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The Solvent as H-Atom Donor in Organic Electrochemical Reactions. Reduction of Aromatic Halides

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Abstract: The first step following the initial formation of the anion radical in the electrochemical reduction of aromatic halides is the cleavage of the C–X bond leading to the neutral Ar· radical. The latter species undergoes three concurrent reactions: H-atom abstraction from the solvent and electron transfer at the electrode and/or from the initial anion radical. The quantitative analysis of this threefold competition allows one to predict the effect of the intrinsic (rate constants) and operational (concentration, stirring rate, cell geometry) parameters. It is the basis on which the results of deuterium incorporation by deuterated water or solvent can be used as a tool to investigate the reaction mechanism and to determine the characteristic rate constants. This is illustrated by the study of the chloro, bromo, and iodo derivatives of three aromatic residues (9-anthryl, 1-naphthyl, and 4-cyanophenyl) in Me_2SO and acetonitrile. It is shown that the proposed reduction mechanism is indeed followed in each case and the degree of competition between the three concurrent steps can be evaluated. Using the values obtained independently (by cyclic voltammetry or redox catalysis) for the cleavage rate of the anion radicals of the chloro compounds, the corresponding rates for the bromo and iodo derivatives are determined as well as the rates of H-atom transfer to the three aromatic radicals and the magnitude of the corresponding deuterium isotope effects.

Introduction

The chemical interference of the solvent in the mechanisms of organic electrochemical reactions is classically thought to involve its acid–base and/or nucleophile–electrophile properties.

The anion radicals and species formed upon further reduction may abstract protons from the solvent or react on it insofar as it possesses an electrophilic character. Conversely, the cation radicals and further oxidized species formed upon oxidation may transfer a proton to the solvent or add a solvent molecule if it possesses a sufficient nucleophilic character. There has been consequently a continuous effort in the development of organic electrochemistry to select solvents of low acidity and electrophilicity for reductions and low basicity and nucleophilicity for oxidations. A first interest of this is the stabilization of the ion radicals resulting in a more facile approach of the reaction mechanisms. On the other hand, the use of an inert solvent with purposely designed addition of a nucleophile or an electrophile has opened up synthetic routes of great interest (e.g., reductive alkylation and carboxylation, anodic substitution).

The role of the solvent as H-atom donor has been considerably less investigated in the context of organic electrochemical reactions carried out in organic solvents. It is, however, anticipated that as soon as a neutral carbon radical is

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formed by acid–base or electrophilic–nucleophilic reaction of the starting ion radical it may abstract a hydrogen atom from the organic solvent. This is clearly the case in the reduction of aromatic halides since aryl radicals formed upon expulsion of the halogen from the initial anion radicals

$$\mathrm{ArX} + 1\mathrm{e} \rightleftarrows \mathrm{ArX}^{-} \qquad (0)$$

$$\mathrm{ArX}^{-}\cdot \xrightarrow{k_1} \mathrm{Ar}\cdot + \mathrm{X}^{-} \qquad (1)$$

are well known to be able to abstract an hydrogen atom from the organic solvents usually employed in reduction such as acetonitrile (ACN), dimethyl sulfoxide ($\mathrm{Me_2SO}$), and dimethylformamide:[1-3]

$$\mathrm{Ar}\cdot + \mathrm{SH} \xrightarrow{k_2} \mathrm{ArH} + \mathrm{S}\cdot \qquad (2)$$

Reaction 2 has indeed been postulated[4,15] to occur in the reduction of several aromatic halides in order to explain the experimental observation that the ArX reduction wave sometimes involves the exchange of less than the two electrons per molecule which would correspond to further electron-transfer reduction of Ar·:

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

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

followed by protonation of the Ar^- anion:

$$\mathrm{Ar}^{-} + \begin{cases} \mathrm{H_2O}\ (\text{residual}) & \qquad\qquad \mathrm{OH}^{-} \qquad (5a) \\ \mathrm{SH} & \rightarrow \mathrm{ArH} + \mathrm{S}^{-} \qquad (5b) \\ \mathrm{R'CH_2\overset{+}{N}R_3} & \qquad\qquad \mathrm{R'\bar{C}H\overset{+}{N}R_3} \qquad (5c) \end{cases}$$

However, the fate of the solvent radical S· has long remained unknown. It may dimerize

$$2\mathrm{S}\cdot \rightarrow \mathrm{S{-}S} \qquad (6)$$

and/or undergo an electrode or solution electron-transfer reduction

$$\mathrm{S}\cdot + 1\mathrm{e} \rightleftarrows \mathrm{S}^{-} \qquad (7)$$

$$\mathrm{S}\cdot + \mathrm{ArX}^{-}\cdot \rightarrow \mathrm{S}^{-} + \mathrm{ArX} \qquad (8)$$

since it is likely to be much easier to reduce than most of the aromatic halides. The simplest hypothesis that comes to mind in order to explain the tendency toward a one-electron exchange is to assume that reaction 6 is able to compete favorably with reactions 7 and/or 8. However, no S–S dimer has apparently been detected so far in the electrolysis products. Part of the riddle has been solved recently at the occasion of a detailed investigation of the reduction products of 4-bromobenzophenone in $\mathrm{Me_2SO}$.[14] It was shown that S^- is partly incorporated into the substrate by nucleophilic addition on the carbonyl group but also by nucleophilic substitution of the bromine atom. Such nucleophilic substitutions at an aromatic carbon by a soft nucleophile are now well documented[16] and it has been shown that they can be electrochemically induced.[17-19] The dips found on the plateau of the polarographic wave and on the descending branch of the cyclic voltammetric wave of several aromatic halides[14,19,20] may thus be related to these reactions since it has been shown that these phenomena are frequently encountered in electrochemically induced aromatic nucleophilic substitutions.[17-21] If reaction 2 were completely predominating over reactions 3 and/or 4 and if the substitution process

$$\mathrm{Ar}\cdot + \mathrm{S}^{-} \rightarrow \mathrm{ArS}^{-}$$

$$\mathrm{ArS}^{-}\cdot - 1\mathrm{e} \rightleftarrows \mathrm{ArS}$$

$$\mathrm{ArS}^{-}\cdot + \mathrm{ArX} \rightarrow \mathrm{ArS} + \mathrm{ArX}^{-}$$

were itself complete, the apparent number of electrons exchanged per molecule, n_{app}, would be 1. In this context, the observation that addition of water results in an increase of n_{app} leveling off at $n_{\mathrm{app}} = 2$ can be rationalized by the occurrence of the reaction

$$\mathrm{S}^{-} + \mathrm{H_2O} \rightarrow \mathrm{SH} + \mathrm{OH}^{-}$$

which renders S^- unavailable for the substitution process.

