Hydrogen Atom Transfer Oxidation of Primary and Secondary Alcoholates into Aldehydes and Ketones by Aromatic Halides in Liquid Ammonia. A New Electrochemically Induceable Reaction

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Abstract: It is possible to induce the oxidation of alcoholates into the corresponding carbonyl compounds by electrochemical reduction of aromatic halides in liquid ammonia, i.e., to electrochemically trigger the reaction ArX + >CH–O$^-$ → ArH + >C=O + X$^-$. H-Atom transfer from the alcoholate to the aryl radical formed upon reduction of the aryl halide appears as the key step of the oxidation process. The ketyl anion radical thus formed can be oxidized into the parent carbonyl compound, remain electrochemically stable, or be reduced into the dianion depending upon the location of the two corresponding standard potentials toward the reduction potential of the aryl halide. Electricity consumption thus tends toward 0, 1, and 2 F/mol for the three cases, respectively. The reactions competing with H-atom transfer, thus lowering the efficiency of the electrochemical inducement of the oxidation process, are electron transfers to the aryl radical which occur at the electrode surface and/or in the solution. These will play the role of termination steps for the corresponding chain systems involving homogeneous initiation of the reaction. The kinetic analysis of the competition between H-atom transfer and homogeneous or heterogeneous electron transfer allows a detailed investigation of the reaction mechanism by electrochemical techniques such as cyclic voltammetry. This also leads to the determination of the rate constant of H-atom transfer of the alcoholate–aryl radical couple.

Electrochemical inducement of a chemical reaction[2a] is based upon the reactivity of the system being larger at a higher or a lower oxidation level than at the original one. A few examples of such processes have been described in organic or coordination chemistry.[2] This reaction that has been the most extensively studied in this respect is $S_{RN}1$ aromatic nucleophilic substitution,[3] the electrochemical inducement[2a,4a] of which is based on the following reaction sequence:

$$ArX + 1e \rightleftarrows ArX^{-\cdot}$$

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

$$Ar\cdot + Nu^- \rightarrow ArNu^{-\cdot}$$

$$ArNu^{-\cdot} - 1e \rightleftarrows ArNu$$

$$(\text{and/or } ArNu^{-\cdot} + ArX \rightleftarrows ArNu + ArX^{-\cdot})$$

$$\overline{ArX + Nu^- \rightarrow ArNu + X^-}$$

(where Ar represents an aromatic or heteroatomatic residue, X$^-$ a nucleofugal group, and Nu$^-$ a soft nucleophile). Preparative aspects,[4a-d] kinetics, and competing reactions[4d-i] have been extensively investigated. A detailed description of the reaction mechanism was thus given which involved the determination of the rate constants of the key steps of the inducement process.

We describe hereafter another type of reaction that can be induced electrochemically showing similar mechanistic and kinetic features as $S_{RN}1$ aromatic nucleophilic substitution. The principles on which the reaction and its electrochemical inducement are based are as follows. We start again with the electrochemical reduction of an aromatic halide, giving rise to an anion radical which decomposes into a neutral aryl radical. The latter is known to be able to readily abstract a hydrogen atom from a wide variety of organic molecules. In the present case, the source of hydrogen atoms is an alcoholate. H-Atom transfer from organic solvents to aryl radicals is indeed known to be an important pathway in the electrochemical reduction of aromatic halides.[5] On the other hand, alcoholates are good H-atom donors toward aryl radicals, better than the corresponding alcohols.[6] Liquid ammonia is used as a solvent since, due to its poor H-atom donor ability,[7] the alcoholate will be the only source of H-atom transfer. The successive reaction steps, occurring at the reduction wave of the aromatic halide, are thus predicted to be:

$$ArX + 1e \rightleftarrows ArX^{-\cdot} \quad (0)$$

$$ArX^{-\cdot} \rightarrow Ar\cdot + X^- \quad (1)$$

$$Ar\cdot + \ >CH—O^- \rightarrow ArH + \ >\dot{C}—O^- \quad (2)$$

The last product is the anion radical of the carbonyl compound corresponding to the starting alcoholate. If the ketone (or aldehyde)/anion radical couple has a standard potential negative to the reduction potential of the starting aromatic halide, the anion radical, when produced, will be immediately reoxidized into the parent carbonyl compound, either at the electrode

$$>\dot{C}—O^- - 1e \rightleftarrows \ >C=O \quad (3)$$

or in the solution

$$>\dot{C}—O^- + ArX \rightleftarrows \ >C=O + ArX^{-\cdot} \quad (4)$$

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(2) (a) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323 and references cited therein. (b) Praefcke, K.; Weichsel, C.; Falsig, M.; Lund, H. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 403. (c) Rieke, R. D.; Kojima, H.; Ofele, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 538. (d) Clennan, E. L.; Simmons, W.; Almpen, C. W. *J. Am. Chem. Soc.* **1981**, *103*, 2098.

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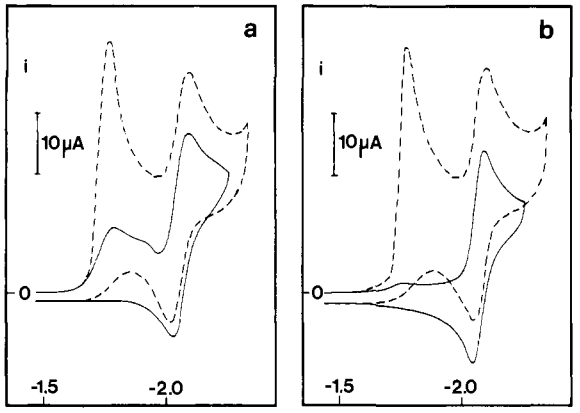

Figure 1. Cyclic voltammetry of 1-chloronaphthalene in liquid NH_3 at −40 °C in the presence of alcoholates: (a) cyclohexanolate, 2.5×10^{-2} M, sweep rate 0.3 V s^{-1}; (b) ethylate, 5×10^{-2} M, sweep rate 0.2 V s^{-1}. 1-Chloronaphthalene concentration: 4.3×10^{-3} M (a), 5.2×10^{-3} M (b). Dashed line: reduction of 1-chloronaphthalene in the absence of alcoholate.

The overall reaction will then amount to oxidizing the alcoholate into the corresponding aldehyde or ketone. The aromatic halide serving as oxidant is reduced into the corresponding hydrocarbon with concomitant expulsion of the halide ion:

$$ArX + >CH—O^- \rightarrow ArH + X^- + >C{=}O \qquad (i)$$

This involves no net exchange of electrons. Under such conditions, setting the electrode potential at the reduction wave of the starting ArX will result in an electrocatalysis of the chemical reaction (i). The consumption of electricity will be vanishingly small if there is no side reaction and if the successive steps are fast within the time scale of the experiment.

However, different inducement situations can be met according to the location of the standard potentials of the ketone (aldehyde)/anion radical (E_1^0) and of the anion radical/dianion (E_2^0) couples. If E_1^0 is positive to the reduction potential of ArX while E_2^0 is negative to that value, the formation of $>\dot{C}—O^-$ is anticipated with correspondingly the consumption of 1 faraday per mol of ArX and alcoholate converted. If E_1^0 and E_2^0 are both positive to the reduction potential of ArX, the formation of the dianion, $>C^-—O^-$, with the consumption of 2 faradays per mol is expected.

