somewhat roughly) by EPR together with their kinetic parameters. Some important classes of radicals are represented by only a single clock, but many more are completely unrepresented. Few readers will be lucky enough to find in this table a clock reaction of use to them in their current research. We hope, therefore, that this Account will stimulate additional EPR kinetic studies on unimolecular radical reactions and that many horlogeries will become well stocked during the coming decade.

Catalysis of Chemical Reactions by Electrodes

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An early example of catalysis of an organic reaction by an electrode was given by the observation that the nucleophilic substitution reaction of 4-bromobenzophenone (ArX) with thiophenolate (Nu^-) can be triggered electrochemically, the electrode potential being set in a region corresponding to reduction of the substrate (Scheme I). Evidence for such a reaction mechanism was provided by cyclic voltammetry but also by preparative-scale experiments in which the yield of substitution product was 80% and the number of faradays passed through the electrolytic cell per mole of starting material was 0.2. The latter figure clearly pointed to the catalytic character of the electrochemical process.

Scheme I

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

$$ArX^{-}\cdot \rightleftarrows Ar\cdot + X^{-} \qquad (1)$$

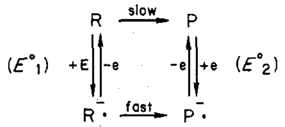
$$Ar\cdot + Nu^{-} \longrightarrow ArNu^{-}\cdot \qquad (2)$$

$$ArNu^{-}\cdot - e \rightleftarrows ArNu \qquad (3)$$

$$\text{(and/or: } ArNu^{-}\cdot + ArX \rightleftarrows ArNu + ArX^{-}\cdot\text{)} \qquad (4)$$

$$ArX + Nu^{-} \longrightarrow ArNu + X^{-}$$

Scheme II



R, reactant; P, product

This reaction can be viewed as an example of a general class of processes in which a chemical reaction that would proceed slowly under normal thermal conditions is accelerated by the presence of an electrode set up at a suitable potential. Such electrochemical inducements are based upon the greater reactivity of a lower or higher oxidation state than of the starting system.

Scheme II represents inducement of reaction by a reduction–oxidation cycle but is immediately transposable to an oxidation–reduction process. The reaction at the −1 oxidation state need not necessarily be a single-step reaction. In Scheme I it is indeed a two-stage reaction: cleavage of the anion radical (eq 1) and then nucleophilic attack of the resulting neutral radical (eq 2).

More generally, one can view the processes going on at each electrode of any electrochemical cell as adding up to a balanced overall chemical reaction. If the standard free energy, ΔG°, of this reaction is positive, electrolysis will involve the conversion of electrical energy into chemical energy leading thus to an actual *electrosynthesis*. The amount of electrical energy required to carry out the synthesis will generally be larger than ΔG° owing to the necessity of overcoming activation barriers in both electrode reactions.

In the reverse situation where $\Delta G^\circ < 0$, the generation of electricity is in principle possible. The activation barriers may, however, be so high that no electricity can be obtained. An *electrochemical activation* of the reaction can then be obtained by providing a finite, stoichiometric, amount of electricity which serves to overcome the activation barriers.

An actual *electrocatalytic* situation is met when, ΔG° still being negative, the number of faradays required to drive the reaction to completion tends toward zero.

With reference to Scheme II, two opposite situations can be encountered differing in the sequencing of the characteristic potentials. These are pictured in Figure 1 in the framework of a cyclic voltammetric analysis of the problem.

In the first case (Figure 1a) the reduction potential of the reactant (wave R) is positive with respect to the reduction potential of the product (wave P). Under such conditions, electrochemical inducement of the reaction will be obtained by setting the electrode potential just after the first wave. The process is then clearly electrocatalytic since at this potential, $P^-\cdot$ is reoxidized into P. The catalytic efficiency will depend upon the competition offered by side reactions. An estimation of its magnitude within the time scale of cyclic voltammetry can be obtained from the heights of the R and P waves: an infinitely efficient process would correspond to complete disappearance of the R wave and full development of the P wave while a completely inefficient process would lead to the reverse situation.

In the reverse case, where the reduction potential of the reactant is negative to the standard potential of the (product)/(product)$^-\cdot$ couple (Figure 1b), electrolysis at

