_1, λ_2, λ, and γ). However, as discussed in detail elsewhere,[16,17] in virtually all the cases where redox catalysis is applied to the equilibrium and rate characterization of irreversible systems, the concentration of species B can be regarded as stationary, i.e.

$$k_1 C_A C_Q = k_2 C_B C_P + k C_B$$

i.e., in dimensionless terms

$$\lambda_1 aq = \lambda_2 bp + \lambda b$$

($a = C_A/C_P{}^0$, $b = C_B/C_P{}^0$, $p = C_P/C_P{}^0$, $q = C_Q/C_P{}^0$).

The kinetics of the catalytic system then depends upon only three parameters which can be chosen as λ_1, λ/λ_2 ($=k/k_2 C_P{}^0$), and γ.

In this context, two limiting situations can be reached as far as the kinetic control of the catalytic system is concerned:

(i) If $k \gg k_2 C_P{}^0$ the kinetic control is by forward reaction (1 sol). The system then depends upon only two parameters, λ_1 and γ; $i_p/\gamma i_{pd}$ is given as a function of λ_1 by a set of working curves, one for each value of γ (Figure 3 in ref 17). They can be used for deriving λ_1 and thus k_1 from measured values of $i_p/\gamma i_{pd}$. A diagnostic criterion that the kinetic control is actually by forward reaction (1 sol) derives from the effect of the catalyst concentration, $C_P{}^0$, keeping the excess factor, γ, constant. A variation in $C_P{}^0$ results in a proportional variation of λ_1 which leads to an increase of the $i_p/\gamma i_{pd}$ ratio as predicted by the working curve corresponding to the given value of γ.[17] Therefore, the observation of a constant value of k_1 from the application of the above procedure, for a given $C_P{}^0$ range, provides evidence that kinetic control is actually by forward reaction (1 sol) within this concentration range.

(ii) If $k \ll k_2 C_P{}^0$, the kinetic control is by reaction 2, reaction (1 sol) remaining at equilibrium. The system again depends upon only two parameters: γ and $\lambda\lambda_1/\lambda_2 = (kk_1/k_2) \cdot (RT/Fv)$. $i_p/\gamma i_{pd}$ is given as a function of the latter parameter by a set of working curves (Figure 5 in ref 17). These can be used to obtain $\lambda\lambda_1/\lambda_2$ and thus kk_1/k_2 from $i_p/\lambda i_{pd}$. A diagnostic criterion that the kinetic control is actually by reaction 2 is again provided by the effect of $C_P{}^0$ for a given value of γ. The parameter $\lambda\lambda_1/\lambda_2$ is indeed independent of $C_P{}^0$. The observation, in a given $C_P{}^0$ range, that i_p/i_{pd} does not depend upon $C_P{}^0$ therefore provides evidence that the kinetic control is by reaction 2 within this concentration range.

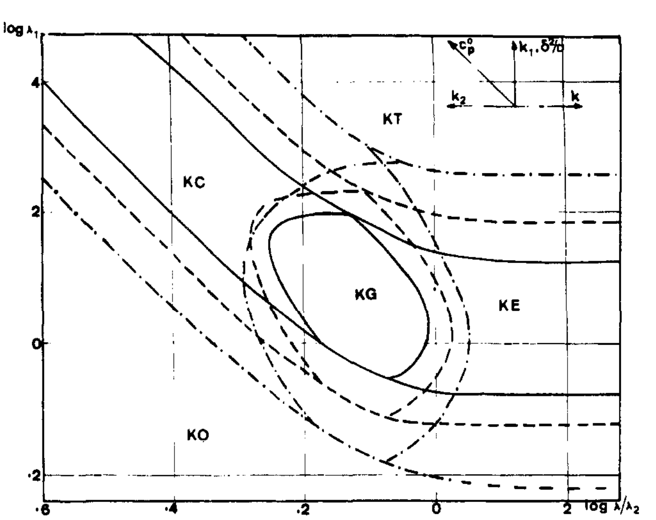

Figure 2. Kinetic zone diagram: KE, kinetic control by forward reaction (1 sol); KC; kinetic control by reaction 2 with reaction (1 sol) at equilibrium; KG, mixed kinetic control; KO, negligible catalysis; KT, total catalysis. γ = 1 (—), 4 (- - -), 20 (-·-·)

For intermediate values of $k/k_2 C_P{}^0$, both reactions (1 sol) and (2) control the overall kinetics. The parameter ranges in which the two limiting situations are reached within experimental uncertainty are shown in Figure 2 on the basis of a 5% error on peak current measurement for various values of the excess factor, γ. It is seen that the effect of an increase of sweep rate is essentially to decrease the $i_p/\gamma i_{pd}$ ratio with little change in the kinetic control. On the contrary, variations in $C_P{}^0$, for a given value of γ, may shift the system from one type of kinetic control to the other: an increase of $C_P{}^0$ tends to shift the system from kinetic control by (1 sol) to mixed kinetic control and from there to kinetic control by (2).