As in the case of the $S_{RN}1$ reaction in liquid ammonia, due to the fact that the Ar· radical is easy to reduce, electrode or solution electron transfers

$$Ar\cdot + 1e \rightleftarrows Ar^- \qquad (5)$$

$$Ar\cdot + ArX^{-}\cdot \rightarrow Ar^- + ArX \qquad (6)$$

are anticipated to compete with the H-atom transfer reaction 2. This decreases the yield of the carbonyl compound or of its one- or two-electron reduction product. The yield in ArH will remain the same since ArH is the final product of either reaction 2 or reactions 5 and 6, Ar^- being ultimately protonated by ammonia:

$$Ar^- + NH_3 \rightarrow ArH + NH_2^- \qquad (7)$$

The reaction sequence (0) + (1) + (5) + (6) + (7) involves the consumption of 2 faradays per mol, representing the classical reductive cleavage of the starting aromatic halide in liquid ammonia in the absence of H-atom donor.[8] Thus, in the catalytic case, the consumption of electricity will vary from 0 to 2 faraday per mol, reflecting the competition between H-atom transfer resulting in ketone (or aldehyde) formation and electron transfer resulting in reductive cleavage into ArH. In the case where E_1^0 > ArX reduction potential > E_2^0, the electricity consumption will be between 1 and 2 faradays per mol, while for the case where

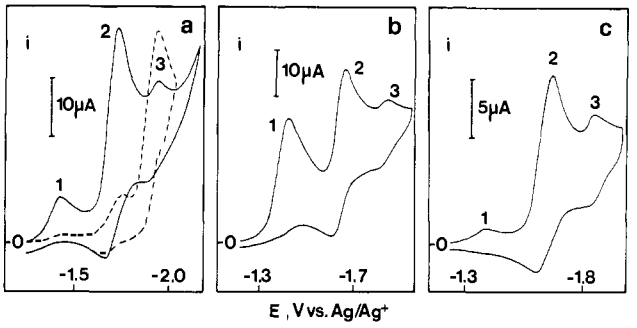

Figure 2. Cyclic voltammetry of 2-chloroquinoline (QCl) in liquid NH_3 at −40 °C in the presence of alcoholates: (a) ethylate, 4.6×10^{-2} M, [QCl] = 7×10^{-3} M, (—) 2 min after mixing and (---) 31 min after mixing; (b) cyclohexanolate, 2.5×10^{-2} M, [QCl] = 5×10^{-3} M, 40 min after mixing; (c) $H_2N(CH_2)_4O^-$, 4.8×10^{-2} M, [QCl] = 3.5×10^{-3}M, 3 min after mixing. Sweep rate: 0.2 V s^{-1}. (1) Reduction peak of 2-chloroquinoline, (2) quinoline peak, (3) 2-alkoxyquinoline peak.

$E_1^0 > E_2^0 >$ ArX reduction potential, the number of faradays per mole will be 2 whatever the extent of the competition between H-atom transfer and electron transfer.

Electrochemical Inducement. Electron Stoichiometry

Zero-Electron (Catalytic) Systems. The reduction of 1-chloronaphthalene in the presence of aliphatic alcoholates (Figure 1) such as cyclohexanolate (Figure 1a) or ethylate (Figure 1b) provides a typical example of electrochemical inducement of the carbonyl formation reaction corresponding to a catalytic situation. The cyclic voltammetry of 1-chloronaphthalene in the absence of alcoholate shows a two-electron irreversible wave corresponding to reductive cleavage of the chlorine–carbon bond followed by the one-electron reversible reduction wave of the resulting naphthalene. Addition of the alcoholate results in a decrease of the first wave, the second wave remaining unchanged. Upon addition of increasing amounts of alcoholate, the first wave eventually disappears.

These observations are compatible with the reaction scheme sketched out in the introduction, involving as the key step H-atom transfer from the alcoholate to the aryl radical (reaction 2), and show that the oxidative conversion of alcoholates into the corresponding ketones aldehydes by means of an aromatic halide, which is known not to occur spontaneously,[9] can be electrocatalyzed by setting the electrode potential at the wave of the aromatic halide.

However, the same general behavior would also be observed if the aryl carbanion resulting from the successive up-take of two electrons (reactions 0 + 1 + 5 and/or 6, would abstract a proton from the alcoholate leading to a dianion that would be reoxidized to the anion radical:

$$Ar^- + >CH—O^- \rightarrow ArH + >C^-—O^- \qquad (8)$$

$$>C^-—O^- - 1e \rightarrow >\dot{C}—O^- \qquad (9)$$

and/or

$$>C^-—O^- + ArX \rightarrow >\dot{C}—O^- + ArX^{-}\cdot \qquad (10)$$

and finally to the ketone or aldehyde through reactions 3 and or 4. Indeed, aliphatic aldehydes and ketones give rise to very negative waves or even to no wave at all in the available potential range so that, at the potential of the first ArX wave, reactions 3, 4, 9, and 10 would certainly be largely in favor of the right-hand sides. Although the key step of this process, reaction 8, is unlikely to be very efficient in the case of aliphatic alcoholates, for both thermodynamic and kinetic reasons, this possible reaction pathway

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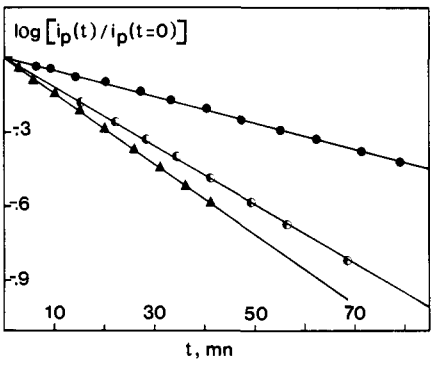


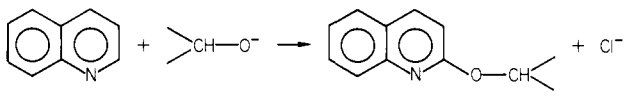
Figure 3. SNAr substitution of 2-chloroquinoline by isopropylate in liquid NH_3 at −40 °C. Time decay of the peak current of the quinoline wave. Isopropylate concentration: (●) 2.42×10^{-2} M; (◐) 5.52×10^{-2} M; (▲) 6.42×10^{-2} M.

will be further discussed on the basis of kinetic data that will be given in the next section.

