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ARTICLES

Homogeneous Reduction of Haloacetonitriles by Electrogenerated Aromatic Radical Anions: Determination of the Reduction Potential of $^{\bullet}CH_2CN$

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The mechanism of homogeneous reduction of XCH_2CN (X = Cl, Br, I) by organic radical anions ($D^{\bullet -}$) has been investigated in DMF. All three haloacetonitriles undergo a concerted dissociative electron transfer with formation of a fragment cluster in the solvent cage. The interaction energy D_p of the fragment cluster has been determined by applying the "sticky" dissociative electron-transfer model to the kinetic data obtained for the reaction between each XCH_2CN and a series of donors. The interaction energies lie in the range from 0.19 to 1.67 kcal mol^{-1} and decrease from Cl to Br and to I. Both the smallness of D_p values and their dependence on the bulkiness of X^- confirm the electrostatic character of these interactions. The intermediate radical stemming from the dissociative electron transfer to XCH_2CN reacts with $D^{\bullet -}$ either by radical coupling (k_c) or by electron transfer (k_{et}). Examination of the competition between these reactions, which can be expressed by a dimensionless parameter $q = k_{et}/(k_c + k_{et})$, as a function of $E^\circ_{D/D^{\bullet -}}$ allows determination of the standard reduction potential of $^{\bullet}CH_2CN$ ($E^\circ = -0.69$ V vs SCE) as well as the reorganization energy λ of the redox process. A significant contribution of internal reorganization to λ has been found, indicating a change of structure from $^{\bullet}CH_2CN$ to $^{-}CH_2CN$.

Introduction

Electron transfer (ET) to organic molecules, bearing suitable leaving groups such as halides, is quite often accompanied by fragmentation of a σ-bond. There are two possible reaction mechanisms for such reductive cleavages. ET and bond breaking can occur either in a stepwise manner with the intermediate formation of a radical anion (eqs 1 and 2) or in a concerted way in which two fragments, a radical and an anion, are produced in a single step (eq 3).

$$RX + e \rightleftharpoons RX^{\bullet -} \tag{1}$$

$$RX^{\bullet -} \rightarrow R^{\bullet} + X^- \tag{2}$$

$$RX + e^- \rightarrow R^{\bullet} + X^- \tag{3}$$

A large body of examples of both types of mechanisms has been reported for various classes of compounds.[1] In the case of alkyl halides, both homogeneous[2−4] and heterogeneous[2,5−7] reductive cleavages follow a concerted mechanism. According to the dissociative ET theory developed by Savéant,[8] the kinetics of the concerted reductive cleavage process can be described by eq 4:

$$\Delta G^\ddagger = \Delta G_0^\ddagger\left(1 + \frac{\Delta G^\circ}{4\Delta G_0^\ddagger}\right) \tag{4}$$

where $\Delta G^\ddagger$ is the activation free energy, ΔG° is the reaction free energy, and $\Delta G_0^\ddagger$ is the intrinsic barrier, i.e., the activation free energy at zero driving force. The intrinsic barrier is given by $\Delta G_0^\ddagger = (D_{RX} + \lambda_o)/4$, where D_{RX} is the R−X bond dissociation energy and λ_o is the solvent reorganization energy.

A very important issue of the concerted dissociative ET is whether the two fragments of the reaction may form a stable cluster. Quantum chemical calculations[6a,9,10] indicate that dissociative electron attachment on alkyl halides in the gas phase may give rise to strongly interacting radical ion pairs, especially if electron-withdrawing groups are attached to the α-C of the radical moiety. Several γ-ray irradiation experiments carried out on alkyl halides in the gas phase[10] or in rigid organic matrixes[11] have evidenced the formation of fragment clusters. These interactions are expected to decrease or even to disappear in the liquid phase, especially in polar solvents capable of solvating the ionic fragment. There is, however, growing evidence that fragment clustering plays a nonnegligible role in concerted dissociative ET to alkyl halides even in solvents as polar as *N,N′*-dimethylformamide (DMF) or acetonitrile.[6,7,12]