A first approach to the determination of k, i.e., of the lifetime of B, is based on the latter observation. If for a certain range of $C_P{}^0$ concentrations the system is under the kinetic control of (1 sol), λ_1 can be determined as described above. If now the system can be shifted into the mixed kinetic control situation by increasing $C_P{}^0$, a working curve can be computed for the value of λ_1 just obtained as a function of the parameter λ/λ_2.[17] It can then be used to determine λ/λ_2 and thus k/k_2. As will be seen later on, k_2 is then frequently at the diffusion limit, k_{dif}. It follows that k can finally be obtained once k_{dif} is known. Another type of situation may be encountered in which k can also be determined at least in principle. It involves the system being under the kinetic control of reaction 2 for a given range of $C_P{}^0$. This allows the determination of $\lambda\lambda_1/\lambda_2$. If the system can be shifted into the mixed control region by decreasing the concentration, λ/λ_2 can be determined by a procedure similar to that used in the preceding case. This again leads to the value of k once $k_2 = k_{dif}$ is known.

Another approach, not involving the shift of the system from one kinetic zone to the other, may be followed by using the kinetic data pertaining to the electrode uncatalyzed reaction as derived from, e.g., cyclic voltammetry. This requires that a range of sweep rates exists in which the electrode reaction is under the kinetic control of the chemical reaction (2).[18] Then the peak potential is a function of the standard potential of the A/B couple, $E°_{AB}$, and of k:

$$E_p = (RT/F)[\ln (RT/F) - 0.78] + E°_{AB} + (RT/2F) \ln (k/v) \quad \text{(I)}$$

If now the catalytic system is under the kinetic control of reaction (1 sol), one has access to k_1. By carrying out this type of determination for several catalyst couples the standard potential $E°_{AB}$ can be obtained as already discussed elsewhere.[14] Once $E°_{AB}$ is known the measurement of the peak potential in cyclic voltammetry leads to the value of k through eq 1. If conversely the catalytic system is under the kinetic control of reaction 2, $kk_1k/_2$ can be determined. On the other hand

$$(RT/F) \ln (kk_1/k_2) = E°_{AB} - E°_{PQ} + (RT/F) \ln k \quad \text{(II)}$$

Since $E°_{PQ}$ is known, eq II provides the value of $E°_{AB} + (RT/F) \ln k$. The application of eq I to the peak potential measurements provides $E°_{AB} + (RT/2F) \ln k$. Solving the ensuing two unknowns–two equations system finally leads to $E°_{AB}$ and to k.

Several examples of the application of these two approaches to the determination of the lifetimes of anion radicals in the haloaromatic series are given in the following. It must be noted, however, that the reduction of these compounds does not follow a mechanism as simple as the EC reaction scheme. The electrode uncatalyzed reduction rather occurs according to the reaction sequence consisting of the above (1 el) to (8) steps. The catalytic process involves the same steps, (1 el) being replaced by (1 sol). Moreover, the solution electron transfer to Ar· and S· may involve the reduced form of the catalyst, Q, as electron source instead of $ArX^{-}·$:

$$Ar· + Q \rightarrow Ar^- + P \quad (4')$$

$$S· + Q \rightarrow S^- + P \quad (8')$$

Despite the complexity of this reaction sequence it has been shown[13,16,17] that the catalytic peak current can be simply derived from its EC expression according to

$$i_p(\lambda_1, \lambda/\lambda_2, \gamma) = i_p^{EC}(\lambda_1, \lambda/\lambda_2, 2\gamma) \quad \text{(III)}$$

The validity of this relationship results from the following characteristics of the reaction mechanism. Ar· is reduced at a potential much more positive than ArX and also than the catalysts giving rise to detectable catalytic currents. The same is true for the radical deriving from the solvent, S·. It follows that reactions 4, 4′, 8, and 8′ are irreversible and that their rates are limited by diffusion. On the other hand, the selection of the catalyst couples and of the sweep rate is such that the catalytic efficiency is significantly lower than its maximal value ($i_p/\gamma i_{pd} = 1.365$) in order for the measurements not to be affected by the overlapping of the catalyst and substrate waves. In such conditions the kinetic parameter featuring the rate-determining step of the catalytic sequence is not very large. It follows that intermediates such as Ar· and S· are formed relatively far from the electrode surface. They have thus no time to diffuse back to the electrode and be reduced according to reactions 3 and 7 before reacting on $ArX^{-}·$ or Q according to (4), (4′) and (8) (8′), respectively. Lastly, the stationary-state concentration of $ArX^{-}·$ is much less than that of Q since it rapidly decomposes according to reaction 2. The solution reduction of Ar· will therefore follow reaction 4′ with practically no interference of (4). The same is true for (8′) and (8).

Table I. Redox Catalyzed Reduction of 1-Chloronaphthalene in Me_2SO (0.1 M Et_4ClO_4)

Catalyst 4-Methoxybenzophenone ($E°_{PQ} = -1.75$ V)								
C_P^0	2×10^{-3}	2×10^{-3}	4×10^{-3}	4×10^{-3}	10^{-2}	10^{-2}	2×10^{-2}	2×10^{-2}
v, V s^{-1}	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05
γ	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$i_p/2\gamma i_{pd}$	1.07	1.11	1.11	1.22	1.20	1.37	1.31	1.49
k_1	110	100	95	102	73	78	62	57

Catalyst Anthracene ($E°_{PQ} = -1.86$ V)				
C_P^0	10^{-3}	10^{-3}	2×10^{-3}	2×10^{-3}
v, V s^{-1}	2	5	1	5
γ	0.5	0.5	0.5	0.5
$i_p/2\gamma i_{pd}$	1.20	1.06	1.38	1.11
k_1	8000	7800	8000	8500