Similar cyclic voltammetric behaviors were found with 6-chloroquinoline in the presence of ethylate and also with 2-chloroquinoline for which the reaction with seven different alcoholates, CH_3O^-, $C_2H_5O^-$, $(CH_3)_2CHO^-$, $(CH_3)_2CHCH_2CH_2O^-$, $(c\text{-}C_6H_{11})O^-$, $NH_2(CH_2)_4O^-$, $NH_2(CH_2)_5O^-$, was investigated. In the case of 2-chloroquinoline an additional phenomenon appears besides the electrochemical inducement of the conversion of the alcoholate into the corresponding ketone or aldehyde (Figure 2). Upon addition of the alcoholate the first wave of 2-chloroquinoline decreases instantaneously with the successive reversible wave of quinoline remaining constant as in the preceding cases. However, both waves slowly decrease with time while a third, almost reversible wave appears and increases concomitantly. This third wave features the reduction of the corresponding 2-alkoxyquinoline as checked by comparison with authentic samples. There are thus two superimposed phenomena: electrochemical inducement of the conversion of the alcohalate into the ketone or aldehyde in the close vicinity of the electrode and substitution of the chloride by the alkoxy ion in the bulk of the solution.

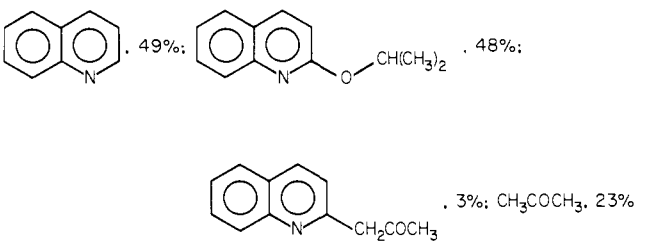
The height of the reduction peak of quinoline is proportional at any time to the bulk concentration of 2-chloroquinoline. This was used to follow the the bulk substitution reaction. The data plotted on Figure 3 indicate that the reaction is first order in both ArX and >CH—O⁻. The resulting second-order rate constants are listed in Table I.

The bulk substitution reaction



which is not electrocatalyzed, is of the S_NAr type,[10] requiring an activated carbon–halogen bond to occur. The 2 position of quinoline is indeed activated by accommodation of a negative charge on the nitrogen while the 6 position is not. In 1-chloronaphthalene there is no such activation. This rationalizes the fact that the $S_{NA}r$ substitution of the halogen by the alcoholate is observed in the case of 2-chloroquinoline but not with 6-chloroquinoline and 1-chloronaphthalene. The 2-alkoxyquinolines were identified as described in the Experimental Section. In the case of methylate, the reaction is qualitatively the same as for the other alcoholates and the rate constant is of the same order of magnitude. No quantitative data were however derived since, due to the poor solubility of methylate and the presence of residual water, its exact concentration is not known.

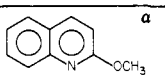
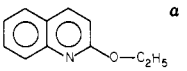
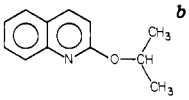
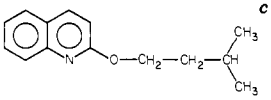
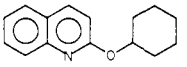
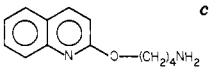
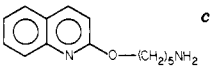
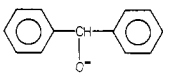
Turning back to the electrochemical inducement of the conversion of alcoholates into the corresponding carbonyl compound acompanied by the reduction of ArX into ArH, a further confirmation of the occurrence of this process was obtained from preparative scale experiments. Electrolysis of a mixture of 2-chloroquinoline (0.3 M) and isopropylate (1 M) in liquid NH_3 at −40 °C, at the wave of 2-chloroquinoline, led to the following product distribution (estimated from NMR titration with reference to the starting 2-chloroquinoline)



with the consumption of only 0.04 faraday/mol demonstrating the catalytic character of the electrochemical inducement process. It is seen that about half of the starting 2-chloroquinoline is converted into the 2-alkoxy derivative by S_NAr substitution while the other half mainly yields quinoline. About half of the expected acetone was lost upon workup or gave rise to heavier products probably resulting from the fact that acetone is produced in a highly alkaline medium. A small amount of the starting 2-chloroquinoline is converted into the $S_{RN}1$ product, 2-propanone-1 (2-quinolinyl), by means of the acetone enolate[11] resulting from the acetone, itself produced by the H-atom transfer reaction.

One-Electron Systems. A typical example of electrochemical inducement of the alcoholate–ketone (or aldehyde) conversion with the standard potentials of the ketone/ketyl couple and of the ketyl/dianion couple being respectively positive and negative to the reduction potential of the starting halide is given by the reduction of 6-chloroquinoline in the presence of diphenyl-

Table I

alcoholate	product	E_p[d]	$10^3 k_{(S_NAr)}$, $M^{-1}\ s^{-1}$
CH_3O^-	 [a]	−1.82	
$C_2H_5O^-$	 [a]	−1.80	22
$(CH_3)_2CHO^-$	 [b]	−1.85	8.5
$(CH_3)_2CHCH_2CH_2O^-$	 [c]	−1.81	31
$C_6H_5O^-$	 [b]	−1.84	3.8
$NH_2(CH_2)_4O^-$	 [c]	−1.84	24
$NH_2(CH_2)_5O^-$	 [c]	−1.83	25
			

[a] Identified by VPC (comparison with an authentic sample). [b] Identified by coupled VPC–mass spectrometry. [c] Not formally identified, the voltammograms and their time-variations are similar to the other cases. [d] In V at 0.2 V s^{-1}; reversible voltammogram.

(11) (a) Hay, J. V.; Hudlicky, T.; Wolfe, J. F. *J. Am. Chem. Soc.* **1975**, *97*, 374. (b) The formation of 3% of the $S_{RN}1$ product implies that the rate constant of the nucleophilic attack of acetone enolate on the 2-quinolyl radical is about 10 times larger than the value resulting from a previous rough estimate.[4d] The reasons for this underestimation of the rate constant have already been discussed.[4i]

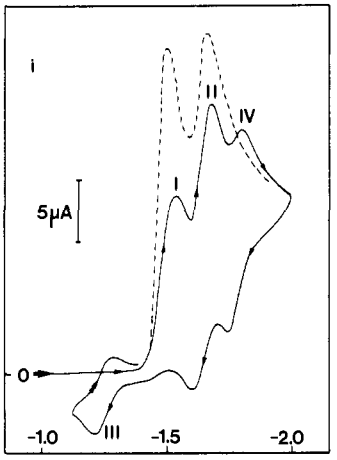


Figure 4. Cyclic voltammetry of 6-chloroquinoline (3×10^{-3} M) in the presence of diphenylcarbinolate (2.5×10^{-2} M) in liquid NH_3 at −40 °C (full line). Dashed line: 6-chloroquinoline (3×10^{-3} M) in the absence of alcoholate. Sweep rate, 0.2 V s^{-1}.