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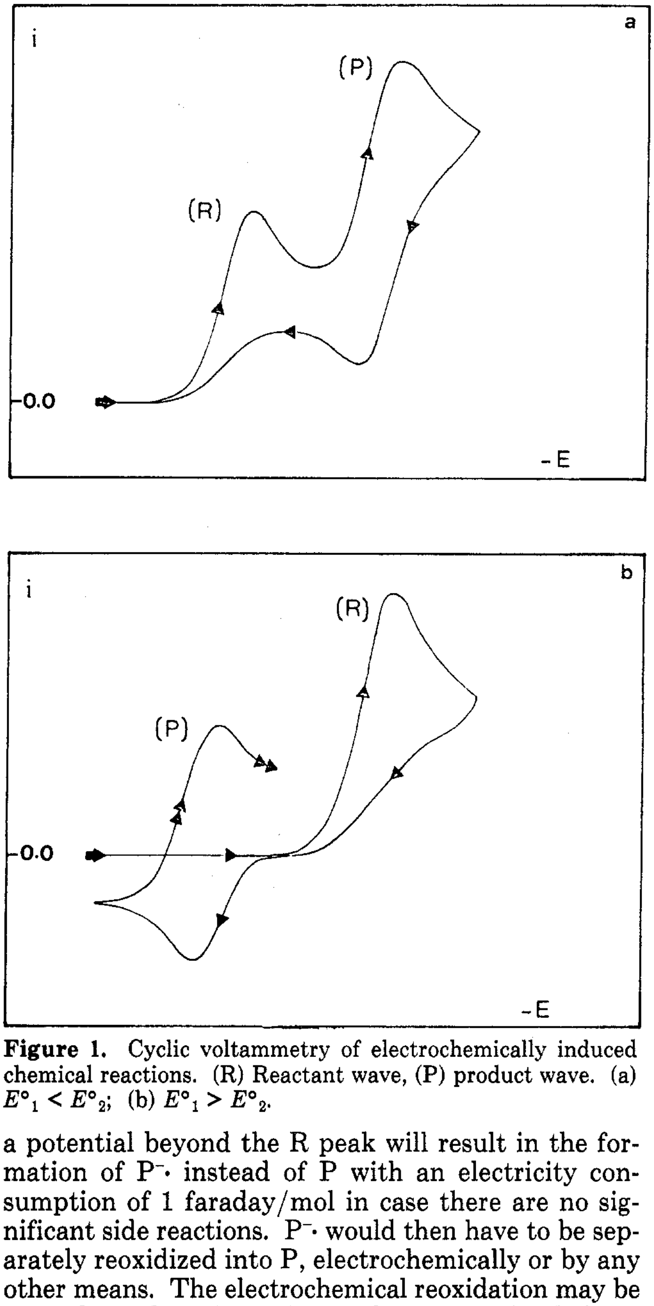

Figure 1. Cyclic voltammetry of electrochemically induced chemical reactions. (R) Reactant wave, (P) product wave. (a) $E^\circ_1 < E^\circ_2$; (b) $E^\circ_1 > E^\circ_2$.

a potential beyond the R peak will result in the formation of $P^{-}\cdot$ instead of P with an electricity consumption of 1 faraday/mol in case there are no significant side reactions. $P^{-}\cdot$ would then have to be separately reoxidized into P, electrochemically or by any other means. The electrochemical reoxidation may be carried out directly at the anode in an undivided cell with the cathode potential set up at a value negative to the R peak and the anode potential a value positive to the $P/P^{-}\cdot$ standard potential. This would involve the consumption of 1 mol of electron/mol of R converted into P. The system is therefore clearly not catalytic but rather of the electroactivation type.

However, as discussed in detail below, such a system can be rendered catalytic through a different programming of the electrode potential.

Besides the example just cited, a few other investigated systems appear to be potentially catalytic along the lines discussed above: cis–trans isomerization of olefinic compounds,[2-6] cycloaddition of indene derivatives,[7] and rearrangement of tetramethyl 1,3-dithione into the β-dithio lactone.[8] There are also a few examples in coordination chemistry involving ligand exchange[9] and isomerization reactions.[10,11]

Although generally more indirect, several other electrochemically induced processes can be formally viewed as belonging to the same class of reactions: electropolymerization[12] and the electrogeneration of bases[13-15] or transition-metal complexes[16-23] able to catalyze organic reactions.

Of chemical reactions effected by direct electrochemical stimulation as pictured by Scheme II, $S_{RN}1$ aromatic nucleophilic substitution,[24] which is based upon the electrophilic reactivity of aryl radicals on nucleophiles,[25] has been the most extensively investigated insofar as synthetic aspects, mechanism, kinetics, and side reactions are concerned.[1,26-31] The following discussion will focus on such reactions, pointing out a series of problems that are important for the $S_{RN}1$ reaction itself but also to the understanding of other electrochemically induced reactions.

Electrochemical Inducement of Aromatic Nucleophilic Substitution

The preparative-scale results that have been reported so far[1,26,27,30,31] are listed in Table I. They were obtained by electrolysis of the substrate–nucleophile solution at the potential of the substrate reduction wave. In cases in which the reduction potential of the substrate is positive to the standard potential of the $ArNu/ArNu^{-}\cdot$ couple, e.g., with $Nu^{-} = PhS^{-}$, ArNu is obtained directly.