On the other hand, the amount of substitution will also depend upon the electrophilic character of the transient Ar· radical. This is anticipated to be less with unactivated aromatic halides than with those that bear an electron-withdrawing group such as $\mathrm{NO_2}$, RCO, etc. The former should therefore lead more easily to an uncomplicated $n_{\mathrm{app}} = 2$ behavior with 100% formation of ArH.

It is not, however, completely excluded that reaction 6 may be in some cases responsible for n_{app} being smaller than 2. Also, the possible formation of the Ar–Ar dimer should be taken into account. Small amounts of bipyrenyl and bianthranyl have indeed been detected in the reduction products of halopyrenes[13] and 9-haloanthracenes.[22] The interference of these two types of dimerization is expected to be dependent upon the electrolysis conditions (concentration, current density) and upon the nature of the haloaromatic through the magnitude of the decomposition rate of its anion radical.

The work reported hereafter deals with systems belonging to the large family of aromatic halides that are amenable to an $n_{\mathrm{app}} = 2$ – ArH = 100% behavior by addition of a small amount of water to the solution. Within this framework, the aim of the work was to carry out a detailed investigation of the competition between H-atom transfer from the solvent to Ar· (reaction 2) and electron-transfer reduction of Ar· either at the electrode (reaction 3) or in the solution (reaction 4), leading to quantitative conclusions. One of the outcomes of this study is intended to be the determination of the rate constants for the H-atom transfer reaction and for the cleavage of the initial anion radical.

Method of Investigation

The method is based upon the determination of the amount of deuterium replacing the halogen atom upon electrolysis in the presence of either 10% $\mathrm{D_2O}$ in the nondeuterated solvent or 10% $\mathrm{H_2O}$ in the perdeuterated solvent. It is assumed that water will provide hydrogen ions and no hydrogen atom while the organic solvent will act oppositely. That water is a negligible H-atom source as compared to organic solvents such as ACN and $\mathrm{Me_2SO}$ has been established beyond reasonable doubt. The validity of the assumption that the organic solvent provides a negligible amount of proton as compared to 10% water, although likely, is less obvious. It is known that protonation of aromatic hydrocarbon dianions by organic solvents is negligible as compared to water even in trace amount. This is shown by the fact that these dianions become stable toward protonation upon careful drying of the solvent, using activated alumina.[23] The Ar^- anions involved in the present case are, however, likely to be more basic than aromatic hydrocarbon dianions. If the $\mathrm{ArH/Ar^-}$ $\mathrm{p}K_\mathrm{a}$s were considerably more negative than those of the organic solvents, one could conceive that the protonation rates by water and by the organic solvent might both become close to the diffusion limit even though the $\mathrm{p}K_\mathrm{a}$ of the solvent is much less than that of water and the protonation rates by carbon acids are certainly much less than by oxygen acids. Consistency of the results obtained under this assumption will therefore have to be checked.

Under the two above assumptions, the amount of Ar^- formed by electron transfer to Ar·—concurrently to the conversion of the latter species into ArH through H-atom abstraction—is given by the amount of ArD obtained upon

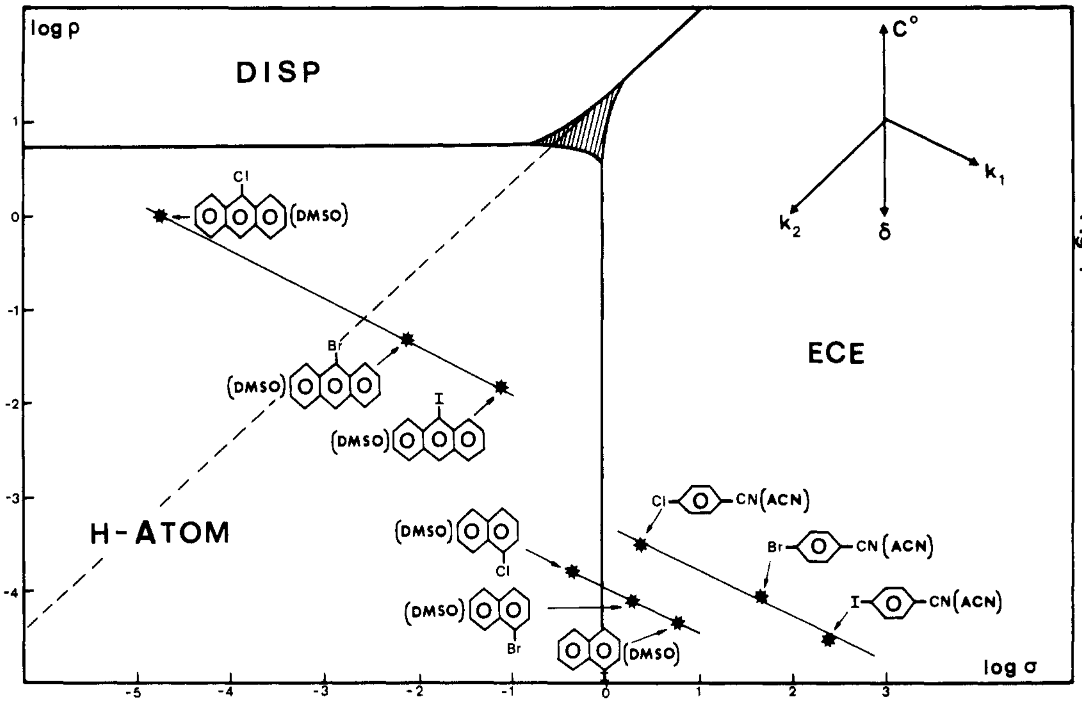


Figure 1. Kinetic zone diagram for the competition between H-atom transfer and electron transfer. The boundary lines correspond to the ArH_{et} and ArH_{at} fractions being 50% each.