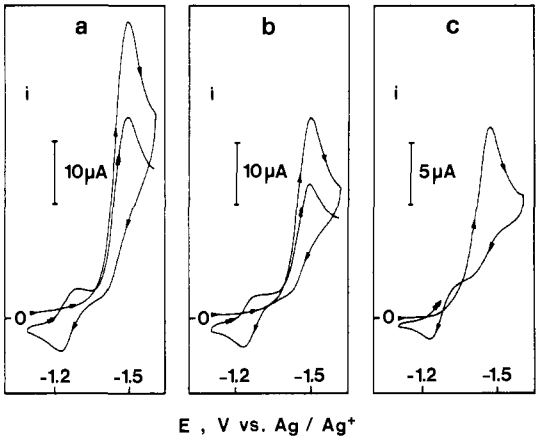
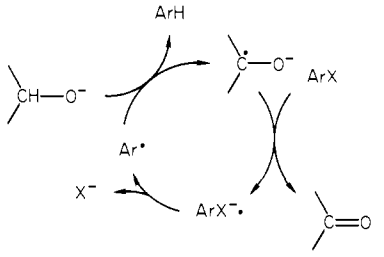


Figure 5. Trace crossing in the cyclic voltammetry of 2-chloroquinoline (5.9×10^{-3} M) in the presence of diphenylcarbinolate (2.5×10^{-2} M) in liquid NH_3 at −40 °C. Sweep rate: 0.5 (a), 0.2 (b), 0.05 (c) V s^{-1}.

carbinolate (Figure 4). Both the anion radical and the dianion of benzophenone are stable in liquid ammonia.[8,12] The two-electron wave (I), which features the reductive cleavage of 6-chloroquinoline into chloride and quinoline, decreases upon addition of diphenylcarbinolate but not below a value corresponding to one electron. The quinoline wave (II) remains constants and two additional reversible waves appear corresponding to the benzophenone/ketyl (III) and ketyl/dianion (IV) couples.

The electrochemical inducement of the alcoholate/ketone conversion is further confirmed by a preparative scale experiment in which a 2.8×10^{-3} M solution of 6-chloroquinoline was electrolyzed at the potential of the first wave in the presence of 2.5×10^{-2} M diphenylcarbinolate. The number of faradays per mole was closed to 1 (1.09) and the yield in quinoline and benzophenone measured by VPC and HPLC was quantitative.

A similar behavior is observed for 2-chloroquinoline upon addition of the same alcoholate. We note in that case the appearance of trace crossing upon scan reversal as the sweep rate is decreased (Figure 5). This is exactly of the same type as observed previously in the case of the $S_{RN}1$ reactions for a "noncatalytic" system.[4f] In the framework of the H-atom transfer mechanism this indicates that the ketyl anion radical formed upon scanning the potential on the reduction wave of 2-chloroquinoline (reactions 0, 1, and 2), being electrochemically stable in this potential range, is able to trigger the following chain process:



in the diffusion layer under the conditions of cyclic voltammetry. The chain process may well propagate outside the diffusion layer toward the bulk of the solution in preparative scale electrolysis.[4h,i]

These observations are again compatible with the reaction mechanism based on H-atom transfer between the alcoholate and the aryl radical. However, here also, the alternative possibility of deprotonation of the alcoholate into the ketone dianion being the key step of the inducement process should be examined. This is even less unlikely to occur than in the case of aliphatic alcoholates. The benzophenone dianion is indeed stable in liquid ammonia,[8,12] which implies that the alcoholate could be deprotonated by Ar^- or even by NH_2^- resulting from the reaction of Ar^- on NH_3.

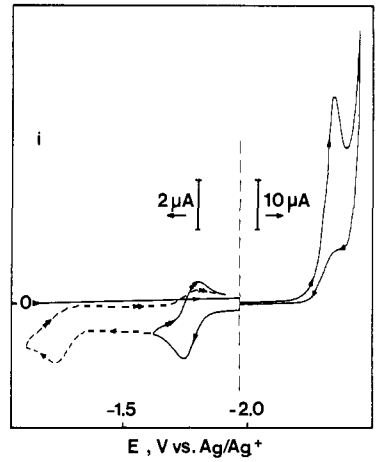


Figure 6. Cyclic voltammetry of chlorobenzene (2.7×10^{-3} M) in the presence of diphenylcarbinolate (2.5×10^{-2} M) in liquid NH_3 at −40 °C. Sweep rate: 0.2 V s^{-1}. Note the change in vertical scale after scan reversal.

Two-Electron Systems. Figure 6 shows the reduction of chlorobenzene in the presence of diphenylcarbinolate. The two-electron irreversible wave of chlorobenzene remains unaffected by the addition of the alcoholate while two waves corresponding to the benzophenone/ketyl and the ketyl/dianion couples appear largely in front of the chlorobenzene wave upon scan reversal. This is compatible with the H-atom transfer mechanism since the benzophenone anion radical thus formed at the chlorobenzene wave would be reduced into the corresponding dianion, the standard potential for this couple being significantly more positive. It is noted that the formation of the benzophenone dianion at the reduction wave of chlorobenzene is not very efficient. Its reoxidation waves are indeed rather small as compared to the height of chlorobenzene reduction wave (note in Figure 6 the expansion of the vertical scale by a factor of 5 after scan reversal). It is also observed that the second reoxidation wave of the dianion of benzophenone formed upon reduction of chlorobenzene is not reversible as if the benzophenone formed was not stable under the conditions of the experiment. The latter observation can be explained by the fact that the NH_2^- formed at the chlorobenzene reduction wave are able to react on benzophenone giving rise to a nonreducible adduct.

The cyclic voltammetry of 1-chloronaphthalene in the presence of the same diphenylcarbinolate (Figure 7) shows an analogous

(12) Demortier, A.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 3495.

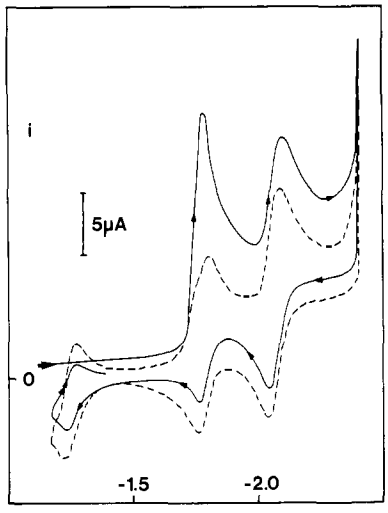


Figure 7. Cyclic voltammetry of 1-chloronaphthalene (2.55×10^{-3} M) in the presence of diphenylcarbinolate (2.5×10^{-2} M) in liquid NH_3 at −40 °C. Full line: first cycle. Dashed line: after 10 cycles. Sweep rate: 0.2 V s^{-1}.

behavior although the anion radical/dianion standard potential is now located almost at the same place as the ArX wave. The formation of the dianion is significantly more efficient than in the preceding case. The reoxidation waves are about two times higher than in the case of chlorobenzene relative to the ArX two-electron reduction wave. After ten cycles, the cyclic voltammogram is pratically the same as for an equimolar mixture of benzophenone and naphthalene, featuring the complete conversion of the alcoholate into benzophenone in the vicinity of the electrode. It is also noticed that the reoxidation wave of the anion radical into benzophenone is almost reversible at low sweep rate. This is compatible with the formation of a lower amount of NH_2^- at the chloronaphthalene two-electron reduction wave.

All these observations are compatible with an H-atom transfer mechanism corresponding to a two-electron situation. However, the alternative possibility of proton transfer from the diphenylcarbinolate to the electrogenerated Ar^- should obviously be envisaged in the present case too.