As regards the electrode reaction, it is noted that the rate-determining step of the set of follow-up chemical reactions is reaction 2 as in the EC reaction scheme. However, the exact expression of the peak potential as a function of the rate of this reaction depends upon the competition between the electrode (reactions 3 and 7) and the solution electron transfer (reactions 4 and 8). When the first of these predominates, one has an ECE-type process and DISP-type mechanism in the reverse situation.[19] The theory of this competition has been worked out for simpler systems not involving reactions 6–8 in the context of cyclic voltammetry.[19] It can be readily shown that the same results will be obtained with the present system provided $k_4 = k_8$. This is what we already assumed, regarding these two rate constants as equal to the diffusion limit since both Ar· and S· are much easier to reduce than A. An increase of $C°_P$ will favor the DISP pathway owing to its second-order character as opposed to the first-order character of the ECE process. The magnitude of the cleavage rate constant, k, is on the other hand a crucial parameter in the ECE-DISP competition: if k is large, Ar· will be formed close to the electrode surface where it will diffuse back and be reduced before having time to react on $ArX^{-}·$; an opposite situation will be met when k is small. Quantitatively, the competition then depends upon the dimensionless parameter $p = k_{dif}C°_P(Fv/RT)^{1/2}/k^{3/2}$. Within 3-mV uncertainty on peak potential measurements, the ECE mechanism will be followed if $p < 1$ and the DISP situation will be reached if $p > 4$.[19] In the first case the peak potential is given by eq I[18,19] while in the second the expression is[18,19]

$$E_p = (RT/F)[\ln (RT/F) - 0.78] + E°_{AB} + (RT/2F) \ln (k/2v) \quad \text{(IV)}$$

Confusion between the ECE and DISP situations would lead to a value of k in error by a factor of 2.

Reduction of Aromatic Halides. Lifetimes of the Anion Radicals

Kinetic Control by Forward Reaction (1 sol). A first example is the reduction of 1-chloronaphthalene in Me_2SO with 0.1 M Et_4NClO_4 as supporting electrolyte. The results obtained with 4-methoxybenzophenone as redox catalyst ($E°_{PQ} = -1.75$ V) are summarized in Table I (all the potentials here and in the following are referred to the aqueous saturated calomel electrode). For $C_P^0 < 4 \times 10^{-3}$ M, the kinetic control is by forward reaction (1 sol) as seen from the constancy of the k_1 values as derived from the working curves corresponding to the kinetic by forward reaction (1 sol) (Figure 3 in ref 17 modified by eq III). k_1 is thus found as equal to 100 M^{-1} s^{-1}.

The cyclic voltammograms are completely irreversible in the range 0.1–1000 V s^{-1}. The peak potential shifts by 28 mV/decade of sweep rate with a peak width of 65 mV, showing that the electrode process is kinetically controlled by reaction 2. From the determination of the peak potential in this sweep rate range and assuming that the electrode reaction follows an ECE mechanism it is found that $E°_{AB} + 0.029 \log k = -1.97$ V.

On the other hand, raising the catalyst concentration above 4×10^{-3} M shifts the system into the region of mixed kinetic control (Table I). Corresponding to $\gamma = 0.5$, $C_P^0 = 2 \times 10^{-2}$ M, and $v = 0.1$ V s^{-1}, i.e., to $\lambda_1 = 5 \times 10^{-1}$, a working curve has been computed giving $i_p/2\gamma i_{pd}$ as a function of $\log (\lambda/\lambda_2)$, which allows the determination of the latter parameter as

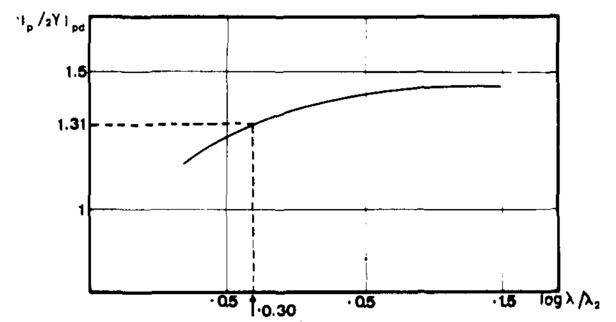

Figure 3. Reduction of 1-chloronaphthalene in Me_2SO as catalyzed by 4-methoxybenzophenone. Mixed kinetic control, $\gamma = 0.5$, $v = 0.1$ V s^{-1}, $C°_p = 2 \times 10^{-2}$ M. Working curve for $\lambda_1 = 5 \times 10^{-1}$ and determination of λ/λ_2.

shown in Figure 3. Log (λ/λ_2) is found as equal to -0.30 and therefore $k/k_2 = 10^{-2}$ M. One has thus four equations:

$$k_1 = 100\ M^{-1}\ s^{-1}$$

$$E°_{AB} + 0.029 \log k = -1.97\ V$$

$$0.058 \log (k_1/k_2) = E°_{AB} - (-1.75)$$

$$k/k_2 = 10^{-2}\ M$$

for determining k_1, k_2, k, and $E°$. The values of $E°$ and k thus found are those figured in Table VI. It is seen that the magnitude of k is such that the assumption of an ECE mechanism for the electrode reaction is perfectly correct ($p = 5 \times 10^{-4} \ll 1$). k_2 is found as equal to 5×10^9 M^{-1} s^{-1}, i.e., a value practically the same as the average value of the diffusion limit for the present types of organic molecules.[20] That k_2 is at the diffusion limit can be rationalized as follows. For chlorobenzene it has been shown[14] that the diffusion limit is met for $E°_{PQ} - E°_{AB} > 420$ mV.[14] The standard rate constant of homogeneous electron transfer, k_S^{sol}, is certainly higher for 1-chloronaphthalene than for chlorobenzene since the charge concentration and thus the solvation energy in the anion radical is less for the first compound than for the second. The above condition is therefore a fortiori true for 1-chloronaphthalene. It can thus be concluded that diffusion control of the backward electron transfer is achieved in the present case since $E°_{PQ} - E°_{AB} \simeq 450$ mV. This conclusion can also be reached more directly starting from the electrochemical data obtained for 1-chloronaphthalene. The electrode reaction is indeed kinetically controlled by the follow-up reaction (2) up to at least 50 V s^{-1}. This provides a lower limit for the apparent standard rate constant of the electrode electron transfer:[18] $k_S^{el,ap} > 2$ cm s^{-1}, which leads to the evaluation of the standard rate constant of the homogeneous electron transfer between the catalyst and 1-chloronaphthalene according to the Hush-Marcus relationships[14] as $k_S^{sol} > 10^{8.4}$ M^{-1} s^{-1}. In these conditions, diffusion control will prevail over activation control as soon as $E°_{PQ} - E°_{AB} > 150$ mV. This last condition is fulfilled in the present case, showing that the backward homogeneous electron transfer is diffusion controlled.

The reduction of 1-chloronaphthalene as catalyzed by 4-methoxybenzophenone offers the most favorable situation for the determination of the rate constants. The catalytic system can indeed be observed under both pure kinetic control by reaction (1 sol) and mixed kinetic control by (1 sol) and (2) and usable rate data can be derived from the analysis of the electrode behavior. This is the reason why all three rate constants (k_1, k_2, and k) could be determined. Such an ideal situation may not be encountered with other substrates and catalysts. However, the determination of k and $E°$ can be carried out as soon as one of the two following sets of less restrictive conditions is fulfilled. (i) The catalytic system can be observed under pure kinetic control by reaction (1 sol) and the electrode reaction is kinetically controlled by step (2) while data on the mixed kinetic control of the catalytic process are not available. (ii) The catalytic system can be observed under both pure (1 sol) control and mixed kinetic control while the electrode reaction is under mixed (1 el)-(2) control.

An illustration of the first case is provided by the reduction of the same 1-chloronaphthalene as catalyzed by anthracene ($E°_{PQ} = -1.86$ V) in the same medium. From the pure kinetic control catalytic data, k_1 was found to be 8200 M s^{-1} (Table I). The $E°_{PQ} - E°_{AB}$ difference being 340 mV in the present case, it follows from above evaluation carried out in the case of 4-methoxybenzophenone that k_2 is here again at the diffusion limit. Taking $k_2 = k_{dif} = 5 \times 10^9$ M^{-1} s^{-1}, $E°_{AB}$ is derived from $0.058 \log (k_1/k_2) = E°_{AB} - E°_{PQ}$ and k from $E°_{AB} + 0.029 \log k = -1.97$ (electrochemical data) leading to $E°_{AB} = -2.19$ V and $k = 8 \times 10^7$ s^{-1}. These results are in fair agreement with those obtained with 4-methoxybenzophenone as the catalyst. The latter data are likely to be more accurate since there is less overlapping between the catalyst and substrate wave.

Table II. Reduction of 4-Chlorobenzonitrile as Catalyzed by Phthalonitrile ($E°_{PQ} = -1.69$ V vs. SCE), $\gamma = 1$, $v = 0.1$ V s^{-1}

C_P^0, M	1×10^{-3}	2×10^{-3}	4×10^{-3}	2×10^{-2}	4×10^{-2}
$i_p/2\gamma i_{pd}$	0.530	0.545	0.615	0.905	1.00
$\log (k_1)$	2.0	1.9	2.0	1.9	1.8

The reduction of 4-chlorobenzonitrile as catalyzed by phthalonitrile ($E°_{PQ} = -1.69$ V) in CH_3CN with 0.1 M $(n\text{-}C_6H_{13})_4NI$ as supporting electrolyte is an example of the second type of situation. The kinetic control is by forward reaction (1 sol) as long as $C_P^0 < 4.10^{-3}$ M, the resulting value of k_1 being 100 M^{-1} s^{-1} (Table II). Tetrahexylammonium iodide was used as supporting electrolyte since it shifts negatively the reduction potential of 4-chlorobenzonitrile as compared to smaller chain quaternary ammoniums. More space is thus available for the selection of a catalyst. The cyclic voltammograms are irreversible in all the accessible sweep rate range. The peak potential shifts negatively upon passing from tetraethyl- to tetrabutyl- and tetrahexylammonium featuring the effect of the double-layer structure on the kinetics, hence showing that the kinetic control is at least partially by electron transfer. This is the case even with Et_4N^+, where the peak potential shift with sweep rate was found to be 75 mV/decade, indicating that the electrode reaction is under the mixed kinetic control of reactions (1 el) and (2).[18] No usable relationship between $E°$ and k such as eq I can therefore be derived from the electrochemical data. However, upon raising the concentration, the catalytic system shifts from pure (1 sol) control to mixed kinetic control (Table II). k/k_2 can thus be determined following the same procedure as for 1-chloronaphthalene (Figure 2), leading to $k/k_2 = 2.4 \times 10^{-2}$ M. If it is then assumed that $k_2 = k_{dif}$ ($= 2 \times 10^{10}$ M^{-1} s^{-1}), the resulting values of $E°_{AB}$ and k are those figured in Table VI. This assumption is supported by the comparison between 4-chlorobenzonitrile and chlorobenzene ($k_S^{sol,4ClPhCN} > k_S^{sol,PhCl}$, $k_2^{PhCl} = k_{dif}$ as soon as $E°_{PQ} - E°_{AB} > 420$ mV;[14] in the present case $E°_{PQ} - E°_{AB} = 490$ mV, therefore $k_2^{4\text{-}ClPhCN} = k_{dif}$). It is noted that it is more difficult to shift the system from pure to mixed kinetic control in the present case than for 1-chloronaphthalene as expected from k being larger for the former than for the latter compound.