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Table I
Electrochemically Induced Aromatic Nucleophilic Substitution (Preparative-Scale Experiments)

substrate (concn, M)	solvent	nucleophile (concn, M)	electrolysis potential[a]	no. of faraday/mol	ArNu, %	ArH, %	ArH unreacted, %	ref
4-bromobenzophenone (10^{-2})	CH_3CN	$PhSNBu_4$ (0.1)	−1.8	0.2	95	3	0	1
(10^{-3})	Me_2SO	PhSNa + dB18C6 (3×10^{-2})	−1.8	1.4	40	29	0	26a
(10^{-3})	Me_2SO	*t*-$BuSNBu_4$ (0.1)	−1.8	0.3	60	0	0	26a
(10^{-2})	CH_3CN	CH_3SNBu_4 (0.1)	−1.9	1.7	5	75	0	26a
(10^{-2})	CH_3CN	$CNNEt_4$ (1.0)	−1.7	0.25	95	3	0	26a
4-bromobenzonitrile (10^{-2})	CH_3CN	$PhSNBu_4$ (0.1)	−2.1	0.2	80	10	4	26a
4-iodobenzonitrile (10^{-2})	CH_3CN	(0.1)	−1.7	1.5	20	80	0	26a
4-bromonaphthalene (10^{-2})	Me_2SO	(0.1)	−2.2	0.3	100	0	0	26a
(10^{-2})	CH_3CN	(0.1)	−2.2	1.2	32	40	0	26a
(10^{-2})	Me_2SO	$CNNEt_4$ (0.1)	−2.2	0.5	0	55	45	26a
4-bromoacetophenone (1.8×10^{-2})	CH_3CN (+10% H_2O)	$PhSNEt_4$	−1.7[b]	0.2	95		0	31
2-chloroquinoline (10^{-2})	Me_2SO	$PhSNBu_4$ (0.1)	−2.05	0.4	77	15	0	26b
(3.5×10^{-3})	Me_2SO	(6.10^{-2})	−1.43	0.10	96	4	0	27
2-chloroquinoline (1.55×10^{-2})	Me_2SO	$(EtO)_2POK$ (0.663)	programmed (see text)	0.01	100	0	0	29

[a] In V vs. Ag/Ag^+ (10^{-2} M) unless otherwise stated. [b] V vs. SCE.

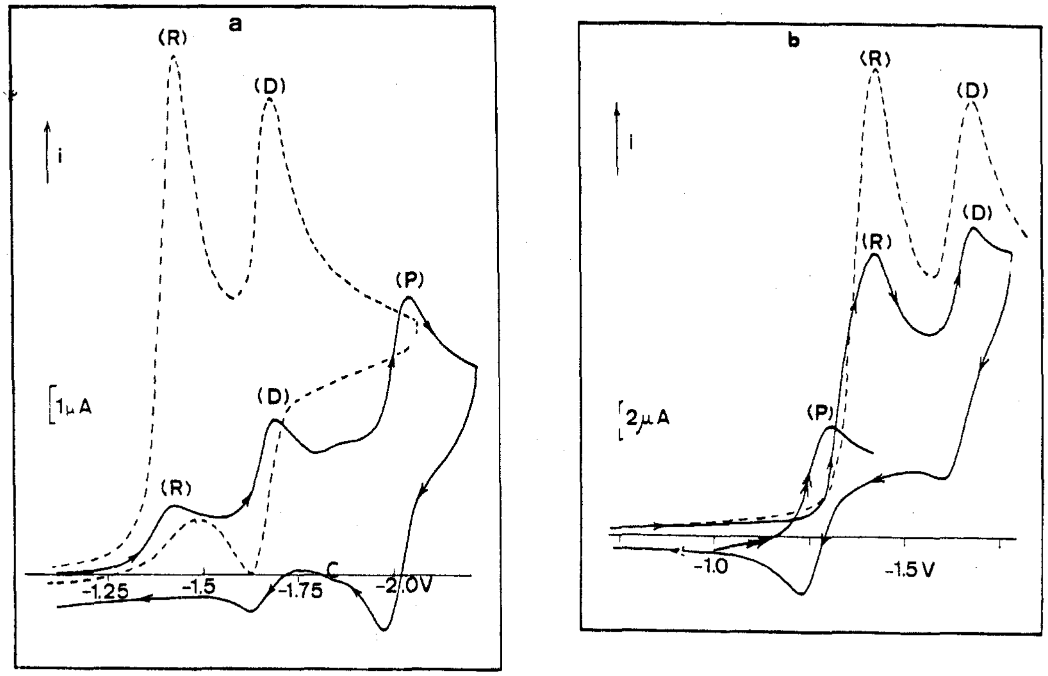

Figure 2. Cyclic voltammetry of 2-chloroquinoline in liquid NH_3 at −40 °C. Sweep rate 0.2 V s^{-1}.. (- -) Without nucleophile added, (—) in the presence of the nucleophile. (a) 1.75×10^{-3} M, 2.5×10^{-2} M $CH_3COCH^-_2$. (b) 3.3×10^{-3} M, 9.4×10^{-2} M $(EtO_2)PO^-$.

In the reverse case, e.g., with the 4-bromobenzophenone–cyanide system, the substitution product was partly obtained in the form of $ArNu^-\cdot$ which had to be independently reoxidized, either electrochemically or by exposure of the electrolyzed solution to air. It was, however, noted that the process has partial catalytic character despite the unfavorable potential relationship. In such a case, the system can even be completely catalytic, as in the reaction of 2-chloroquinoline with diethyl phosphite ion in liquid ammonia where a different strategy for the imposition of the electrode potential was followed. In every case, electrochemical inducement was shown to be effective by the fact that the substitution process fails to occur spontaneously within several hours while it takes on the order of 10 min as a maximum to go to completion in the electrochemical cell.