Kinetics. Side Reactions. Mechanism

The kinetics of the electrochemical inducement process was investigated systematically in the case of *2-chloroquinoline* in the presence of *aliphatic alcoholates* (catalytic systems) and of *diphenylcarbinolate* (one-electron system) in the framework of the H-atom transfer mechanism. It is then anticipated that electron transfer to Ar· at the electrode (reactions 5) or in the solution (reaction 6) will compete with the H-atom transfer reaction 2. The kinetics of this three-cornered competition will be different if electron transfer essentially occurs either at the electrode (ECE type process) or in the solution (DISP type process). In all cases the concentration of alcoholate was made large enough for the H-atom transfer reaction to be pseudo-first order. The kinetics are formally the same as for another electrochemically induced reaction, $S_{RN}1$ aromatic nucleophilic substitution; the nucleophilic attack on the Ar· radical

$$Ar\cdot + Nu^- \rightarrow ArNu^{-}\cdot$$

being replaced by the H-atom transfer reaction 2 and the reoxidation of the $ArNu^{-}\cdot$ anion radical

$$ArNu^{-}\cdot - 1e \rightarrow ArNu$$

and/or

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

by the reoxidation of the $>\dot{C}—O^-$ anion radical (reactions 3 and 4). The kinetic analyses carried out for electrochemically induced

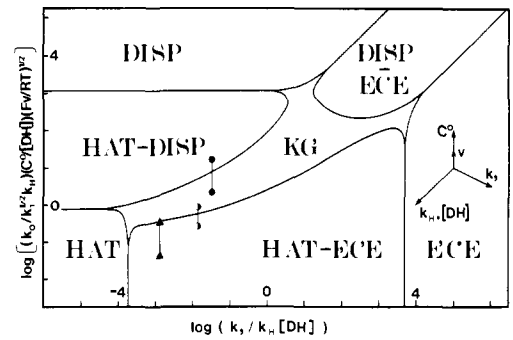


Figure 8. Kinetic competition zone diagram (based on 1% accuracy on peak current measurements). The three limiting situations, HAT, DISP, and ECE, correspond to complete predominance (≥99%) of H-atom transfer and homogeneous and heterogeneous electron transfer to Ar·, respectively. The HAT-DISP, HAT-ECE, DISP-ECE zones correspond to the transition between the limiting situations. KG represents a situation in which the three competing pathways interfere simultaneously, none being negligible. The effect of the various intrinsic (rate constants) and operational (sweep rate, ArX concentration) parameters is shown on the right-hand side. Symbols refer to the experiments plotted in Figures 9a and 9b for the systems: 2-chloroquinoline, (●) cyclohexanolate, 2.5×10^{-2} M, (◑) ethylate, 10^{-2} M, and (▲) ethylate, 9.7×10^{-2} M.

$S_{RN}1$ aromatic substitution[4a-g] can therefore be used straightforwardly in the present case.

The three-cornered competition between H-atom transfer and the two modes of electron transfer is thus conveniently represented by a kinetic zone diagram[4e] (Figure 8) involving two independent dimensionless parameters:

$$\rho = k_D C^0 (Fv/RT)^{1/2}/(k_1^{1/2} k_H[DH]), \quad \sigma = k_1/k_H[DH]$$

(k_1 is the rate of cleavage reaction 1, k_H is the H-atom transfer second-order rate constant, [DH] is the alcoholate concentration, C^0 is the ArX concentration, v is the sweep rate, k_D is the diffusion limit of second-order rate constants in liquid NH_3 at −40 °C, $k_D \approx 3 \times 10^{10}$ M^{-1} L s^{-1} [7]) which shows, based on a 1% accuracy on peak current determinations, the various zones corresponding to the predominance of either H-atom transfer or ECE or DISP electron transfer processes and the transition zones where the system depends upon a single parameter, ρ and σ, respectively. In the H-atom/DISP zone a working curve is available[4e] that relates the peak current rates, i_p/i_p^0 (i_p is the observed peak current, i_p^0 is the peak current in the absence of alcoholate) to the parameter ρ (Figure 9a). For the H-atom/ECE transition, i_p/i_p^0 is simply expressed as $i_p/i_p^0 = [\sigma^{1/2}/(1 + \sigma^{1/2})]$.[4e]

In the case of 2-chloroquinoline, the cleavage rate k_1 is not too large, $k_1 = 1.7 \times 10^4$ s^{-1},[4d] so that the system is anticipated to be in an H-atom–Disp situation provided v and C^0 are large enough and [DH] not too large. This is indeed what was observed with cyclohexanolate, 2.5×10^{-2} M (Figure 9a). The efficiency of the catalytic process is thus found to depend, besides alcoholate concentration, upon sweep rate and ArX concentration, in agreement with the predicted kinetics for an H-atom–DISP competition. By use of the corresponding working curve[4e] it is then possible to derive the value of $k_D/(k^{1/2}k_H)$ by fitting the experimental data plotted as a function of $v^{1/2}C^0/[DH]$ with the working curve which is represented in terms of $\rho = (k_D/k_1^{1/2}k_H)(Fv/RT)^{1/2}C^0/[DH]$ (Figure 9a). $k_D/(k_1^{1/2}kH)$ is thus found equal to 11.5 $s^{1/2}$, $k_1 = 1.7 \times 10^4$ s^{-1} as determined previously,[4d] and k_D is taken as equal to the diffusion limit[4d,e] 3×10^{10} M^{-1} s^{-1} which leads to the value of k_H reported in Table II.

For large catalytic efficiencies, i.e., for small values of i_p/i_p^0, corresponding to small values of C^0 and v the experimental data depart from the H-atom–DISP behavior. The experimental curve tends toward a nonzero limiting horizontal line. This corresponds to the system passing from an H-atom–DISP situation to an H-atom–ECE situation as pictured on the zone diagram in Figure 8 where the points corresponding to each value of C^0 and v have been located on the basis of the previously determined values of

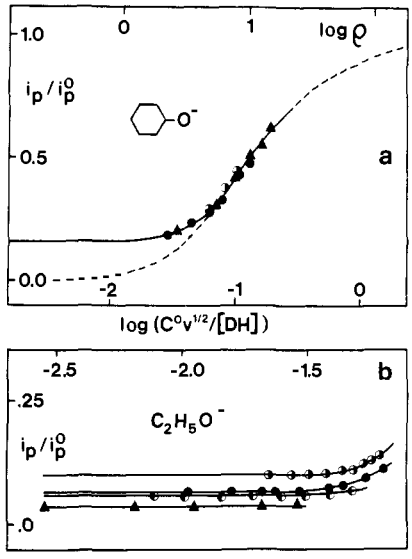
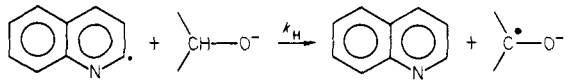


Figure 9. Variation of the peak current of 2-chloroquinoline upon addition of cyclohexanolate (a) and ethanolate (b). The data for part a are given in the order sweep rate (V s^{-1}), symbol, successive values of C^0 (mM) descending the curve: 0.108, ◑, 7.6, 6.0, 4.5; 0.200, ●, 7.6, 6.0, 4.5, 3.4, 2.5, 1.6; 0.295, ▲, 8.8, 7.6, 6.0, 4.5, 3.4, 1.6. Cyclohexanolate concentration: 2.5×10^{-2} M. Dashed line: working curve i_p/i_p^0 vs. log ρ, $\rho = (k_D/k_1^{1/2}k_H)(C^0/[DH])(Fv/RT)^{1/2}$. The data for part b are given in the order ethanolate concentration (M), symbol, successive values of C^0 (mM) descending the curve: 10^{-2}, ◑, 1.35, 1.25, 1.15, 1.05, 0.95, 0.83, 0.7, 0.6, 0.5; 3×10^{-2} ● 4.1, 3.5, 2.9, 2.5, 1.9, 1.5, 1.4, 1.05, 0.7; 3.9×10^{-2}, ◐, 4.0, 3.3, 2.7, 2.1, 1.6, 1.2, 0.9, 0.65; 9.7×10^{-2}, ▲, 6.0, 4.5, 2.5, 1.4, 0.6. $v = 0.215$ V $\times$ s^{-1}.