electrolysis with 10% D_2O in the unlabeled solvent. Conversely, the amount of Ar· converted into ArD by D-atom transfer—concurrently to its electron-transfer reduction into Ar^-—will be given by the amount of ArD formed upon electrolysis in the deuterated solvent with 10% H_2O. Other proton or H-atom sources, besides the solvent and water, should be avoided. This led us to employ lithium perchlorate as supporting electrolyte instead of the usual tetraalkylammonium salts, the cation of which might act as both a proton and an H-atom source. Previous results[14,24,25] as well as those of a preliminary study of the present aromatic halides have indeed shown that deuterium incorporation may be different whether a lithium or a quaternary ammonium salt is used as supporting electrolyte. For the same reasons, the effect of residual water should be examined in the experiments with D_2O and unlabeled solvent.

In order to derive a quantitative description of the reaction mechanism from the measurements of deuterium incorporation one has to establish the relationships existing between the yields of ArH resulting from protonation of Ar^- (ArH_{et}) and of ArH resulting from H-atom transfer to Ar· (ArH_{at}) on one hand and the rate constants of the concurrent steps on the other. It must be clearly realized that the problem does not involve a direct competition between H atom and proton transfer but rather a competition between H-atom transfer (2) and electron transfer (3, 4) to Ar·. The latter reaction may occur at the electrode surface (3) and/or in the solution (4). There is therefore a threefold competition concerning species that are involved in a diffusional transfer from or to the electrode surface. Since, as will be seen later on, the starting chemical step (1) is fast, the formation of Ar· and its conversion into ArH by reactions 2–5 occur in a reaction layer adjacent to the electrode the thickness of which is certainly much smaller than that of the diffusion layer. A complete mathematical analysis of the polarization problem thus set has been carried out[26] leading to the following essential points.

The sum of the ArH fractions, ArH_{et} and ArH_{at}, is equal to one. Each of them depends upon two dimensionless parameters:

$$\sigma = k_1/k_2 \qquad \rho = (k_D/k_2k_1^{1/2})(C^0D^{1/2}/\delta)$$

D is the diffusion coefficient of ArX, C^0 is its initial concentration, and δ is the thickness of the diffusion layer. It is a decreasing function of the stirring rate. δ can be estimated experimentally for each particular electrolysis cell, from the time required to consume a given fraction of the starting material:

$$\delta = (SDt/V)/\log\,(C^0/C^t)$$

S is the surface area of the working electrode; V is the volume of solution; C^0 is the initial concentration; C^t is the concentration at time t; the C^0/C^t ratio can be determined by, e.g., cyclic voltammetry.

Since Ar· is assumed to be much easier to reduce than ArX, the rate of reaction 4 can be considered to be at the diffusion limit: $k_4 = k_D$. The competition between the three reactions is best represented by a kinetic zone diagram (Figure 1) featuring the various types of kinetic control in a log σ–log ρ plane with the boundary lines corresponding to a 50% yield for each route leading to ArH. Four zones thus appear on the diagram: "H atom" corresponds to $ArH_{at} > 50\%$, "DISP" to the ArH_{et} yielded by reaction 4 being larger than 50%, and "ECE" to the ArH_{et} yielded by reaction 3 being larger than 50%.[26] The hatched central zone corresponds to mixed control by all reactions 2–4. The competition between (2) and (4) depends upon the magnitude of ρ. σ plays a similar role for the competition between (2) and (3). The ECE-DISP competition, (3) vs. (4), depends upon[27,28]

$$p = \rho/\sigma = (k_D/k_1^{3/2})(C^0D^{1/2}/\delta)$$

For small values of p, the competition involves reactions 2 and 3 with negligible interference of reaction 4. For given values of C^0 and δ, this situation will be reached for high values of k_1. Indeed, when k_1 is large, Ar· is formed close to the electrode and has thus time to diffuse back and pick up one electron before encountering an $ArX^{-}\cdot$ molecule. The competition with reaction 2 then depends upon the magnitude of k_2:

$$ArH_{et} = \sigma^{1/2}/(1 + \sigma^{1/2}),\ ArH_{at} = 1/(1 + \sigma^{1/2}) \qquad (1)$$

The ArH fractions are then independent of the initial con-

Table I. Coulometry of the Aromatic Halides in the Presence of 10% Water

aromatic halide	electrolysis potential, V vs. SCE	solvent	n_{app}	Ar H%
1-chloronaphthalene	−2.00	Me_2SO	2.0	100
1-bromonaphthalene	−2.00	Me_2SO	2.0	100
1-iodonaphthalene	−1.60	Me_2SO	2.0	100
4-chlorobenzonitrile	−2.00	ACN	2.2	97
4-bromobenzonitrile	−2.00	ACN	2.0	97
4-iodobenzonitrile	−1.50	ACN	1.9	98
9-chloroanthracene	−1.75	Me_2SO	2.0	98
9-bromoanthracene	−1.65	Me_2SO	2.0	95
9-iodoanthracene	−1.60	Me_2SO	1.9	95

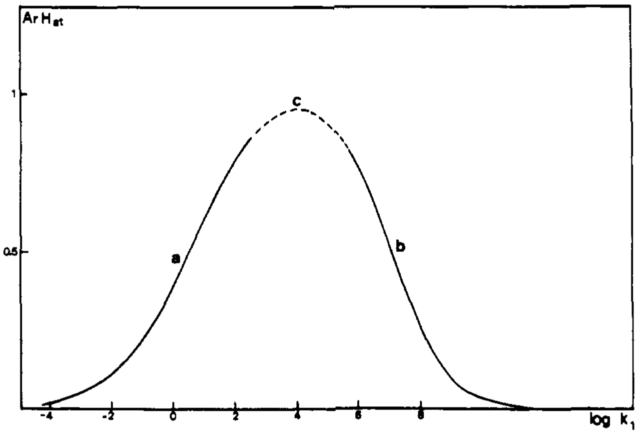


Figure 2. Effect of the anion radical cleavage rate on the yield in H-atom transfer product. $k_2 = 10^7\ s^{-1}$, $k_D = 5 \times 10^9\ M^{-1}\ s^{-1}$, $D = 10^{-5}\ cm^2\ s^{-1}$, $C^0 = 10^{-2}$ M, $\delta = 2.8 \times 10^{-3}$ cm.

centration and the diffusion layer thickness, i.e., from the stirring rate and the geometry of the cell.