Rough estimates of substrate–nucleophile reactivity have been obtained for other systems by means of cyclic voltammetry. They derive from observation of how the cyclic voltammogram of the substrate changes upon addition of the nucleophile. Two typical examples, shown on Figure 2, concern the substitution of 2-chloroquinoline by acetone enolate and diethyl phosphite ions. Each of them corresponds to one of the two types of potential relationship represented in Figure 1. An additional wave, D, is visible; it is for the reduction of ArH into $ArH^-\cdot$, as verified by independent investigations of the ArH electrochemical reduction. Wave D features the formation of ArH by reductive cleavage of the carbon–halogen bond of the substrate as seen on the voltammogram of 2-chloroquinoline in the absence of nucleophile (dashed lines on Figure 2). When the nucleophile is added, the magnitudes of the three waves reflect the reactivity of the substrate–nucleophile system toward substitution: the lower waves R and D and the higher wave P, the more reactive the system. Three qualitative degrees of reactivity may thus be defined: "unreactive", corresponding to no appreciable change of the cyclic voltammogram upon addition of the nucleophile; "reactive", corresponding to a significant lowering of waves R and D and appearance of wave P; "very reactive", corresponding to spontaneous substitution or to bulk substitution after a few cycles. According to these criteria, 2-haloquinolines are *unreactive* with the anions CN^-, SCN^-, OH^-, PhO^-, $EtC(COOEt)_2^-$, $MeCONMe^-$, and $MeCONH^-$; *reactive* with PhS^-, p-$ClC_6H_4S^-$, $(EtO)_2PO^-$, $CH_3COCH_2^-$, and $PhCOCH_2^-$; and *very reactive* with CH_2CN^-, Ph_3C^-, and lutidine carbanion. Also, 1-iodonaphthalene is *reactive* with $(EtO)_2PO^-$.

These data and those in Table I show that the efficiency of nucleophiles is related to their "softness", as it is for the $S_{RN}1$ aromatic nucleophilic substitution reactions that occur spontaneously or under light or dissolved alkali metal stimulation.[24,32]

General Features of the Mechanism; Electrode and Solution Electron Transfers; Competing Reactions

The very fact that the substitution reaction is triggered by setting the potential at the reduction wave of the substrate is a strong argument in favor of the $S_{RN}1$ mechanism[24] for this reaction. Among the species resulting from this first electron transfer, the best candidate to be attacked by a nucleophile is the neutral radical $Ar\cdot$ formed upon cleavage of the initial anion radical. The formation of $Ar\cdot$ by such cleavage is well documented, and rate data have been obtained for a large number of aromatic halides by direct or indirect electrochemical methods.[33-37]

The mechanism of the electrochemical inducement would then involve the sequence of reactions 0–4. The situation thus resembles what occurs with similar substrate/nucleophile systems in substitutions stimulated by dissolved alkali metals in liquid ammonia.[24]

Two distinct advantages of the electrochemical approach are immediately apparent. First, one can adjust the reducing power of the stimulator by programming the electrode potential so as to trigger the substitution process without going to such negative values as to induce further reductions of the products. Second, evaluation of the catalytic character of the inducement process can be readily derived from the current characteristics revealed by cyclic voltammetry and from the amount of electricity passed for a given conversion in preparative scale electrolysis.

It is to be noted that the anion radical $ArNu^{-}\cdot$ formed by addition of the nucleophile to the neutral radical $Ar\cdot$ may be oxidized to the final substitution product competitively at the electrode (reaction 3) as well as in the solution by electron transfer to a substrate moleule (reaction 4). The second of these pathways is the same as in the chain propagation process for homogeneously stimulated reactions[24] while the first is specific for heterogeneous stimulation. Which of these two competitive modes of $ArNu^{-}\cdot$ reoxidation predominates is essentially a function of the rates of reactions 1 and 2. When these are large, $ArNu^{-}\cdot$ is formed at a short distance from the electrode. Mostly, the $ArNu^{-}\cdot$ can then diffuse back and be reoxidized at the electrode surface before encountering a substrate molecule to which to lose its electron. The heterogeneous reoxidation will then predominate over the homogeneous reoxidation. The opposite will tend to occur when the rates are small.

In cases in which the yield of substitution product approaches 100% and the amount of electricity required to induce the reaction tends toward zero, the $S_{RN}1$ mechanism as described by the (0)–(4) sequence thus appears as the likely route to substitution. One might seek to invoke radical–radical coupling as the key step instead of nucleophilic addition of Nu^- to $Ar\cdot$. It is indeed conceivable that the $Nu\cdot$ radical could be formed by electron transfer from $Ar\cdot$:

$$Nu^- + Ar\cdot \rightarrow Nu\cdot + Ar^-$$

$$Nu\cdot + Ar\cdot \rightarrow ArNu$$

However, this can be ruled out because the balanced equation for the electrochemically induced process would then be

$$ArX + e + 0.5Nu^- \rightarrow 0.5ArNu + 0.5Ar^- + X^-$$

and ArNu would be formed in only 50% yield after the passage of 1 faraday/mol of ArX consumed.