The existence and magnitude of the ion radical interactions strongly influence the dynamics of the dissociative electron transfer to the parent molecule. In fact, when fragment clustering is significant, the dissociative ET theory in its original form does not fit satisfactorily the experimental data, the $\Delta G^\ddagger$ values predicted by the theory being considerably greater than the experimental ones. The theory has been recently revised to take into account possible interactions in the products stemming from dissociative ET.[6a,12] The improved model of the dissociative ET (the "sticky" model), which is based on Morse-type energy profiles for both reagent and product system, gives the following activation driving force relationship:

$$\Delta G^\ddagger = \frac{(\sqrt{D_{RX}} - \sqrt{D_P})^2 + \lambda_o}{4}\left(1 + \frac{\Delta G^\circ - D_P}{(\sqrt{D_{RX}} - \sqrt{D_P})^2 + \lambda_o}\right) \tag{5}$$

where D_P is the interaction energy of the ion radical pair. As

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seen in eq 5, the reaction kinetics is strongly influenced by the presence of weak interactions because D_P not only modifies the driving force, as would do a product work term, but also it decreases the intrinsic barrier (standard activation energy).

Equation 5 has been applied successfully to the heterogeneous reductive cleavage of carbon−halogen bonds in a few alkyl halides. Application of the "sticky" model to these systems also made possible the precise determination of the halide ion radical interaction in the fragment cluster. The experimental examples of dissociative ET with fragment clustering are quite limited and are mostly concerned with electrochemical reactions at inert electrodes.[6,7,12] Here we report on the homogeneous reduction of three haloacetonitriles by electrogenerated organic radical anions. The process is shown to follow a concerted dissociative ET mechanism with the formation of interacting fragments, with interaction energies depending on the dimension of the leaving halide ion. This study provides the first examples of a homogeneous concerted dissociative ET in which interaction of the product fragments plays an important role in the dynamics of the process.

A second interesting aspect of the homogeneous reduction of haloacetonitriles concerns the cyanomethyl radical. Indeed, such a radical is formed as an intermediate in many processes where the solvent CH_3CN is engaged in H-atom transfer reactions. This is the case, for example, for many electrochemical processes in which very reactive odd-electron species are generated.[13] Besides being the simplest of the cyanoalkyl radicals, which are intermediates in many reactions, $^{\bullet}CH_2CN$ is also of great interest in interstellar cloud chemistry.[14] Much attention has been therefore dedicated to this interesting radical. Various studies on its thermodynamic properties[15] as well as its spectroscopic[16] characterization have been reported. Despite importance, the redox properties of $^{\bullet}CH_2CN$ have never been examined. In the course of the homogeneous reduction process, the intermediately formed cyanomethyl radical may further react with $D^{\bullet-}$ according to the following reaction pathways:

$$D^{\bullet-} + {}^{\bullet}CH_2CN \rightarrow D - CH_2CN^- \qquad (6)$$

$$D^{\bullet-} + {}^{\bullet}CH_2CN \rightarrow D + {}^{-}CH_2CN \qquad (7)$$

where $D^{\bullet-}$ is the reduced form of the donor molecule D. Kinetic analysis of the competition between the above reactions, which depends on $E^{\circ}_{D/D^{\bullet-}}$, makes possible the determination of E° of the $^{\bullet}CH_2CN/^{-}CH_2CN$ couple.[17]

Experimental Section

Chemicals. *N,N*-Dimethylformamide (DMF) (Janssen, 99%) was kept over anhydrous Na_2CO_3 for several days and stirred from time to time. It was then fractionally distilled under reduced pressure under N_2 twice and stored in a dark bottle under N_2. Tetra-*n*-butylammonium perchlorate (Fluka 98%) was recrystallized twice from a 2:1 water−ethanol mixture and dried at 60 °C under vacuum. The haloacetonitriles and the aromatic compounds used as mediators were all commercially available and were used as received.