Conversely, for large values of p, the competition involves reactions 2 and 4 with negligible interference of reaction 3. This situation tends to be met for small values of k_1. Ar· is then formed relatively far from the electrode. It will pick up an electron from $ArX^{-}\cdot$ before having time to diffuse back to the electrode. The competition between (2) and (4) will then be the more in favor of (2) the larger k_2 but also the larger k_1. This can be rationalized as follows. When k_1 increases, although remaining low enough for the ECE situation not to be reached, the concentration of $ArX^{-}\cdot$ in the reaction layer becomes smaller and smaller, which favors reaction 2 at the expense of reaction 4. ArH_{at} is then given by

$$ArH_{at} = (1/2^{1/2}p) \int_0^{2^{1/2}p} [\ln(1 + \eta)]\, d\eta/\eta \qquad (II)$$

The ArH fractions are now depending upon the initial ArX concentration and the diffusion layer thickness, i.e., upon the stirring rate and the cell geometry.

In both the "H-atom/ECE" and "H-atom/DISP" limiting situations the yields in deuterium incorporation give access to information regarding the rate constants. In the first case, σ, i.e., the ratio k_1/k_2, can be derived using eq I. In the second, p can be derived using eq II, which leads, knowing C^0 and δ, to $k_1^{1/2}k_2$. In a series of haloaromatics involving the same Ar and different X, independent determination of k_1 for one ArX will thus lead to the determination of k_2 and then of k_1 for the other ArX. It is noted that k_2 features H-atom transfer from the solvent in the 10% D_2O-solvent experiments and D atom transfer from the perdeuterated solvent in the other series of experiments. Comparison between these two types of results will thus give access to the deuterium isotope effect of the H-atom transfer reaction.

The arrows in Figure 1 show how the system will shift from one limiting kinetic control to the other. As expected an increase of k_2 will favor reaction 2 in all cases. The effect of k_1 is more subtle: an increase of k_1 first increases the efficiency of reaction 2 at the expense of reaction 4 and then decreases it to the benefit of reaction 3 as shown in Figure 2. This situation may be found when passing from Cl to Br and to I with the same Ar since k_1 is known to increase along this sequence.

There have been several previous studies of deuterium incorporation upon reductive electrolysis of aromatic halides.[11,13,14,24,25] None of them, however, provides a systematic investigation of the reaction mechanism using deuterium incorporation as a tool. The previous investigations regarding iodoanisoles and toluene[24] and halonaphthalenes[11] had more a synthetic than a mechanistic aim. The possible interference of the solution electron transfer (4) was not considered in the previous study[13] of a series of halopyrenes, benzophenones, fluorenes, 4-chlorostyrylpyridines, and 4'-methoxybenzaniline carried out in the presence of tetrapropylammonium perchlorate as supporting electrolyte. It is noted that the total yield of ArH is very significantly lower than 100% in most cases. In the case of 4-bromobenzophenone the H(D)-atom transfer reaction to Ar· largely predominates over electron transfer through either (3) or (4) in DMF,[13] ACN,[14] and Me_2SO[14] both with tetraalkylammonium[13,14] and lithium[14] salts as supporting electrolyte. In a recent study of iodobenzene reduction in DMF,[25] the eventual competition of H-atom transfer from the solvent was not taken into account. This might be justified according to the above discussion, given the fact that k_1 is then certainly very high, which would result in reaction 3 predominating over reactions 2 and 4. Since the exact value of k_1 is not known H-atom transfer from either the solvent or the tetraalkylammonium cations cannot, however, be completely excluded. The possible interference of spatial concentration effects should also be taken into account since the reaction layer thickness may well be on the same order as that of the diffuse double layer.

Results and Discussion

All the aromatic halides studied in the present work gave rise upon electrolysis in the presence of 10% H_2O to an apparent number of electrons practically equal to 2 and a yield of ArH close to 100% (Table I). With the exception of 9-chloroanthracene all the aromatic halides listed in Table I show a completely irreversible behavior in cyclic voltammetry. In the former case reversibility was reached at 10 V s^{-1} in Me_2SO. The rate constant, k_1, for the decomposition of the anion radical of 9-chloroanthracene could then be evaluated by this technique leading to the results reported in Table IV. For the other aromatic halides k_1 is thus larger than 10^4–10^5 s^{-1}. A certain number of k_1 values could, however, be determined using the redox catalysis method leading to the results reported in Table IV. A detailed account of the application of the redox catalysis method to the determination of the lifetimes of the anion radicals for these aromatic halides is given elsewhere.[28] The deuterium incorporation results are given in Table II.

1-Halonaphthalenes in Me_2SO. The deuterium incorporation from D_2O increases in the sequence Cl, Br, I and the deuterium incorporation from CD_3SOCD_3 decreases in the same order as expected for an H-atom/ECE competition with k_1 increasing from Cl to Br and I. That the electron transfer to Ar· essentially occurs at the electrode with negligible interference of reaction 4 is further substantiated by the value of k_1 for the chloro derivative as found by the redox catalysis method (Table IV).[28] Taking $k_D = 5 \times 10^9\ M^{-1}\ s^{-1}$, $D = 10^{-5}\ cm^2\ s^{-1}$, $C^0 = 2 \times 10^{-2}$ M, and $\delta = 10^{-3}$ cm then leads to $p = 9 \times 10^{-4}$.