The preparative-scale results (Table I) show that the ArNu yield is sometimes significantly different from 100% and that the apparent number of electrons is far from zero in a number of cases. At the same time formation of a significant amount of the hydrogenolysis product, ArH, is observed. This points to the possibility that reduction of $Ar\cdot$ competes with the addition of Nu^- and thus with the substitution process. Two modes of $Ar\cdot$ reduction are conceivable. In an organic solvent (SH), H-atom abstraction may occur:

$$Ar\cdot + SH \rightarrow ArH + S\cdot \qquad (5)$$

Aryl σ radicals are indeed able to abstract a hydrogen atom from a wide variety of organic molecules containing C–H aliphatic bonds.[38] On the other hand, electron transfer to $Ar\cdot$ is generally easier than to the substrate ArX.[33,34,36] This implies that, at the potential of the ArX wave, $Ar\cdot$ can pick up one electron from the electrode:

$$Ar\cdot + e \rightleftarrows Ar^- \qquad (6)$$

It also follows that $ArX^{-}\cdot$ can concurrently transfer one

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electron to Ar· in the solution:

$$\mathrm{Ar\cdot} + \mathrm{ArX^{-}\cdot} \rightarrow \mathrm{Ar^{-}} + \mathrm{ArX} \qquad (7)$$

These reactions are completed by proton abstraction from the solvent or from residual water, leading to ArH.

Electrochemical control of the process again provides a convenient approach to analysis of the competition between substitution and Ar· reduction. This point has practically not been discussed for homogeneously stimulated systems[24] although the same side reactions should also interfere in this case. In this connection, it is noted that liquid ammonia is the solvent of choice for $S_{RN}1$ substitution,[24] presumably in part because of its ability to stabilize anionic nucleophiles and in part because it is a poor H-atom donor.[39-41]

Kinetics of Competition with Electron Transfer. Characteristic Rate Constants

The competition between substitution and electron transfer to Ar· is one of the most important mechanistic problem in $S_{RN}1$ reactions stimulated by an electron-donor agent such as an electrode or a dissolved metal. It is indeed a built-in problem in the sense that as soon as the substitution process is triggered by the presence of an electron source able to produce ArX· and then Ar·, there is at the same time the possibility for Ar· to be immediately destroyed by the electron source. The same device which induces the substitution process is able to kill it!

An important objective was thus to find experimental conditions in which no other side reactions interfere. This was achieved by using liquid ammonia as the solvent,[27,28] taking advantage of its poor H-atom donor ability.[39,42] In such conditions, reaction 5 can be neglected and the competition between substitution and hydrogenolysis of the ArX bond is completely within the reaction sequence (0) + (1) + (2) + (3) + (4) + (6) + (7). It is immediately apparent that the kinetic situation will be quite different when the electron transfer to Ar· occurs predominantly at the electrode (reaction 6) from when it occurs in solution (reaction 7). In the former case we deal with a competition between two first-order reactions ($\mathrm{Nu^-}$ is added in sufficient excess for pseudo-first-order kinetics to be achieved) while in the latter competition is between a first- and a second-order reaction.

A prerequisite for the analysis of this rather complex problem is a good understanding of the competition between heterogeneous (eq 6) and homogeneous (eq 7) electron transfer when reaction 2 and therefore reactions 3 and 4 are absent. This has been arrived at recently in the context of several electrochemical methods.[42-45] For present purposes, the main conclusion from these studies is that the competition between heterogeneous (ECE) and homogeneous (Disp) electron transfers in cyclic voltammetry is dependent upon the parameter.

$$p = k_D C^\circ (Fv/RT)^{1/2} k_1^{-3/2}$$

v is the sweep rate, C° is the substrate concentration, k_1 is the rate constant of the cleavage reaction 1, and k_D is the rate constant of reaction 7 which can be regarded as diffusion controlled since the standard potential of the $\mathrm{Ar\cdot/Ar^-}$ redox couple is much more positive than that of the $\mathrm{ArX/ArX^{-}\cdot}$ couple. Large values of p correspond to predominance of the Disp pathway and small values to the predominance of the ECE mechanism. The magnitude of the cleavage rate k_1 is of particular importance in this connection. If cleavage is fast, p is small and the Ar· radical is formed at a short distance from the electrode. It will diffuse back and pick up an electron from the electrode (eq 6) rather than from $\mathrm{ArX^{-}\cdot}$ (eq 7). Conversely, if cleavage is slow, p is large and the Ar· radical is formed far from the electrode where it will then pick up an electron from $\mathrm{ArX^{-}\cdot}$ before it has time to diffuse back to the electrode surface.