Instrumentation. The electrochemical measurements were made with a PAR model 173 potentiostat equipped with a PAR 175 universal programmer and a Nicolet 3091 digital oscilloscope. All experiments were conducted in a three electrode glass cell, thermostated at 25 °C. A glassy carbon (Tokai GC-20) electrode, prepared and activated before each measurement as previously described,[18] was used as the working electrode and a platinum wire as the counter electrode. The reference electrode was Ag/AgI/$(n\text{-}C_4H_9)_4NI$ 0.1 M DMF, calibrated after each experiment against the ferrocene/ferricinium couple. The standard potential for ferrocene oxidation in DMF + 0.1 $(n\text{-}C_4H_9)_4NClO_4$ is 0.475 V against the KCl saturated calomel electrode (SCE). In the article, all of the potential values are reported against SCE. Digital simulations were performed by using the program DigiSim 2.1 (Bioanalytical Systems).

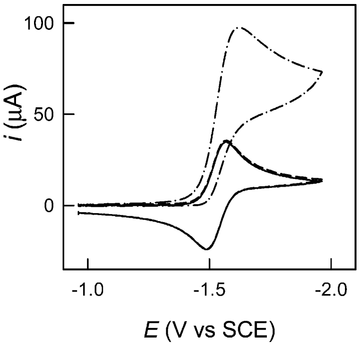

Figure 1. Cyclic voltammetry of 1.25 mM 1,4-dicyanobenzene in DMF + 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at a glassy carbon electrode at $v = 0.2$ Vs^{-1} in the absence (———) and presence of either 3.04 mM phenol (– – –) or 3.04 mM phenol + 2.52 mM $ClCH_2CN$ (– · –).

Results and Discussion

Kinetics of the Homogeneous Reduction of Haloacetonitriles. The kinetics of the homogeneous reduction of haloacetonitriles by a series of electrochemically generated organic radical anions $(D^{\bullet-})$ was investigated by cyclic voltammetry. This indirect method, known as homogeneous redox catalysis, has been already described in detail and applied to the electron transfer to many compounds.[2−4,19,20] In the case of an alkyl halide RX the following reaction sequence takes place:

$$D + e^- \rightleftharpoons D^{\bullet-} \qquad (8)$$

$$D^{\bullet-} + RX \rightarrow D + R^{\bullet} + X^- \qquad (9)$$

$$D^{\bullet-} + R^{\bullet} \rightarrow D + R^- \qquad (10)$$

$$D^{\bullet-} + R^{\bullet} \rightarrow DR^- \qquad (11)$$

The initial step of the reaction is a rate-determining concerted dissociative ET from the radical anion to the alkyl halide. The alkyl radical $R^{\bullet}$ reacts with $D^{\bullet-}$ according to two competitive reaction pathways: (i) ET to give R^- (eq 10) or (ii) radical−radical coupling leading to alkylation of the mediator (eq 11). The competition between reduction and coupling depends on the standard reduction potentials of both D and $R^{\bullet}$.

The various aromatic compounds used as mediators all give rise to a reversible cyclic voltammetric wave, and their standard potentials $(E^{\circ}_{D/D^{\bullet-}})$, measured as the midpoint between the cathodic and anodic peaks, are gathered in Table 1. Figure 1 shows a typical example of the voltammetric behavior of a mediator and the catalytic effect observed upon addition of a halide. Catalysis results in a loss of reversibility and an enhancement of the cathodic peak current. We have previously shown that reduction of XCH_2CN is an overall $2e^-$ process (eq 12) yielding the carbanion $^{-}CH_2CN$, which is then protonated by the starting material (eq 13).[21]

$$XCH_2CN + 2e^- \rightarrow {}^{-}CH_2CN + X^- \qquad (12)$$

$$^{-}CH_2CN + XCH_2CN \rightarrow CH_3CN + {}^{-}CH(X)CN \qquad (13)$$

TABLE 1: Electron Transfer Rate Constants and q Values for the Reactions between Haloacetonitriles and Various Radical Anions in DMF + 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at 25 °C