The reduction of 1-bromonaphthalene in Bu_4NClO_4 (0.1 M)-Me_2SO follows the same general pattern as that of 4-chlorobenzonitrile. Using 4-methylthiobenzophenone as the catalyst ($E°_{PQ} = -1.65$ V), the same analysis leads to the $E°_{AB}$ and k values figured in Table VI.

Kinetic Control by Reaction (2) with (1 sol) at Equilibrium. A first example of this situation is the reduction of 2-chloro-

Table III. Redox Catalyzed Reduction of 2-Chloroquinoline in DMF with Et_4NClO_4 as Supporting Electrolyte

Catalyst Benzo[*c*]cinnoline, $v = 0.033\ V\ s^{-1}$, $\gamma = 5$			
C_P^0	10^{-3}	2×10^{-3}	5×10^{-3}
$i_p/2\gamma i_{pd}$	0.127	0.170	0.171
$\log kk_1/k_2$	−2.4	−2.0	−2.0
Catalyst Terephthalonitrile, $v = 0.033\ V\ s^{-1}$, $\gamma = 0.5$			
C_P^0	10^{-3}	2×10^{-3}	5×10^{-3}
$i_p/2\gamma i_{pd}$	1.11	1.21	1.36
$\log kk_1/k_2$	−1.3	−1.1	−0.9
Catalyst Perylene, $v = 0.33\ V\ s^{-1}$, $\gamma = 0.5$			
C_P^0	10^{-3}	2×10^{-3}	
$i_p/2\gamma i_{pd}$	1.74	1.73	
$\log kk_1/k_2$	+0.6	+0.6	

Table IV. Redox Catalyzed Reduction of 2-Chloroquinoline in DMF with Et_4NClO_4 as Supporting Electrolyte

catalyst	benzo[*c*]cinnoline	terephthalonitrile	perylene
kk_1/k_2, s^{-1}	$10^{-2.1}$	$10^{-0.9}$	$10^{0.6}$
$E°_{AB}$ + 0.058 log *k*	−1.75	−1.75	−1.75
$E°_{AB}$ + 0.029 log *k*	−1.585	−1.573	−1.585
$E°_{AB}$, V vs. SCE	−1.915	−1.922	−1.915
k, s^{-1}	5×10^5	9×10^5	5×10^5

quinoline in DMF with 0.1 M Et_4NClO_4 as supporting electrolyte. The cyclic voltammograms featuring the uncatalyzed reduction were found to be irreversible from 0.1 to 2000 V s^{-1}, showing that $k > 10^4\ s^{-1}$. The peak characteristics in this sweep range at 22 °C were the following: shift of the peak potential $\partial E_p/\partial \log v = -30$ mV; peak width $\Delta E_p = 50$ mV.

This clearly indicates a kinetic control at the electrode by reaction (2) (theoretical values for 22 °C: $\partial E_p/\partial \log v = -29.3$ mV, $\Delta E_p = 47$ mV).[18] The redox catalysis experiments were carried out with three catalyst couples: perylene ($E°_{PQ} = -1.61$ V), terephthalonitrile ($E°_{PQ} = -1.52$ V), and benzo[*c*]cinnoline ($E° = -1.465$ V). The results are shown in Table III: kk_1/k_2 was computed from the experimental $i_p/2\gamma i_{pd}$ values for several values of C_P^0 using the working curves corresponding to the kinetic control by reaction 2 (Figure 5 in ref 17 modified by eq III). The values of kk_1/k_2 thus obtained are approximately constant when varying C_P^0 as long as $C_P^0 > 2 \times 10^{-3}$ M. This shows that within this concentration range the kinetic control is by reaction 2 with (1 sol) as preequilibrium. It is noted that under these conditions $\log kk_1/k_2$ is a linear function of $E°_{PQ}$ (Figure 4) with a slope close to $(-1/58)\ mV^{-1}$ as expected from eq II. The resulting values of $E°_{AB} + 0.058 \log k$ are given in Table IV for the three catalysts.

On the other hand, $E°_{AB} + 0.029 \log k$ was obtained from the peak potentials of the cyclic voltammograms in the range 0.1–50 V s^{-1} assuming an ECE-type mechanism for the electrode reaction. This finally leads to the values of $E°_{AB}$ and *k* given in Table IV. The results obtained with perylene can be regarded as less accurate than those obtained with the two other catalysts owing to partial overlapping of the catalyst and substrate waves. The values found for *k* allow the assumption of an ECE-type electrode reaction to be justified. For the highest sweep rate used in catalytic efficiency determination (0.33 V s^{-1}), the value of the competition parameter *p* is indeed found as 0.1, showing that the ECE pathway is actually followed with negligible interference of the DISP process within experimental uncertainty.