Table II. Deuterium-Incorporation Experiments[a]

aromatic halide	solvent	water 0%	ArD	run
1-chloronaphthalene	CH_3SOCH_3	D_2O	0.40	1
	CD_3SOCD_3	H_2O	0.33	2
1-bromonaphthalene	CH_3SOCH_3	D_2O	0.56	3
	CD_3SOCD_3	H_2O	0.21	4
1-iodonaphthalene	CH_3SOCH_3	D_2O	0.66	5
	CD_3SOCD_3	H_2O	0.11	6
	CD_3SOCD_3	D_2O	0.96	7
	CH_3CN	D_2O	0.89	8*
4-chlorobenzonitrile	CH_3CN	D_2O	0.58	9
	CD_3CN	H_2O	0.14	10
	CD_3CN	D_2O	0.93	11
4-bromobenzonitrile	CH_3CN	D_2O	0.82	12
	CD_3CN	H_2O	0.04	13
4-iodobenzonitrile	CH_3CN	D_2O	0.89	14
	CD_3CN	H_2O	0.02	15
	CD_3CN	D_2O	0.94	16
9-chloroanthracene	CH_3SOCH_3	D_2O	0.21	17
	CH_3SOCH_3	D_2O	0.26	18*
	CD_3SOCD_3	H_2O	0.39	19*
	CH_3CN	D_2O	0.08	20
9-bromoanthracene	CH_3SOCH_3	D_2O	0.08	21
	CH_3CN	D_2O	0.07	22
9-iodoanthracene	CH_3SOCH_3	D_2O	0.21	23
	CH_3CN	D_2O	0.35	24

[a] Concentration of substrate $C^0 = 10^{-2}$ M except for the runs labeled with an asterisk ($C^0 = 2 \times 10^{-2}$ M). The electrolysis potentials were the same as in Table I.

This implies that the formation of Ar^- by reaction 4 would be less than 10^{-3} the formation of Ar^- by reaction 3. The same a fortiori holds for bromo- and iodonaphthalene, for which k_1 is larger than for the chloro derivative. The deuteration data can therefore be treated in the context of the H-atom/ECE competition for all three compounds.

Let us first correct the data for the effect of residual water. It was noted that the deuterium incorporation in an electrolysis of iodonaphthalene in Me_2SO with 5% H_2O and 5% D_2O is approximately half that obtained in run 5 (Table II) showing that the deuterium isotope effect is negligible in the protonation/deuteration reaction in agreement with previous results.[24] The effect of residual water is visible in run 7 (Table II) from the fact that deuterium incorporation is 96% instead of 100%. Thus

$$[H_2O]/([H_2O] + [D_2O]) = 0.04$$

and therefore $[H_2O] \simeq 0.4\%$, which is close to the amount of residual water currently found by Karl Fischer titration in the electrolysis solution where no special care was taken to dry the solvent and prevent water dissolution from the purging nitrogen stream.

From the results of runs 1, 3, and 5 corrected for the effect of residual water as determined above and from those of runs 2, 4, and 6 one obtains the following data by application of eq 1:

	k_1/k_2^H	k_1/k_2^D	k_1^{rel} (av)	k_2^H/k_2^D
1-chloronaphthalene	0.51	4.1	1	8
1-bromonaphthalene	1.95	14.2	3.6 ± 0.2	7
1-iodonaphthalene	4.8	65.5	12 ± 3	13

where k_1^{rel} is the rate constant for the decomposition of the anion radical relative to that for the chloro derivative. Starting from the k_1 value for the latter compound determined by the redox catalysis method[28] the absolute rates are finally obtained (Table IV). The isotopic effect for the H(D)-atom abstraction reaction k_2^H/k_2^D is found as satisfactorily constant in view of the accuracy of the deuterium incorporation measurements.

Table III. 9-Chloroanthracene in Me_2SO. H-Atom/DISP Competition as a Function of the Initial Concentration

C^0, mM	ArH_{et} fraction[a]	δ, cm	ρ	$\rho\delta/C^0 = k_D D^{1/2}/k_1^{1/2}k_2$	k_2, s^{-1}
20	0.27	2.4×10^{-3}	1.32	0.16	8.1×10^6
10	0.22	1.4×10^{-3}	0.95	0.14	9.2×10^6
5	0.16	1.5×10^{-3}	0.58	0.17	7.6×10^6
2	0.07	2.8×10^{-3}	0.23	0.29	4.5×10^6

[a] Corrected for the effect of residual water.

4-Halobenzonitriles provide a second example of a H-atom/ECE competition. In ACN, the deuterium incorporation from D_2O increases monotonically from Cl to Br and I and the deuterium incorporation decreases in the same sequence (Table II). The value of k_1 for 4-chlorobenzonitrile is higher than for 1-chloronaphthalene (Table IV). The contribution of the solution electron transfer (4) is therefore certainly negligible. This again holds a fortiori for the 4-bromo- and iodobenzonitriles. Runs 11 and 16 (Table II) show that the effect of residual water corresponds to a concentration of 0.065%. The same treatment of data (runs 9, 12, 14 and 10, 13, 15) as for the 1-halonaphthalenes leads to the following results:

	k_1/k_2^H	k_1/k_2^D	k_1^{rel} (av)	k_2^H/k_2^D
4-chlorobenzonitrile	2.9	41	1	14
4-bromobenzonitrile	47	576	15 ± 1	12
4-iodobenzonitrile	259	4312	97 ± 9	16

The absolute values of k_1 for the bromo and iodo derivatives as derived from k_1^{rel} and the k_1 value for the chloro compound obtained by redox catalysis[28] are given in Table IV. The isotopic deuterium effect is again found as satisfactorily constant.