Table II. Rate Constants of the H-Atom-Transfer Reaction:



alcoholate	k_H, M^{-1} s^{-1}	alcoholate	k_H, M^{-1} s^{-1}
$C_2H_5O^-$	1.2×10^8	$(CH_3)_2CHO^-$	2.2×10^8
$(CH_3)_2CH(CH_2)_2O^-$	9.3×10^7	$(c\text{-}C_6H_{11})O^-$	2×10^7
$H_2N(CH_2)_4O^-$	3.7×10^8	$(Ph)_2CHO^-$	1.6×10^7
$H_2N(CH_2)_5O^-$	1.6×10^8		

$k_D/(k_1^{1/2}k_H)$. It is indeed clearly seen that when the sweep rate and the ArX concentration are decreased, the representative points tend to cross the KG zone, from the HAT–DISP zone and toward the HAT–ECE zone. When the latter situation is reached i_p/i_p^0 no longer depends upon sweep rate and substrate concentration reflecting that the competition is between first-order processes while in the HAT-DISP case it is between a second and a pseudo-first-order reaction.

A very similar behavior was found in the case of methylate, again displaying the transition from the HAT-DISP to the HAT–ECE situations upon decreasing sweep rate and ArX concentration. No k_H value is however reported in Table II for this case since the exact concentration of methylate is not known for the reasons mentioned earlier. It is roughly estimated as being of the same order or magnitude as for the other alcoholates.

The passage into the HAT–ECE situation is even more clearly visible in the case of ethanolate as shown in Figure 9b where the variation of the peak current with ArX concentration is represented for four different values of the ethanolate concentration. For the HAT–ECE competition it is predicted[4e] that

$$(i_p^0 - i_p)/i_p = (k_H[DH]/k_1)^{1/2}$$

involving a square root dependency upon the alcoholate concentration. This is what is found for ethanolate as shown on Figure 10 which allows the determination of k_H (Table II).

The other aliphatic alcoholates display the same type of behavior. In the HAT–ECE region the above relationship was also

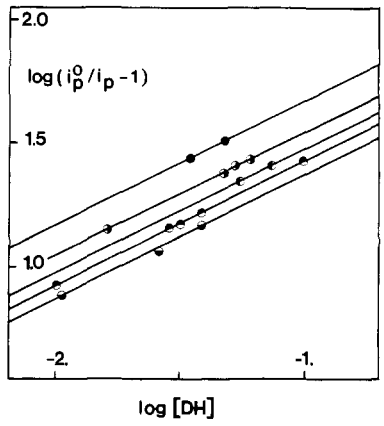


Figure 10. Variations of the peak current of 2-chloroquinoline (QCl) upon addition of aliphatic alcoholates in the framework of a HAT–ECE competition: (●) $H_2N(CH_2)_4O^-$; (◑) $(CH_3)_2CHO^-$; (◐) $H_2N(C\text{-}H_2)_5O^-$; (⊖) $CH_3CH_2O^-$; (⊖) $(CH_3)_2CH(CH_2)_2O^-$. [DH] in M, sweep rate $v = 0.215$ V s^{-1}. [QCl] between 10^{-3} M and $5\ 10^{-4}$ M.

shown to hold (Figure 10), allowing again the determination of k_H (Table II).

The fact that the peak height varies with sweep rate and substrate concentration as shown on Figure 9a reflects a competition between a first- and a second-order process. This is compatible with the H-atom transfer mechanism under HAT–DISP conditions while it is not with the proton transfer mechanism 0 + 1 + 5 + 6 followed by the two competitive reactions

$$Ar^- + >CH—O^- \rightarrow ArH + >C^-—O^- \quad (8)$$

$$Ar^- + NH_3 \rightarrow ArH + NH_2^- \quad (8')$$

themselves followed by reactions 9 and/or 10 and reactions 3 and/or 4. In that case, indeed, the competition would be between two pseudo-first-order reactions implying no dependence of the peak current upon sweep rate and ArX concentration. This conclusion is actually not very surprizing since the aliphatic $>CHO^-/>C^-—O^-$ couple is likely to be much less acidic than the NH_3/NH_2^- and even the ArH/Ar^- couples.

The reaction of *2-chloroquinoline with diphenylcarbinolate* is an example of a noncatalytic system as discussed in the preceding section (Figure 5); at the level of the ArX wave the electrochemically stable form of the carbonyl compound is the ketyl anion radical. The apparent numer of electrons for the ArX wave is thus expected to be located between 1 and 2 depending upon the respective efficiencies of the H-atom transfer reaction and the further electron transfer reduction of the aryl radical. This is indeed what is found as shown on Figure 11a which represents the variations of i_p/i_p^0 with the sweep rate and the ArX concentration for a given value of the diphenylcarbinolate concentration.

It is observed that the experimental data fit the working curve corresponding to a HAT-DISP competition in the context of a noncatalytic situation.[4e] This allows the determination of the rate constant of H-atom transfer (Table II) along the same procedure as for the reaction of 2-chloroquinoline with cyclohexanolate. As in the latter case, it is seen that the system shifts toward an HAT-ECE situation when decreasing v and C^0. This limit is represented on Figure 11a by a horizontal line which corresponds to a peak-current ratio independent of sweep rate and ArX concentration.

The very fact that the observed kinetics depends upon v and C^0, reflecting the existence of a competition between a first- and a second-order reaction, provides evidence against the proton transfer mechanism for the same reasons as already discussed in the catalytic cases (aliphatic alcoholate).