RX	donor	$E^\circ_{D/D^{\bullet-}}$ (V vs SCE)	q	k_9/M^{-1} s^{-1}
$ClCH_2CN$	fluoranthene	−1.736	1.0	5.62×10^5
	perylene	−1.634	1.0	9.33×10^4
	methyl 4-cyanobenzoate	−1.580	1.0	1.51×10^4
	2,3-benzanthracene	−1.538	0.9	1.29×10^4
	1,4-dicyanobenzene	−1.532	0.9	6.61×10^3
	4-nitroanisole	−1.222	0.9	2.51×10^1
	nitrobenzene	−1.105	0.9	1.95
$BrCH_2CN$	4-nitroanisole	−1.222	0.9	4.68×10^4
	nitrobenzene	−1.105	0.9	3.98×10^3
	1-nitronaphthalene	−1.036	0.9	4.57×10^2
	methyl 3-nitrobenzoate	−0.990	0.8	2.40×10^2
	3-nitrobenzonitrile	−0.889	0.6	2.82×10^1
	1,3-dinitrobenzene	−0.834	0.4	1.70×10^1
	4-nitrobenzaldehyde	−0.786	0.2	4.79
ICH_2CN	1-nitronaphthalene	−1.036	0.8	2.19×10^5
	methyl 3-nitrobenzoate	−0.990	0.8	1.20×10^5
	3-nitrobenzonitrile	−0.889	0.6	1.48×10^4
	1,3-dinitrobenzene	−0.834	0.4	1.16×10^4
	4-nitrobenzaldehyde	−0.786	0.3	1.15×10^3
	2-methyl-1,4-naphthoquinone	−0.684	0.1	4.17×10^2
	2,6-di-*tert*-butyl-1,4-benzoquinone	−0.630	0.0	2.24×10^2
	1,4-dinitrobenzene	−0.589	0.0	3.17×10^1

Such a father−son reaction would have the effect of diminishing the catalytic efficiency since it subtracts a fraction of the starting material from the catalytic cycle. Equation 13 can be suppressed if a proton donor stronger than XCH_2CN is added to the solution. Strong proton donors, however, may also protonate the radical anion of the mediator ($D^{\bullet-}$), severely hampering the catalytic process. Phenol was found to fulfill the required conditons, i.e., it protonates rapidly $^-CH_2CN$ but its reaction with $D^{\bullet-}$ is too slow (see Figure 1) to interfere with the catalytic process. A slight excess of phenol is required to suppress completely the father−son reaction, and thus most of the catalysis experiments were carried out in the presence of phenol at a c_{PhOH}/c_{RX} ratio of ca. 1.2.[22] Cyclic voltammetry of the mediator alone was first run at different scan rates in the range from 0.1 to 50 Vs^{-1}. The necessary quantity of acid was then added, and the cyclic voltammteric measurements were repeated. In this manner it was always possible to check the effect, if any, of the acid on the voltammetric behavior of the mediator. The halide was then added, and the experiment was completed.

The kinetics of the process was analyzed by cyclic voltammetry according to published procedures.[4] Working curves relating the current ratio i_p/i_{pd}, where i_p and i_{pd} are the peak currents measured for the mediator in the presence and absence of the halide, respectively, with a dimensionless kinetic parameter (p) were constructed by digital simulation of the reaction sequence shown in eqs 8−11. The kinetic parameter is given by $p = RTc_Dk_9/F\upsilon$, where c_D is the concentration of the mediator and υ is the scan rate. The competition between the two reactions of the radical $R^\bullet$ (eqs 10 and 11) is expressed by another kinetic parameter, q, defined as

$$q = k_{et}/(k_{et} + k_c) \tag{14}$$

where k_{et} and k_c are the rate constants of the ET (eq 10) and the radical−radical coupling (eq 11) reactions, respectively. Working curves with different values of q, which can vary from 0 to 1, were therefore constructed by digital simulation. For each particular value of the ratio c_{RX}/c_D a set of 11 $\log(i_p/i_{pd})$ versus $\log p$ plots with q values varying from 0 to 1 in 0.1 increments was obtained. An example of a set of theoretical working curves and fitting of some experimental data is illustrated in Figure 2. For convenience of presentation only seven of the 11 theoretical curves are included in the figure. For each mediator/halide couple, the values of k_9 and q, obtained from the best fitting of the data points on the appropriate theoretical curve, are collected in Table 1.