9-Chloroanthracene is anticipated to give rise to an H-atom/DISP competition. The anion radical decomposes indeed rather slowly: $k_1 = 150\ s^{-1}$ in Me_2SO as determined by cyclic voltammetry. The parameter p featuring the ECE-DISP competition is thus $p = 8606$ taking for δ 10^{-2} cm, which is a maximal value for currently used electrochemical cells. The formation of Ar^- from electrode reduction of $Ar\cdot$ is therefore negligible as compared to the electron transfer from $ArX^-\cdot$.[29] For such a system, it is expected that the H-atom/DISP competition will depend upon the initial substrate concentration, H-atom transfer being favored at the expense of electron transfer by a decrease of C^0. This is what was indeed found in the series of experiments reported in Table III, where the initial concentration was varied from 2 to 20 mM. ρ was evaluated for each concentration using the working curve[26] giving ArH_{et} as a function of ρ (eq 11). The quantity $\rho\delta/C^0 = k_D D^{1/2}/k_1^{1/2}k_2$ is found to be satisfactorily constant with the exception of the experiment at the lowest concentration which corresponds to a very small amount of ArH_{et} and therefore to a poor accuracy on the determination of ρ. This shows that the experimental results do follow the predicted kinetic behavior for an H-atom/DISP competition. Taking $k_D = 5 \times 10^9\ M^{-1}\ s^{-1}$, $D = 10^{-5}\ cm^2\ s^{-1}$, and $k_1 = 150\ s^{-1}$, $k_2^H = 8.5 \times 10^6\ s^{-1}$ as an average value for the first three experiments. It is clearly seen that the initial concentration can be used for such H-atom/DISP systems as an operational parameter to shift the competition ratio toward values where the yield of ArH_{et} is significantly different from either 0 or 1 so as to meet a reasonable accuracy in rate determination. A similar treatment of the data obtained with CD_3SOCD_3 with 10% H_2O (run 19 in Table II) leads to $k_2^D = 1.4 \times 10^6\ s^{-1}$.

The 9-haloanthracene series provides an illustration of the transition between an H-atom/DISP and an H-atom/ECE situation. Comparison between runs 17, 21, and 23 (Table II) shows that the ArH_{et} yield first decreases and then increases when passing from Cl to Br and to I as predicted theoretically

Table IV. C-X Cleavage Rate Constants of the ArX Anion Radicals

		k_1, s^{-1}	
compd	solvent	from cyclic voltammetry (a) or redox catalysis (b)	from deuterium incorporation experiments[a]
9-chloro-anthracene	Me_2SO	(a) 1.5×10^2	
	ACN	(a) 2.6×10^2	
9-bromo-anthracene	Me_2SO	(b) 3×10^5	$7. \times 10^4$
	ACN		1.5×10^5
9-iodo-anthracene	Me_2SO		$7. \times 10^5$
	ACN		$6. \times 10^6$
1-chloro-naphthalene	Me_2SO	(b) $5. \times 10^7$	
1-bromo-naphthalene	Me_2SO	(b) $3. \times 10^8$	$2. \times 10^8$
1-iodo-naphthalene	Me_2SO		$6. \times 10^8$
	ACN		$4. \times 10^{10}$
4-chloro-benzonitrile	ACN	(b) $5. \times 10^8$	
4-bromo-benzonitrile	ACN		$1. \times 10^{10}$
4-iodo-benzonitrile	ACN		$5. \times 10^{10}$

[a] Deuterium incorporation measurements lead to $k_1^{\mathrm{ArX}/=\mathrm{Cl}}/k_1^{\mathrm{ArCl}}$; k_1^{ArCl} is given by the cyclic voltammetry or redox catalysis data.

(Figure 2). Within an H-atom/DISP competition, an increase of k_1 leads to a decrease of ArH_{et} while the variation is completely reversed in the case of an H-atom/ECE competition. It can thus be stated that the type of competition changes from DISP to ECE when going from Cl to I. The location of the bromo derivative can be derived from the effect of concentration on the ArD yield upon electrolysis in Me_2SO with 10% D_2O:

C^0, mM	ArD
2	0.08
5	0.07
10	0.08

These data show that 9-bromoanthracene reduction involves an H-atom/ECE competition with H-atom abstraction being predominant over electrode reduction. Another piece of evidence pointing to the same conclusion is the fact that k_1 would be equal to 10^3 s^{-1} if an H-atom/DISP competition were assumed to occur. This figure is in complete disagreement with the observation that the cyclic voltammogram of 9-bromoanthracene does not exhibit any reversibility up to sweep rates of several thousands volts per second. The competition becomes less in favor of H-atom transfer when passing to the iodo derivative. The rate-constant ratios can then be determined for these two compounds from the data of runs 21 and 23 (Table II) using eq I as in the case of the halonaphthalenes and benzonitriles which leads to k_1 using the value found for k_2^H in the case of 9-chloroanthracene.

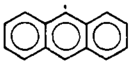
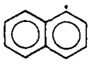
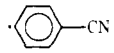
	k_1/k_2^H	k_1, s^{-1}
9-bromoanthracene	0.0084	7.1 10^4
9-iodoanthracene	0.080	6.8 10^5

Solvent Effects. The deuterium-incorporation measurements with 10% D_2O in the unlabeled solvent were repeated with acetonitrile in the 9-haloanthracene series (runs 20, 22, and 24 in Table II) and for 1-iodonaphthalene (run 8). For 9-chloroanthracene which involves an H-atom/DISP competition, the decrease in ArH_{et} when passing from Me_2SO to ACN reflects a decrease of ρ caused by an increase of both k_1 (see Table IV, third column) and k_2^H. The ratio of the H-atom transfer rate constants is found as

$$k_2^{\mathrm{H,ACN}}/k_2^{\mathrm{H,Me_2SO}} = 2.3$$

which is very close to the previously determined value for the phenyl radical.[2] For 9-bromoanthracene, which involves an H-atom/ECE competition, the increase in k_1 is not very different from the increase in k_2^H as can be derived from the fact that the ArH_{et} yield is about the same in both solvents. For 9-iodoanthracene the increase in k_1 from Me_2SO to ACN is larger. In the case of 1-iodonaphthalene it is not possible to exactly determine k_1 since the $k_2^{\mathrm{H,ACN}}/k_2^{\mathrm{H,Me_2SO}}$ ratio has not been measured for the naphthyl radical. Assuming that it is close to 2 for the phenyl and the anthryl radical leads, however, to an estimation of k_1 is this case. The values of k_1 in ACN as computed from the above data are listed in Table IV.