The reaction thus appears to follow an H-atom transfer rather than a proton transfer mechanism despite the fact that the diphenylcarbinolate can certainly be deprotonated by Ar^- and even by NH_2^- from a thermodynamic point of view since the dianion of benzophenone is stable in liquid NH_3. Deprotonation is ap-

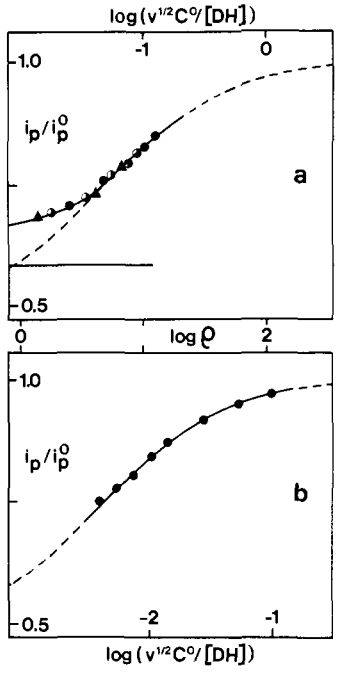


Figure 11. Variations of the peak current of 2-chloroquinoline upon addition of diphenylcarbinolate (a) or of diphenyl carbinolate + diphenylcarbinol (b). Sweep rate: (●) 0.387 V s^{-1}, (◑) 0.204 V s^{-1}, (▲) 0.117 V s^{-1}. [DH] = concentration of diphenylcarbinolate (a) or of diphenylcarbinolate + diphenylcarbinol (b) (see text). Dashed line: working curve i_p/i_p^0 vs. log ρ, $\rho = (k_D/k_1^{1/2}k_H)(C^0/[DH])(Fv/RT)^{1/2}$.

parently unable to compete kinetically with H-atom transfer which is indeed a rather fast reaction (Table II).

This conclusion is further confirmed by a series of experiments involving again 2-chloroquinoline and diphenylcarbinolate but now in the presence of a large excess of water and diphenylcarbinol. At equilibrium of the reaction

$$Ph_2CH{-}O^- + H_2O \rightleftarrows Ph_2CHOH + OH^-$$

the equilibrium constant of which is about 1, the respective concentrations can be estimated as $[Ph_2CH{-}O^-] = 2.5 \times 10^{-3}$M, $[OH^-] = 10^{-2}$ M, $[Ph_2CHOH] = 2.9 \times 10^{-1}$ M, and $[H_2O] = 2.8$ M, amounting to a pH of about 16.5, which approximately corresponds to neutrality in liquid ammonia. Under such conditions, Ar^- when formed would certainly deprotonate H_2O or the diphenylcarbinol rather than the diphenylcarbinolate. The observation that the kinetics of the reaction are of the same type as for diphenylcarbinolate alone (Figure 11b) provides further evidence for the H-atom transfer mechanism. In the presence of diphenylcarbinol, H-atom transfer may involve both the alcoholate (reaction 2) and the alcohol

$$Ar\cdot + Ph_2CHOH \xrightarrow{k'} ArH + Ph_2\dot{C}{-}OH \qquad (2')$$

followed by

$$Ph_2\dot{C}{-}OH + Ph_2CHO^- \rightleftarrows Ph_2CHOH + Ph_2\dot{C}{-}O^-$$

Thus in the context of a HAT–DISP situation the expression of the parameter governing the competition between electron and H-atom transfer will now involve the reaction with the alcohol besides that with the alcoholate:

$$\rho = k_D C^0 (Fv/RT)^{1/2}/\{k_1^{1/2}(k_H[RO^-] + k_H'[ROH])\}$$

i.e.

$$\rho = 10\{k_D C^0 (Fv/RT)^{1/2}/(k_1^{1/2}k_H[DH])\}$$

taking into account the equilibrium concentrations of the alcoholate, $[RO^-]$, and of the alcohol, [ROH], corresponding to the experiment shown in Figure 11b ($[DH] = [RO^-] + [ROH]$ is the total concentration of H-atom donors). Comparing the curves in Figures 11a and 11b, it is found that the contributions of the alcohol and the alcoholate are on the same order in spite of the former being in large excess. More precisely, this results in k_H/k'_H being approximately equal to 11, i.e., of the same order of magnitude as previously determined in the case of methanol.[9] It is thus seen that the diphenylcarbinolate is involved in an H-atom transfer mechanism under conditions where the proton transfer mechanism cannot occur due to the excess of water and diphenylcarbinol.

In the case of the reaction of diphenylcarbinolate on 1-chloronaphthalene and 1-chlorobenzene described in the preceding section (Figures 6 and 7), the height of the ArX reduction wave is of no help since it corresponds to two electrons per molecule whatever the mechanism and the competing reactions involved. We have thus no formal proof that the formation of benzophenone results from an H-atom transfer rather than from a proton transfer reaction. The first mechanism is however not as unlikely as in the case of 2-chloroquinoline. Indeed, dramatic changes of the ratio between the rates of H-atom and proton transfer are not expected when passing from the 2-quinolyl to the 1-naphthyl and phenyl radicals. Furthermore the increase in reactivity, by a factor of about 10, observed when passing from chlorobenzene to 1-chloronaphthalene seems to be better rationalized in the context of the H-atom transfer mechanism than in that of the proton transfer mechanism. In the latter case, this would imply that the ratio of rate constants for the proton abstraction from diphenylcarbinolate (eq 8) and from NH_3 (eq 8′) increases by a factor of 10 when passing from the phenyl to the 1-naphthyl carbanion, which seems unlikely. In the framework of the H-atom transfer mechanism, the explanation of this change in reactivity is as follows. The lifetime of the initially formed anion radical, $ArX^{-}\cdot$, decreases considerably when passing from 1-chloronaphthalene to chlorobenzene. The Ar· radical is thus formed much closer to the electrode surface in the latter than in the former case. For chlorobenzene, a competition HAT–ECE thus occurs under unfavorable conditions for the H-atom transfer reaction while the competition with electron transfer is less severe with 1-chloronaphthalene for which the competition occurs in a HAT–DISP context ($k_1 = 1.5 \times 10^4$ s^{-1} [4e]). Another consequence is that more NH_2^- is formed with chlorobenzene than with 1-chloronaphthalene which matches the observation that the second oxidation wave of the benzophenone dianion is less reversible in the first case than in the second.

Experimental Section

Voltammetric Experiments. The experimental setup, electrochemical cell, and procedures for purifying the solvent were the same as those previously described.[14,15] The working electrode in cyclic voltammetry was a platinum disk of 1-mm diameter. It was polished on alumina before use. The experiments were carried out at −40 °C. The supporting electrolyte was potassium bromide in 0.1 M concentration.

The reference electrode was an $Ag|Ag^+$ 0.01 M electrode in liquid ammonia.[14] A solid-state amplifier potentiostat with positive feedback resistance compensation[16] was used together with a function generator (Tacussel TPPRT) and a storage oscilloscope (Schlumberger OCM 581) or an X–Y chart recorder (Ifelec 2025C). Ohmic drop compensation was required in the cyclic voltammetry experiments since the resistance between reference and working electrode was currently of the order of 4000–5000 Ω.

The alcoholates were prepared "in situ" by reduction of the corresponding alcohol by potassium. As the solubilization of halogenoaromatic compounds in liquid ammonia is relatively slow, in the case when the initial time must be known with accuracy, i.e., in the case when relatively fast $S_{RN}Ar$ reactions occur, the following procedure was followed: the cell was filled with purified ammonia, the alcoholate was prepared, and then the halogenoaromatic dissolved in the minimum amount of the corresponding alcohol was added. The first voltammogram was recorded immediately.