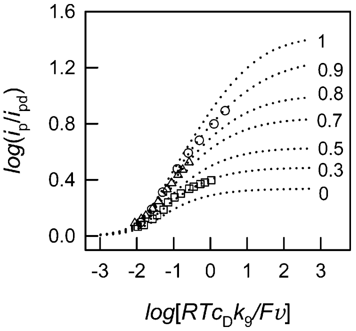

Figure 2. Homogeneous reduction of haloacetonitriles by organic radical anions in DMF + 0.1 M $(n\text{-}C_4H_9)_4NClO_4$. The experimental data are for the catalytic systems: (○) 2,3-benzanthracene + $ClCH_2CN$, (△) methyl 3-nitrobenzoate + $BrCH_2CN$, and (□) 4-nitrobenzaldehyde + ICH_2CN, and they were obtained at $c_{RX}/c_D = 10$. The dotted lines are working curves calculated at the indicated values of the competition parameter q with $c_{RX}/c_D = 10$.

The kinetics of the homogeneous reduction of haloacetonitriles may be analyzed according to the concerted dissociative electron transfer theory.[8] This requires knowledge of the standard free energy $\Delta G^\circ = -F(E^\circ_{RX/R^\bullet+X^-} - E^\circ_{D/D^{\bullet-}})$ and the activation free energy $\Delta G^\ddagger$ of the reaction between XCH_2CN and $D^{\bullet-}$. $\Delta G^\ddagger$ was calculated from the experimental rate constant k_9 according to

$$\Delta G^\ddagger = RT \ln\left(\frac{Z}{k_9}\right) \tag{15}$$

assuming a value of 3×10^{11} M^{-1} s^{-1} for the homogeneous collision frequency Z. The standard reduction potentials of the haloacetonitriles, required for the calculation of ΔG°, cannot be measured experimentally. They can be calculated from the C−X bond dissociation energy D_{RX} and the oxidation potentials of the halide ions according to

$$E^\circ_{RX/R^\bullet+X^-} = -D_{RX} + T\Delta S^\circ - E^\circ_{X^\bullet/X^-} \tag{16}$$

where ΔS° is the bond dissociation entropy. The entropic term in eq 16 has been previously estimated as 6.9 kcal mol^{-1}.[7] Also, the $E^\circ_{X^\bullet/X^-}$ values of all three halides are available in the literature[6a,23] and are listed in Table 2. Unfortunately, the bond dissociation energies of XCH_2CN are not known, and therefore we estimated them as follows. First we calculated D_{RX} of iodoacetonitrile from the enthalpies of formation of ICH_2CN, I, and $^\bullet CH_2CN$ according to the equation

$$D_{RX} = \Delta_f H^\circ(^\bullet CH_2CN) + \Delta_f H^\circ(X) - \Delta_f H^\circ(XCH_2CN) \tag{17}$$

Experimental data on $\Delta_f H^\circ$ of the three species involved in the dissociation of ICH_2CN are available in the literature. The values of 41.2 ± 1.0, 58.5 ± 2.4, and 25.52 ± 0.01 kcal mol^{-1} reported for $\Delta_f H^\circ$ of ICH_2CN,[24] $^\bullet CH_2CN$,[25] and the iodine atom,[26] respectively, give $D_{RX}(I{-}CH_2CN) = 42.8 \pm 2.6$ kcal mol^{-1}. Inspection of literature[27] data on bond dissociation energies of various alkyl halides RX (X = Cl, Br, I) shows that, although D_{RX} values depend on the structure of the alkyl group, for any given R the difference between D_{RX} values of C−Br and C−I is about constant and equal to 14.0 ± 0.7 kcal mol^{-1}. Likewise,

TABLE 2: Thermodynamic and Kinetic Parameters for the Homogeneous Electron Transfer to XCH_2CN in DMF + 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at 25 °C[a]

X	D_{RX}	E°_{X/X^-}	$E^\circ_{RX/R^\bullet+X^-}$	a_{RX}	a_X	a	λ_o	$\Delta G_0^\ddagger$ (exptl)[b]	$\Delta G_0^\ddagger$ (pred.)[c]	D_P
Cl	70.5	1.81	−0.96	2.93	1.81	2.50	17.2	16.2	22.0	1.67 ± 0.12
Br	56.8	1.48	−0.69	3.02	1.96	2.65	16.5	15.5	18.4	0.50 ± 0.06
I	42.8	0.99	−0.57	3.06	2.20	2.82	15.8	13.1	14.7	0.19 ± 0.03

[a] Energies are in kilocalories per mole, potentials in V vs SCE and radii are in angstroms. [b] Experimental value. [c] Predicted value according to a concerted dissociative ET without interaction of product fragments.