Table V. H(D) Atom Transfer Rate Constants

Ar·	solvent	k_2^H, s^{-1}	k_2^D, s^{-1}	k_2^H/k_2^D
	Me_2SO ACN	8.5×10^6 $2. \times 10^7$	1.5×10^6	6
	Me_2SO	$1. \times 10^8$	1.5×10^7	8
	ACN	$4. \times 10^7$	$3. \times 10^6$	14

C-X Cleavage Rate Constants of the ArX Anion Radicals. The rate constants obtained from the preceding deuterium-incorporation experiments starting from the value derived for the chloro derivative by cyclic voltammetry or redox catalysis are summarized in Table IV. For two cases, 9-bromoanthracene and 1-bromonaphthalene in Me_2SO, the results obtained by the deuteration and the redox catalysis methods can be compared. It is seen that the agreement is satisfactory for the latter compound while it is not very good for the former. It must, however, be borne in mind that the determination regarding 9-bromoanthracene was based upon a very low deuterium incorporation (run 21 in Table II), which results in a rather poor accuracy on k_1. It is noted that the deuteration method is able to provide the estimation of lifetimes of extremely unstable ArX anion radicals down to the 0.1-ns time range. For such fast processes the layer where the cleavage reaction occurs is extremely narrow. For, e.g., $k_1 = 10^{10}$ s^{-1} its thickness is on the order of 3 Å, i.e., on the order of molecular size. In such conditions, the cleavage reaction is likely to possess a surface character rather than a volume character. It follows that the determination of k_1 for 4-bromo- and iodobenzonitriles is certainly imprecise. Another reason for this is the fact that the deuterium incorporation ratios are very close to either 100 (10% D_2O-CH_3CN) or 0% (10% H_2O-CD_3CN). It is apparent from the results given in Table IV that there is a definite trend for the cleavage rate of the ArX anion radicals to increase when passing from Me_2SO to ACN. The difference appears as being higher the faster the cleavage.

H-Atom Transfer Rate Constants. The H and D atom abstraction rate constants obtained from the deuterium incorporation experiments carried out for the chloro derivatives using the values of k_1 determined by cyclic voltammetry or redox catalysis are summarized in Table V. It is noted that the k_2 values thus determined are not likely to be indirectly affected by double-layer effects on k_1, since they are based on the k_1 values for the chloro derivatives, which are less than 10^8 s^{-1}, corresponding to a reaction layer thickness larger than 30 Å. There is a remarkable paucity of data in the literature regarding the determination of absolute values for the H-atom transfers to aryl radicals. It has been estimated that the rate constant of the reaction

$$\mathrm{Ph\cdot + CH_3 - Ph}$$

is on the order of 3×10^6 M s^{-1},[30] which would lead to a value of ca. 10^6 M^{-1} s^{-1} for ACN,[2] i.e., about 2×10^7 s^{-1} for the first-order rate constant. Starting from a pulse radiolysis determination of the Ph· + CH_3OH reaction[31] the first-order rate constant would be 3×10^6 s^{-1}. It is not possible to derive from the existing data a reliable value for the Ar·'s studied here. For PhCN, one could think to use the Hammett correlations previously reported.[3] They, however, concern ratios between hydrogen and chlorine atom abstraction rates, both of these being able to vary with the structure of Ar·. Clearly more absolute rate data should be available before any structure-reactivity correlation could be attempted.

The deuterium isotope kinetic effects found in the present study (last column of Table V) are of the same order of magnitude as already reported for similar reactions.[31]

The Solvent as a Possible Proton Source Competing with Water. If the pK_a of the ArH/Ar couple were considerably higher than that of the SH/S^-, one could conceive that, besides water, the solvent could interfere in the protonation of Ar^-. In such a situation, the interference of H transfer in the 10% D_2O-unlabeled solvent experiments as well as that of D transfer in the 10% H_2O-deuterated solvent experiment would be overestimated by the above treatment. This overestimation would clearly be larger in the latter than in the former case resulting in a rapidly increasing underestimation of the deuterium isotope effect. Since the values found in the present work are already somewhat larger than what has been previously found for similar reactions[31] it follows that the interference of the solvent in the protonation of Ar^- is likely to be negligible as compared to 10% water. In other words, the difference in pK_a between the ArH/Ar^- and SH/S^- couples is probably not sufficient to overcome the intrinsic slowness of protonation by a CH acid.

Conclusion

The above results and discussion demonstrate the importance of the role played by organic solvents as H-atom donors in the electrochemical reaction of aromatic halides. A similar situation is likely to exist for other organic electrochemical reactions as soon as an aryl radical or another H-scavenging radical is produced upon chemical transformation of the initially formed ion radical. The competition between H· and H^+ transfer is not a direct one. It actually occurs through the competition between H-atom and electron transfer to the secondary radical. The latter pathway involves concurrently the electrode and the initial ion radical as electron sources. In the first case, the competition between H-atom and electron transfer is independent from the operational parameters, i.e., the initial concentration, the stirring rate, and the volume to surface ratio of the cell. These factors do influence the competition in the second case. Among the intrinsic factors, the cleavage rate of the initial anion radical is the most important one since it largely varies with the structure of the substrate while the H-atom transfer rates, although dependent upon the structure of Ar· and the nature of the solvent, vary in a much less extended range. The effect of these two factors on the competition between H-atom transfer and the two types of electron transfer is illustrated in Figure 1 by the location of the points representing each of the aromatic halides studied in this work on the kinetic zone diagram. The quantitative kinetic analysis of the competition between H-atom and electron transfer not only demonstrates the proposed mechanism, but it also provides a method for deriving from deuterium incorporation experiments two series of rate data. The first of these concerns the cleavage of the aromatic halide anion radical. Relative rate constants are thus obtained which can be converted into absolute values as soon as one member of the halogen series has been characterized by an independent method, e.g., cyclic voltammetry or redox catalysis. Another outcome of the method is the determination of H-atom transfer absolute rate constants, again using independently measured cleavage rates of the initial anion radical.

Experimental Section

Electrochemical Instrumentation and Procedures. Instrumentation and procedures for polarography and cyclic voltammetry have been described elsewhere.[32,33] Electrolyses were performed with a Tacussel Asa 100 potentiostat and a Tacussel IG5 integrator, a milliammeter was placed with the integrator in the circuit of the counterelectrode, and a voltmeter was used to check the potential between the working and the reference electrode. The reference was a Ag/Ag^+ 0.01 M electrode in the solvent used. Two different cells were used for the electrolysis: the first one has a volume of 50 mL, the working electrode is a 30-cm^2 mercury pool, the counterelectrode is a platinum wire separated from the cathodic compartment by a no. 4 sintered disk or a Nafion 125 membrane; the second cell used with deuterated solvents has a volume of 10 mL and the working electrode is a 6-cm^2 mercury pool.