When, now, the nucleophile is added into the solution, a three-cornered competition, ECE–Disp–substitution, occurs. Its outcome depends[28] upon two kinetic parameters involving both rate constants and the operational parameters v, C°, $[\mathrm{Nu^-}]$:

$$\sigma = k_1/k_2[\mathrm{Nu^-}]$$

$$\rho = (k_D/k_1^{1/2}k_2)(C^\circ/[\mathrm{Nu^-}])(Fv/RT)^{1/2}$$

A kinetic zone diagram (Figure 3a) shows the regions of the log ρ–log σ plane where a limiting mechanism, ECE, Disp, or substitution, prevails over the others and how variations of the rate constants and of the operational parameters are predicted to shift the system from one zone to the other. This applies for cyclic voltammetry. However, a very similar zone diagram is obtained for preparative-scale electrolysis. The parameters are the same except that Fv/RT is replaced by D/δ^2 in the expression for ρ, D being the average diffusion coefficient of the various species and δ the diffusion layer thickness which mainly depends upon the stirring rate (the larger the stirring rate, the thinner the diffusion layer).

As expected, an increase of k_2 and $[\mathrm{Nu^-}]$ favors the substitution process whatever the type of electron transfer it competes with. The sweep rate (or the stirring rate) and the initial concentration have no effect in the ECE–subst case, which is appropriate in view of the first-order character of all steps of the reaction scheme. On the contrary, in the Disp–Subst case, the competition between a first-order (eq 2) and a second-order (eq 7) reaction leads to a dependence upon both v (or δ) and C°. C° and $[\mathrm{Nu^-}]$ then do not interfere separately but rather through their ratio. The effect of k_1 is particularly remarkable: starting from an ECE situation, raising k_1 will first lead to an increase and then to a decrease of the substitution ratio, ending with a Disp situation.

One now conceives how the paradox of the electrochemical inducement involving the simultaneous destruction of the active species Ar· can be resolved. In the ECE situation, $k_2[\mathrm{Nu^-}]$ has to be large enough for Ar· to be efficiently trapped by $\mathrm{Nu^-}$, preventing it from diffusing back to the electrode where it would be reduced. Therefore, $k_2[\mathrm{Nu^-}]$ must be larger the faster the cleavage of the ArX bond. Under Disp control, $k_2[\mathrm{Nu^-}]$ is opposed to k_D. A large value of k_1—not too large, however, so as to avoid coming back into the ECE

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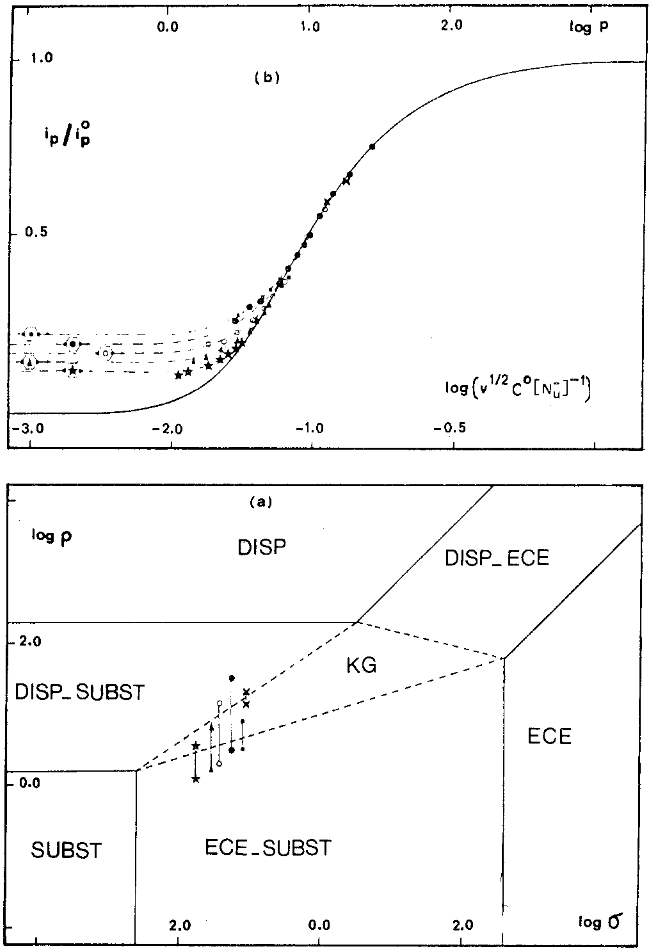

Figure 3. Competition between electrochemically catalyzed aromatic nucleophilic substitution and electron transfer to Ar· in the context of cyclic voltammetry. (a) Kinetic zone diagram. $\sigma = k_1/k_2[\mathrm{Nu}^-]$, $\rho = (k_D/k_1^{1/2}k_2)(C^\circ/[\mathrm{Nu}^-])(Fv/RT)^{1/2}$. (b) Reduction of 2-chloroquinoline in the presence of benzenethiolate in liquid NH_3 at −40 °C. Points, experimental data; each type of points represents data obtained with a given value of C° and Nu^- for different sweep rates: $C^\circ = 1.5 \times 10^{-3}$ M, $[\mathrm{Nu}^-] = 1.3 \times 10^{-2}$ (×), 1.54×10^{-2} M (■); $C^\circ = 2.65 \times 10^{-3}$ M, $[\mathrm{Nu}^-] = 2.12 \times 10^{-2}$ (●), 3.18×10^{-2} (○), 4.08×10^{-2} (▲), 6.62×10^{-2} (☆). i_p, i_p°, peak current in the presence and absence of nucleophile, respectively.

control—then favors substitution since it lowers the efficiency of the solution electron transfer (eq 7).