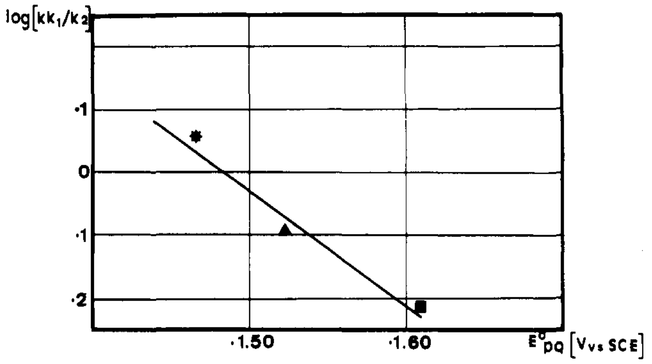

Figure 4. Redox catalyzed reduction of 2-chloroquinoline in DMF, log kk_1/k_2 vs. the standard potential of the catalyst: ∗, perylene; ▲, terephthalonitrile; ■, benzo[*c*]cinnoline.

The experiments carried out at low values of C_P^0 (Table III) show a definite tendency to depart from the behavior corresponding to pure kinetic control by reaction 2 corresponding to the transition to mixed kinetic control. This could be, in principle, used to evaluate λ/λ_2 as discussed in the theoretical section and leads to the determination of k_2. Several attempts to obtain k_2 by this procedure led to values between 10^9 and $10^{10}\ M^{-1}\ s^{-1}$, i.e., compatible with the conclusion that the backward electron transfer is at the diffusion limit. The results derived from the transition from pure to mixed kinetic control were, however, found to be much less accurate than on the side of the kinetic control by (1 sol). This is due to the smallness of the catalytic effect and consequently to the necessity of using catalysts which $E°$s are close to the reduction potential of the substrate resulting in wave-overlapping errors. It follows that the method using both the electrochemical data and the kinetic analysis of the catalytic system under pure (2) kinetic control is to be preferred to that based on the transition between pure and mixed kinetic control. The applicability of the first method, however, requires that the electrode reaction be controlled by reaction 2. This condition is likely to be fulfilled since the solution process is already under the same kind of kinetic control. It is noted that the method does not necessitate the independent knowledge of k_2. That k_2 is, in the present case, at the diffusion limit can be shown as follows. For 2-chloropyridine, diffusion control is achieved when $E°_{PQ} - E°_{AB} > 0.260$ V (see Figure 7 of ref 14). The standard rate constant of electron transfer is certainly higher for 2-chloroquinoline than for 2-chloropyridine since the charge concentration and thus the solvation energy are less for the first compound than for the second. The above condition is therefore a fortiori true for 2-chloroquinoline. Since $E°_{PQ} - E°_{AB} > 0.260$ V for the three catalysts, it follows that diffusion control of the backward solution electron transfer is achieved in each case. The same conclusion can also be reached in the following manner. The electrode reduction of 2-chloroquinoline is kinetically controlled by the follow-up reaction (2) up to at least 50 V s^{-1}. This provides a lower limit of the apparent standard rate constant of the electrode electron transfer[18] ($k_S^{el,ap} > 0.5\ cm\ s^{-1}$), which leads to an evaluation of the standard rate constant of the solution electron transfer between the catalyst and 2-chloroquinoline according to the Hush–Marcus relationships:[14] $k_S^{sol} > 10^{8.1}\ M^{-1}\ s^{-1}$. In these conditions, diffusion control will prevail over activation control as soon as $E°_{PQ} - E°_{AB} > 200$ mV. This last condition is fulfilled by the three catalysts used here showing that the backward electron transfer is diffusion controlled for all three.

The reduction of 9-bromoanthracene in Me_2SO with 0.1 M Et_4NClO_4 as supporting electrolyte provides a second example of kinetic control by reaction 2 with (1 sol) being at equilibrium. The results obtained with nitromesitylene as a catalyst ($E°_{PQ} = -1.305$ V) are summarized in Table V. It is seen that

Table V. Redox Catalyzed Reduction of 9-Bromoanthracene in Me_2SO with Et_4NClO_4 (0.1 M) as Supporting Electrolyte, Catalyst Nitromesitylene

C_P^0	10^{-3}	10^{-3}	5×10^{-3}	5×10^{-3}
v, V s^{-1}	1.0	3.3	1.0	3.3
γ	0.5	0.5	0.5	0.5
$i_p/2\gamma i_{pd}$	1.14	1.06	1.18	1.05
kk_1/k_2	1.6	2.5	1.9	2.2

kinetic control is indeed by reaction 2 in the considered concentration range. kk_1/k_2 is found as equal to 2.0 s^{-1}.

On the other hand, the cyclic voltammograms recorded between 0.1 and 1000 V s^{-1} showed no reversibility. Their peak potential exhibits a 34 mV/decade variation with sweep rate with a 50-mV peak width, indicating that the electrode reaction is under the kinetic control of reaction 2.[18] Assuming that the electrode reaction follows an ECE mechanism, $E°_{AB} + 0.029 \log k$ is found equal to -1.45 V from the measurement of the peak potential. The resulting values of $E°_{AB}$ and k are -1.61 V and 4×10^5 s^{-1}. The ECE-DISP competition parameters are then $p = 0.6$ at $v = 1$ V s^{-1} and $p = 2$ at $v = 10$ V s^{-1}, showing that the system is right in the middle of the transition zone between the ECE and DISP mechanisms. If a pure DISP behavior were assumed to be followed, one would find $k = 2 \times 10^5$ s^{-1} and $p = 1.8$ ($v = 1$ V s^{-1}) and 5.6 ($v = 10$ V s^{-1}), leading to the same conclusion. A reasonable estimation is therefore $k = 3 \times 10^5$ s^{-1}. A more refined value could be obtained from an iteration procedure using the working curve for the transition between ECE and DISP.[19] This would not, however, be presently very meaningful in view of the current accuracy level of the determinations.