Preparative Experiments. The cell was filled with 60 mL of purified ammonia; the working electrode was a platinum grid with about 15 cm^2

(13) Thiébault, A., unpublished results.
(14) Herlem, M. *Bull. Soc. Chim. Fr.* **1967**, 1687.
(15) Herlem, M.; Minet, J. J.; Thiébault, A. *J. Electroanal. Chem.* **1971**, *30*, 203.
(16) Garreau, D.; Savéant, J. M. *J. Electroanal. Chem.* **1972**, *35*, 309.

of surface area. The supporting electrolyte was KBr 0.1 M. After completion of the electrolysis the products were identified by cyclic voltammetry or after extraction according to the following procedure: the solution was neutralized with an excess of NH_4Cl and then 100 mL of diethyl ether was added; the ammonia was allowed to evaporate through a condenser, the central well of which contained 2-propanol held at about -20 °C by occasional addition of pieces of solid CO_2.

6-Chloroquinoline with Benzhydrol Alcoholate. The ether extract was titrated by HPLC on a 25 cm RP 18 column eluted with a 75-25 methanol-water mixture and by gas chromatography on a 3 m 3% OV17 column.

2-Chloroquinoline with Isopropylate. The ether extract was separated into two portions. The first portion was analyzed by gas chromatography and NMR. 2-Propanone-1 (2-quinolinyl) was identified by its mass spectrum obtained by gas chromatography-mass spectroscopy: *m/e* 187 (11), 186 (28), 171 (13), 170 (32), 145 (5), 144 (36), 143 (100), 142 (27), 128 (8), 116 (17), 115 (26), 89 (23). The second portion was treated with 2,4-dinitrophenylhydrazine and the acetone derivative was identified by its melting point and NMR spectrum.

SNAr Reactions. 2-Methoxyquinoline was identified by comparison with an authentic sample[17]—UV spectrum, retention time in VPC (3% OV17), and HPLC (25 cm RP 18, 75-25 $MeOH/H_2O$). Its mass spectrum was identical with that previously published.[17]

2-Ethoxyquinoline was identified by comparison with an authentic sample—HPLC (25 cm Lichrosorb 65-35 $MeOH/H_2O$)—and by its mass spectrum: *m/e* 173 (57) (M), 158 (88) (M - 15), 145 (100) (M - 28), 129 (97) (M - 44), 128 (26) (M - 45), 117 (58), 116 (33), 102 (16) (129 (quinoline) - 27), 101 (12), 90 (42), 89 (66), 76 (11), 75 (19).

2-Isopropoxyquinoline was identified after evaporation of ammonia and extraction of the residue by ether: NMR spectrum ($CDCl_3$) (ppm by reference to Me_4Si) δ 1.38 (doublet, 6 H, CH_3), 5, 6 (septuplet, 1 H, O-C*H*<), 7.0-8.3 (multiplet, 6 H, aromatic protons); mass spectrum 187 (25) (M), 162 (38) (M - 15), 145 (100) (M - 42), 129 (45) (M - 58, quinoline), 117 (73), 102 (73) (quinoline - 27), 101 (15), 90 (66), 89 (73).

2-(Cyclohexyloxy)quinoline was identified through its mass spectrum obtained by gas chromatography-mass spectrometry coupling: 227 (47) (M), 146 (32), 145 (100) (M - C_6H_{11}), 129 (10) (M - 98, quinoline), 128 (10), 117 (22), 116 (9.6), 102 (2), 90 (13), 89 (15).

The other products of the S_NAr reactions were not formally identified but their voltammograms and their kinetics of formation were similar to other cases (see Table I).

Acknowledgment. This work was supported in part by the CNRS (Equipe de Recherche Associée No. 309 "Electrochimie Moléculaire").

Registry No. 2-Chloroquinoline, 612-62-4; 6-chloroquinoline, 612-57-7; methylate, 3315-60-4; ethylate, 16331-64-9; isopropylate, 15520-32-8; 3-methylbutylate, 35730-35-9; cyclohexanolate, 80754-03-6; 4-aminobutylate, 80754-04-7; 5-aminopentylate, 80754-05-8; diphenylcarbinolate, 80754-06-9; 1-chloronaphthalene, 90-13-1; chlorobenzene, 108-90-7; 2-ethoxyquinoline, 46185-83-5; 2-isopropoxyquinoline, 60814-31-5; 2-(cyclohexyloxy)quinoline, 80754-07-0; (2-quinolinyl)-2-propanone, 1531-30-2.

(17) Clugston, D. M.; Mc Lean, D. B. *Can. J. Chem.* **1966**, 44, 781.

Phosphonosulfates. Metal Ion Catalysis in the Hydrolysis of 2-Pyridyl- and 2-Pyridylmethylphosphonosulfate

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Abstract: The hydrolysis rates of phosphonosulfates having a neighboring 2-pyridyl group, 2-pyridyl- (**1**) and 2-pyridylmethylphosphonosulfate (**2**), have been compared with those of the corresponding phenyl- (**3**) and benzylphosphonosulfate (**4**) in a pH range of 1-9. All of the esters were found to undergo the acid-catalyzed reaction via the selective S-O bond cleavage. Under neutral pH conditions, the P-O bond was selectively cleaved in the solvolysis of all the esters regardless of whether Zn^{2+} or Mg^{2+} is present or not. In the absence of metal ion, an intramolecular catalysis by the 2-pyridyl group was observed for the hydrolysis of **2**, but not for that of **1**. The intramolecular catalysis was inhibited by the Zn^{2+} ion. Such an inhibition, however, appears to be largely compensated by the Zn^{2+} ion catalysis which leads to the formation of a pentavalent phosphorus intermediate upon metal chelation. Even more remarkable catalysis by the Zn^{2+} ion was observed for the hydrolysis of **1**.

Phosphosulfates such as adenosine-5′-phosphosulfate (APS) and 3′-phosphoadenosine-5′-phosphosulfate (PAPS) are classified as active sulfates due to biological reasons and taken as the key intermediates for the biological sulfur metabolism.[2] The P-O-S linkage involved in such phosphosulfates undergoes S-O bond cleavage and transfers its sulfate moiety to numerous nucleophiles such as steroids and phenols under biological conditions. Reduction of the sulfate group in the active sulfates also takes place most plausibly via the S-O bond cleavage under certain enzymic conditions. However, information on the enzymic mechanisms of these reactions is very limited up to the present time. Various reactions of biochemical concern have often been enhanced by metal ions under nonenzymatic conditions. Thus, it is meaningful to examine metal-ion catalysis in the cleavage of the P-O-S linkage of the active sulfates and to clarify which bond, P-O or S-O, is selectively cleaved under such catalytic conditions. We have previously reported that the S-O bond of phosphosulfates was selectively cleaved in the acid-catalyzed hydrolysis and the catalysis was enhanced by the Mg^{2+} ion when the reaction was carried out in organic solvents containing low water contents.[3,4] However, the metal-ion catalysis was not detected without acids, partly due to low reactivity of a model substrate under specified conditions.

In this work, we selected another type of active sulfates, phosphonosulfates, and investigated the hydrolysis of 2-pyridyl- and 2-pyridylmethylphosphonosulfate (**1** and **2**) and of the related

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