The deuterium contents were measured by mass spectrometry with a Hitachi Perkin-Elmer RMU6E mass spectrometer operated at low ionization energy (5 eV). The spectra were recorded by M. Brun (Laboratoire de Spectrochimie Moléculaire, Université P et M. Curie). The spectra only show the M and M + 1 peaks. The deuterium content is given by the ratio (SM + 1)/[(SM + 1) + SM] of the peak areas after correction of area of the M + 1 peak for the ^{14}C natural isotopic abundance corresponding to the M peak. The deuterium contents are reproducible within ±1%.

Chemicals. ACN was distilled before use on calcium hydride. Me_2SO was purchased from SNPA (pharmaceutical quality) and used without further purification. The deuterated solvents were obtained from Merck and had a deuterium content higher than 99%. Deuterated water had a deuterium content of 99.75%. The products were of commercial origin except 9-iodo- and 9-fluoroanthracene, which were kindly provided by Dr. O. Hammerich (University of Copenhagen).

Isolation of Products. Benzonitrile obtained through the electrolysis of its halogenated derivatives in ACN is isolated in the following way. The electrolyzed solution is distilled at atmospheric pressure and 76 °C, the residue is treated with water and benzene, the benzenic layer is recovered in a conical tube and slowly evaporated, and benzonitrile is then analyzed by mass spectrometry.

When halonaphthalenes are electrolyzed in ACN, naphthalene is recovered by vacuum evaporation of the solvent and then washed with water. When the electrolyses are carried out in Me_2SO, naphthalene is precipitated with an excess of water and then extracted with ether. The ether layer is then evaporated, and naphthalene is dried and analyzed.

Anthracene is recovered both from Me_2SO and ACN by vacuum distillation of the solvent; the residue is washed with water and dried before analysis.

It was checked that no H/D exchange between the deuterated solvent and water takes place under the basic conditions of the cathodic compartment by analyzing the solvent at the end of the electrolysis by NMR.

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Electrolytic Reduction of 1,4-Dihalonorbornanes at Mercury Electrodes in Dimethylformamide. Evidence for [2.2.1]Propellane as an Intermediate

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Abstract: Low-temperature (−34 °C) electrolytic reduction of 1,4-dibromonorbornane at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates yields norbornane, bis(1-norbornyl)mercury, and 1,1′-binorbornyl; reduction of 1,4-diiodonorbornane results in the same three products along with 1-iodonorbornane and other minor species. At potentials for which the mass balance is 100%, norbornane and bis(1-norbornyl)mercury account for 98% of the electrolysis products and the coulometric *n* value is precisely three. When tetramethylammonium perchlorate is utilized as the supporting electrolyte at −34 °C, there is a range of potentials over which a pronounced polarographic current minimum appears; this low-temperature minimum is attributed to adsorption upon the electrode of complex species consisting of tetramethylammonium cations and halide ions. Three key observations suggest that [2.2.1]propellane is an intermediate in the electrochemical reduction of the 1,4-dihalonorbornanes: (1) norbornane is derived from 1,4-dihalonorbornane via a three-electron process which does not involve 1-halonorbornane as intermediate; (2) bis(1-norbornyl)mercury is produced by electrolytic reduction of 1,4-dihalonorbornane but not by reduction of 1-halonorbornane; and (3) a species apparently obtained by two-electron reduction of 1,4-dihalonorbornanes is capable of undergoing oligomerization. A polarographic wave seemingly attributable to reduction of [2.2.1]propellane is observed.

Electrochemical preparation of a propellane was first accomplished by Rifi,[1] who obtained [3.2.1]propellane by reduction of 1,5-dibromobicyclo[3.2.1]octane at a mercury pool cathode in dimethylformamide containing tetra-*n*-butylammonium perchlorate. In subsequent work, Wiberg and his collaborators[2,3] have attempted to electrosynthesize both [2.2.2]propellane and [2.2.1]propellane; although these two elusive small-ring propellanes have been implicated as intermediates in both chemical and electrochemical reactions, neither compound has been isolated. Wiberg, Epling, and Jason[2] demonstrated the probable intermediacy of [2.2.2]propellane in the electrolytic reduction of 1,4-dibromobicyclo[2.2.2]octane at platinum in dimethylformamide containing tetraethylammonium bromide. After the electrolysis was completed, the catholyte was saturated with chlorine gas and a small amount of 1,4-dichlorobicyclo[2.2.2]octane was recovered, the latter product resulting from addition of chlorine across the propellane bond. Wiberg, Epling, and Jason commented that [2.2.2]propellane is thermally unstable and undergoes a ring-opening reaction to produce 1,4-dimethylenecyclohexane; this diene adds chlorine across both double bonds to yield the tetrachloride.

In an investigation by Wiberg, Bailey, and Jason,[3] the reduction of 1,4-dibromonorbornane at a platinum electrode in dimethylformamide containing tetraethylammonium perchlorate was found to give norbornane, 1,1′-binorbornyl, and a norbornyl adduct of dimethylformamide. Although electrolyses were conducted at −25 °C, the experimental conditions were quite harsh because approximately one half of the supporting electrolyte was reduced along with the dibromide.[4] According to the authors, two different mechanisms could account for the formation of 1,1′-binorbornyl and the norbornyl adduct of the solvent—either coupling of the appropriate radicals or addition of radicals or anions to [2.2.1]propellane—but it was not possible to distinguish between these pathways from the available evidence.

The [2.2.1]propellane has been prepared and trapped (though not isolated or characterized) in the chemical reaction reported by Wiberg, Pratt, and Bailey.[5] Addition of *tert*-butyllithium to 1,4-diiodonorbornane at −77 °C results in an assortment of products, all of which appear to arise from addition of a carbanion to the [2.2.1]propellane.

We have recently undertaken investigations[6-11] of the electrochemical reduction of a number of alkyl halides, uti-

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