It is noted that the value of k is smaller than in the case of 2-chloroquinoline. This explains why it is not practically possible in the present case to shift the system from pure kinetic control by reaction 2 to mixed kinetic control by decreasing the catalyst concentration. It is thus necessary to use the electrochemical data, besides the redox catalysis data, for determining k.

Discussion

The examples discussed above show that the application of the redox catalytic method allows the lifetimes of very short-lived intermediates to be determined. The nanosecond time range becomes accessible leading to a gain of four to five orders of magnitude over the standard application of usual electrochemical techniques.

It is interesting in this connection to estimate the minimal lifetimes that could be determined by the redox catalytic method. When k increases, the catalytic system tends to be kinetically controlled by forward reaction (1 sol). At the same time, the electrode process tends to be under the kinetic control of the electron transfer (1 el). In a typical situation where $\gamma = 4$, $C_P^0 = 10^{-3}$ M, the kinetic control by forward reaction (1 sol) will occur for $k > 10^7$ s^{-1} with $k_2 = 5 \times 10^9$ M^{-1} s^{-1}. For such a value of k, the kinetic control of the electrode process by reaction 2 will be obtained within a reasonable sweep range, say 0.1-1 V s^{-1}, if $k_S^{el,ap} > 0.2$ cm s^{-1}.[18] This is not an exceedingly high value in the context of aromatic molecules[14,20] showing that compounds can be found for which the catalytic system will be under the control of forward reaction (1 sol) while the electrode process is still kinetically controlled by reaction 2. The reduction of 1-chloronaphthalene in Me_2SO was an example of such a situation. It is clear, however, that going to higher and higher k's will nevertheless result in a tendency for the electrode reaction to be controlled, at least partially, by (1 el), thus preventing the knowledge of $E°_{AB} + (RT/2F) \ln k$ as an element for the determination of k. The upper limit of determinable k's hinges therefore upon the possibility of shifting the catalytic system from pure kinetic control by (1 sol) to mixed kinetic control upon raising C_P^0 for a given value of γ. The enlargement of the mixed kinetic control zone when increasing γ (Figure 1) suggests the use of high values of γ for achieving the determination of very small lifetimes. However, this would result in an increased overlapping of the catalyst and substrate wave rendering the accurate determination of the catalytic current uncertain in the context of the presently available mathematical treatments. At present, reasonable estimations of the maximal usable values of γ and C_P^0 are 40 and 5×10^{-2} M, respectively. This leads to the conclusion that the upper limit of k is around 10^9 s^{-1}. Further improvements could probably be obtained through the derivation of mathematical treatments taking the overlapping between the catalyst and substrate waves into account, allowing then the use of larger γ's. They will, however, be limited by the decreasing accuracy resulting from the extraction of a small catalytic current from a large total current.

Table VI. Standard Potentials of Anion Radical Formation and Rate Constants of Decomposition

compd	solvent	$E°_{AB}$, V vs. SCE	k, s^{-1}
2-chloroquinoline	DMF	-1.92	6×10^5
9-chloroanthracene	Me_2SO	-1.67^a	1.5×10^2 ^{a}
9-bromoanthracene	Me_2SO	-1.60	3×10^5
1-chloronaphthalene	Me_2SO	-2.19	5×10^7
1-bromonaphthalene	Me_2SO	-2.13	3×10^8
4-chlorobenzonitrile	CH_3CN	-2.18	5×10^8

[a] Directly derived from cyclic voltammetry of the uncatalyzed electrode reduction (reversibility is reached for $v \geqslant 10$ V s^{-1}).

To conclude, let us examine briefly the trends observed in the correlation between the lifetimes of the anion radicals and the structure of the parent compounds. Inspection of the results given in Table VI supports the validity of the following empirical rules already stated at the occasion of a study of reductive cleavage in the thiocarbonate series.[24] Designating by the leaving group the part of the molecule which leaves with the negative charge (here the halogen) and the remaining group the part which will keep the odd electron (Ar in the present case), the cleavage will be faster, in a series where the remaining groups are the same, the easier the leaving group can accommodate an elementary negative charge. In such a series the cleavage will be faster the more positive the standard potential. Conversely, in a series where the leaving groups are the same, the cleavage will be slower the easier the remaining group can accommodate the charge. Thus the cleavage will be faster the more negative the standard potential.

The first part of the rule is clearly illustrated by the comparison of the chloro and bromo derivatives of the same ArH (anthracene, naphthalene). Br^- is a better leaving group than Cl^- in the anion radical, and the bromo derivatives have more positive standard potentials than the chloro derivatives, as already seen for another series of haloaromatics (Table III in ref 14).