The kinetic zone diagram appears as a useful tool both for selecting the best experimental conditions, especially concentrations and stirring rates, for maximal substitution yield and for predicting how the yield will vary when passing from one substrate to another and from one nucleophile to another. Quantitative predictions would require k_1 and k_2 to be known, which is not generally the case, particularly for k_2. However qualitative predictions can be made, on the basis of intuitive knowledge of compared reactivity for the nucleophiles and for the cleavage of anion radicals (e.g., the leaving group ability). As regards k_1, more precise data can be derived from direct and indirect analysis of the electrochemical behavior of substrates in the absence of nucleophiles.[33-37]

A typical experimental illustration of the kinetics of the ECE–Disp–Subst process is given by the 2-chloroquinoline–benzenethiolate system as shown in Figure 3.[28] For most of the sweep rates and substrate and nucleophile concentrations, the observed kinetics correspond to a Disp–Subst competition (Figure 3b). At high substitution ratios the system shifts into ECE–Subst control (foot of the curves). The shift of the system from one control to the other is illustrated by the vertical lines on the kinetic zone diagram. In contrast, a pure ECE–Subst competition has been found for 2-iodoquinoline with the same nucleophile. This is expected from the cleavage being faster for the iodo than for the chloroquinoline radical anion.

The excellent fit of the observed kinetics with the theory provides definite and detailed evidence of the correctness of the $S_{RN}1$ mechanism in the framework of its competition with heterogeneous and homogeneous electron transfer. On the other hand, quantitative treatment of the kinetic data has allowed determination, for the first time, of rate constants for the addition of nucleophiles to aryl σ radicals (see Table II in ref 27). Cleavage rates of anion radicals that would have been difficult to obtain otherwise have also been derived in the same way.[27]

Competition with H-Atom Transfer

So far there have been no systematic quantitative studies of the competition of substitution with H-atom transfer comparable to what has been done for the competition with electron transfer.

The seriousness of H-atom transfer[46] as a side reaction lowering substitution efficiency can be qualitatively evaluated from data on preparative-scale electrolysis (Table I). For the 1-bromonaphthalene–PhS^- system, the substitution yield is lower in acetonitrile than in dimethyl sulfoxide because the former compound is a better H-atom donor than the latter.[47] Also, in the case of 4-bromobenzophenone reacting with PhSNa in the presence of a crown ether, the yield is less than with $\mathrm{PhSNBu_4}$, which may be related to the good H-atom donor ability of ethers.

Unusual Features of Cyclic Voltammograms. Potential Programming

Unusual cyclic voltammograms are frequently found with systems in which chemical reactions are electrochemically induced according to Scheme II. Two types of unusual behavior are observed. The first of these is the occurrence of a current dip at the foot of the $(P/P^{-}\cdot)$ wave in the case where the product is more difficult to reduce than the reactant.[30] Several examples of this phenomenon are given in Figure 1 of ref 29. The first reaction of any electrochemist confronted with such a phenomenon would be to relate it to passivation processes[48,49] or self-inhibition caused by reactant adsorption.[50,51] It has been shown[30] that these phenomena have nothing to do with reactant adsorption but are actually a reflect of the homogeneous catalytic process itself: as the electrode potential approaches the second wave the ECE–Subst process converts into a Disp–Subst process involving a more efficient substitution.

In the case where the product is easier to reduce than the reactant, another type of unusual voltammogram

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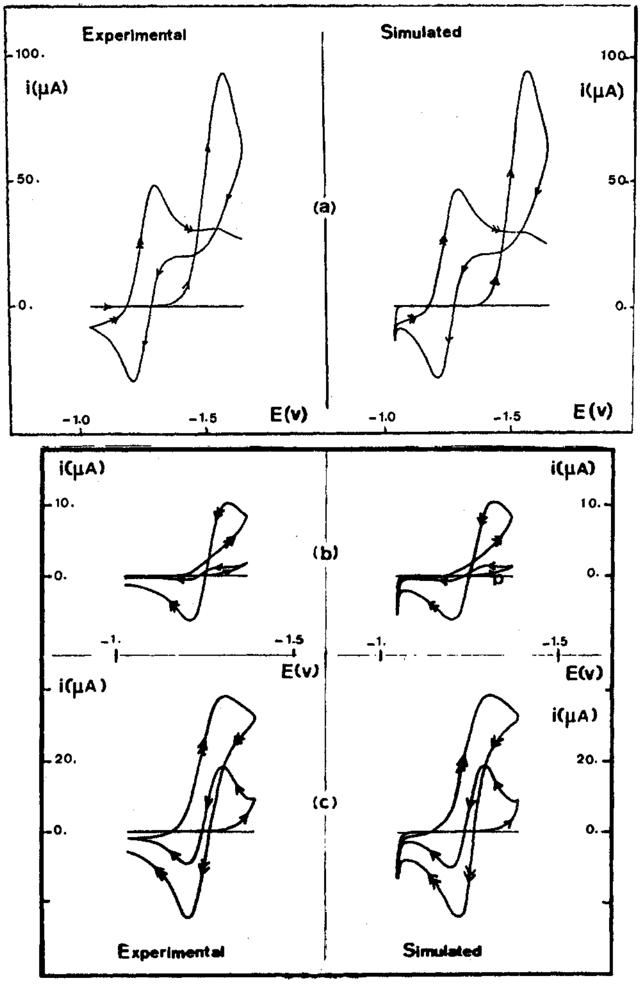