The second part of the rule is illustrated by the comparison of bromoanthracene and naphthalene on one hand and of chloroanthracene, quinoline, and naphthalene on the other. There appears to be one exception to the rule when comparing 1-chloronaphthalene and 4-chlorobenzonitrile. It must, however, be noted that $E°_{AB}$ and k are very close for these two compounds and that the solvent is not the same. There is indeed evidence that for the same aromatic halide k is significantly higher in CH_3CN than in Me_2SO and that the order of reactivity between 1-halonaphthalenes and 4-halobenzonitriles is reversed when considered in the same solvent.[25]

Experimental Section

The electrochemical instrumentation, electrodes, and cell for cyclic voltammetry were the same as already described.[14] Positive feedback compensation of the cell resistance[26] was used for sweep rates above 10 V s^{-1}. The working electrode was a mercury drop hanged at the tip of a gold disk of about 0.8 mm^2 surface area. The reference electrodes were Ag/Ag^+ (Ag^+ 10^{-2} M) in the used solvent (DMF, ACN, Me_2SO) or aqueous saturated calomel electrode. All the potentials were converted to values referred to the aqueous saturated calomel electrode in the corresponding medium.

Chemicals. The aromatic halides, catalysts, solvents, and supporting electrolytes were from commercial origin.[27]

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(20) The average value for the diffusion limit of usual aromatic molecules in DMF can be estimated at 5×10^9 M^{-1} s^{-1} from previous studies.[21] This figure is apparently in error by a factor of 2 since k_{dif} was taken as equal to $4\pi Dd$ (D, diffusion coefficient; d, diameter of the molecule) instead of $4\pi(2D)d$.[22] A more satisfactory value for DMF is then 10^{10} M^{-1} s^{-1}. Taking into account the respective viscosities this would lead to 4×10^9 M^{-1} s^{-1} for Me_2SO and 2×10^{10} M^{-1} s^{-1} for CH_3CN. The ratios between these k_{dif} values in is agreement with the peak heights obtained in cyclic voltammetry for the same compound, fluorenone, in the three solvents. Note also that a previous study by fluorescence quenching led to a value very close to 2×10^{10} M^{-1} s^{-1} for CH_3CN.[23]

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N-tert-Butoxy-*N-tert*-alkylaminyls. A New Class of Persistent Radicals[1]

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Abstract: *N-tert*-Butoxy-*N-tert*-butylaminyl (**1·**) and three related radicals have been generated from their parent hydroxylamines in hydrocarbon solution. In the absence of oxygen these radicals are extremely persistent. Their electronic structures, as indicated by their EPR parameters (a^{14N}, a^{17O}, and a^{13C}, all determined without isotopic enrichment) and the N-H bond strength in **1**-H (measured as 81.0 kcal/mol), show that the effectiveness of conjugative electron delocalization is reduced relative to that in the isomeric nitroxides. This effect is attributed to the greater electronegativity of oxygen compared with nitrogen.

We have been interested for many years in the rates and mechanisms of decay of four classes of isoelectronic radicals: alkylperoxyls (ROO·),[3] alkyl nitroxides (R_2NO·),[4] alkylhydrazyls ($R_2\dot{N}NR$),[5] and alkoxyaminyls ($R\dot{N}OR$).[6] Although persistent *N*-alkoxyarylaminyl radicals[6,7] and a persistent *N*-alkoxy-*N*-vinylaminyl[8] are known, there are no reports of a persistent *N*-alkoxy-*N*-alkylaminyl.[9] Tertiary alkyl groups dramatically increase the persistence of peroxyls, nitroxides, and hydrazyls. Unfortunately we were previously unable to explore this area of $R\dot{O}NR$ chemistry since all our attempts to synthesize *N,O*-di-*tert*-butylhydroxylamine were unsuccessful.[6] This problem has now been overcome since Meesters and Benn[11] have reported an elegant synthesis of this compound and of three other *N-tert*-butoxy-*N-tert*-alkylamines. They very kindly presented us with samples of their hydroxylamines and we have been able to show that the corresponding *N-tert*-butoxy-*N-tert*-alkylaminyl radicals are extremely persistent in solution under oxygen-free conditions.

Experimental Section

Sample Preparation. *N,O*-Di-*tert*-butylhydroxylamine (**1**-H) was prepared according to the procedure of Meesters and Benn[11] and purified by distillation and preparative GLC. *N-tert*-Amyl-, *N-tert*-octyl-, and *N*-(1-adamantyl)-*O-tert*-butylhydroxylamine (**2**-H, **3**-H, and **4**-H, respectively) were liberated from their hydrochlorides under oxygen-free conditions. Normally this reaction was carried out under vacuum directly in the EPR tube by distilling onto 5-25 mg of the solid hydrochloride thoroughly deoxygenated NH_3 and a hydrocarbon solvent (usually benzene or *n*-pentane).

Radical Generation. Radicals **1·**, **2·**, **3·**, and **4·** were generated in hydrocarbon solvents by one of the following methods: (a) UV photolysis of the hydroxylamine in the presence of di-*tert*-butyl peroxide; (b) UV photolysis of the hydroxylamine alone; (c) H abstraction by an inorganic oxidizing agent, e.g., PbO_2 and Ag_2O in the presence of a drying agent, usually $MgSO_4$, and $K_3Fe(CN)_6$ in 2 N NaOH.

If the foregoing procedures were carried out under oxygen-free conditions, using thoroughly degassed solvents and reagents, high concentrations of *N-tert*-butoxy-*N-tert*-alkylaminyl radicals could be generated. The radicals obtained in this way were extremely persistent, there being no detectable decay over very many days at room temperature. However, if oxygen was not carefully excluded, the radicals were very much less persistent, especially when they were generated by photolysis. Decay rates were not reproducible and, during photolysis, an intense spectrum of the corresponding *tert*-butoxy-

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