Figure 4. Experimental and simulated cyclic voltammograms of the electrochemical inducement of the substitution of 4-chlorobenzonitrile by potassium diethyl phosphite (0.663 M) in liquid NH_3 at −40 °C. (a) $C° = 1.55 \times 10^{-2}$ M, $v = 0.215$ V s^{-1}; (b) $C° = 1.08 \times 10^{-3}$ M, $v = 0.115$ V s^{-1}; (c) $C° = 1.55 \times 10^{-2}$ M, $v = 0.115$ V s^{-1}.

is observed.[26,27,29] It involves the crossing of the cathodic and anodic traces as shown on Figure 4a. This type of behavior can be obtained with ECE–Subst as well as with Disp–Subst system. Along the R cathodic wave, $P^{-\cdot}$ is formed through $R + e \rightleftarrows R^{-\cdot}$, $R^{-\cdot} \rightarrow P^{-\cdot}$. $P^{-\cdot}$ is electrochemically stable in this potential region. This is also true during the reverse scan as long as the potential has not crossed $E°_2$. $P^{-\cdot}$ therefore diffuses toward the solution, reacting with R which diffuses toward the electrode according to $P^{-\cdot} + R \rightleftarrows R^{-\cdot} + P$. The latter reaction is endergonic, but its coupling with $R^{-\cdot} \rightarrow P^{-\cdot}$ pulls it toward the right-hand side, resulting in the overall reaction $P^{-\cdot} + R \rightarrow P + P^{-\cdot}$. P is then reduced at the electrode, giving rise to a cathodic current which may result in trace crossing. A typical example of experimental and simulated curves is given in Figure 4a in the case of the substitution of 4-chlorobenzonitrile by diethyl phosphite ion in liquid NH_3.

With the same system, Figure 4b,c shows how the substitution can be induced by programming the potential scan so as to encompass only the $P/P^{-\cdot}$ wave. Thus, a minute concentration of $P^{-\cdot}$, produced by a vanishingly small amount of electricity, is able to trigger the substitution process. This was confirmed by a preparative-scale experiment[29] in which it was found that opening the circuit after a short induction period resulted in an excellent substitution yield (≃ 100%) with a very low electricity consumption (less than 0.01 faraday/mol). It thus appears that when the electrochemical stimulation is a priori noncatalytic ($E°_2 > E°_1$) it may be rendered catalytic by appropriate programming of the electrode potential.

Concluding Remarks

The preceding discussion of the electrochemical stimulation of aromatic nucleophilic substitution shows how electrons from an electrode can be advantageously employed to catalyze a chemical reaction. The possibility of adjusting and even programming the potential appears as particularly useful for the purpose of giving the stimulation a catalytic character and at the same time avoiding further reduction (or oxidation) of the desired product. On the other hand, the current potential curves obtained for such systems in the context of the usual electrochemical techniques, especially cyclic voltammetry, and their variations with operational parameters (concentrations, time scale), allow an easy qualitative estimation of the feasibility of the desired reaction and of the extent of side reactions. Quantitative treatment of these kinetic data renders possible an accurate determination of the reaction mechanism and the measurement of rate constants for key steps in the reaction sequence. Obtaining these data, which are difficult to gather otherwise, opens a route to the establishment of reactivity–structure relationships.

Few reactions have yet been tested in this respect. The use of techniques such as cyclic voltammetry for a rapid estimate of reactivities should facilitate the extension of electrochemical stimulation to other types of reactions both in the organic and inorganic fields. An obstacle may be the existence of large overpotentials for the electrochemical steps that induce the reaction. They may, however, be lowered by redox or chemical catalysis of these electrochemical steps.[52] One may thus envision the possibility of combining catalysis of electrochemical reactions and catalysis by electrochemistry to widen the scope of electrochemical inducement of chemical reactions. Another outcome of increased development of electrochemical stimulation concerns heterogeneous photocatalysis on semiconductors which indeed lies essentially on electrochemical grounds.[53]

I express my appreciation to those co-workers who have contributed to the work that I have discussed, Drs. C. Amatore and J. Pinson. The studies in liquid ammonia were carried out with the expert collaboration of Dr. A. Thiébault and J. Chaussard (Laboratoire de Chimie Analytique de l'ESPCI Paris). The work described in this paper was sponsored in part by the CNRS (Equipe de Recherche Associée 309 "Electrochimie Moléculaire").

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