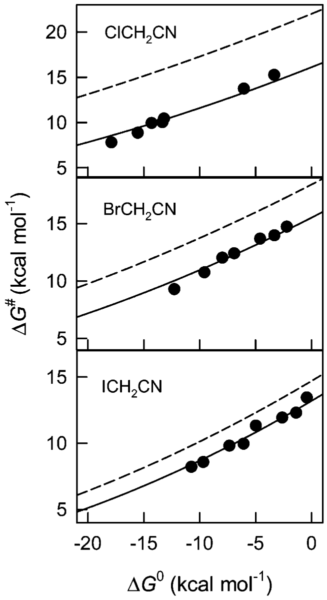

Figure 3. Variation of the activation free energy as a function of the standard free energy of the reaction between $D^{\bullet-}$ and haloacetonitriles in DMF at 25 °C. The dashed and solid lines are the predictions of the classical (eq 4) and "sticky" (eq 5) dissociative electron-transfer models, respectively.

the difference between the values for C−Cl and C−I is approximately constant and equal to 27.7 ± 2.7 kcal mol^{-1}. Thus, starting from the D_{RX} value calculated for ICH_2CN from experimental thermochemical data, we estimated the D_{RX} values of $BrCH_2CN$ and $ClCH_2CN$. The values of D_{RX} together with the values of $E^\circ_{RX/R^\bullet+X^-}$ calculated from eq 16 are listed in Table 2.[28]

The last parameter required for the application of the dissociative ET theory is the solvent reorganization energy λ_o, which was calculated from the hard sphere radii of the reagents using an empirical equation (eq 18) derived[20f] from an extensive set of experimental data.[29]

$$\lambda_o = 95\left(\frac{1}{2a} + \frac{1}{2a_D} - \frac{1}{a + a_D}\right) \tag{18}$$

where a and a_D are the effective radius of XCH_2CN and the hard sphere radius of the donor, respectively. The effective radii of the halides were calculated from the equation[8] $a = (2a_{RX} - a_X)a_X/a_{RX}$, while an average value of 3.7 Å was used for the radius of the donors. The calculated λ_o values are reported in Table 2.

Figure 3 shows the dependence of $\Delta G^\ddagger$ of the ET between each XCH_2CN and a series of donors on ΔG° of the reaction. Comparison of the experimental data with the theoretical predictions (dashed curves) according to eq 4 shows that the predicted values of $\Delta G^\ddagger$ are considerably larger than the experimental ones and the discrepancy between theory and experiment increases from I to Br and to Cl. This observation is in good agreement with the results on the heterogeneous reduction of the same halides at inert electrodes.[7] As in the case of the heterogeneous ET, ion−dipole interactions in the solvent cage, which have the effect of lowering $\Delta G^\ddagger$, may be responsible of the observed discrepancy. Therefore, we examined the applicability of the "sticky" dissociative ET model (eq 5). All other parameters in eq 5 being already defined (Table 2), the fitting was achieved by adjusting the interaction energy D_P until a best fit of the experimental data was obtained. The best fitting results are illustrated in Figure 3 (solid curves), and the corresponding values of D_P are gathered in Table 2.

The "sticky" dissociative electron-transfer model fits very well the experimental data, and therefore we conclude that, as in the heterogeneous case, homogeneous reduction of XCH_2CN by aromatic radical anions follows a concerted dissociative ET with a weak interaction of the fragments in the solvent cage. It is noteworthy that the values of the interaction energy D_P derived from the fitting are quite small and decrease with increasing radius of the leaving ion. Both the smallness of the D_P values and their dependence on the radius of the halide anion suggest that interaction in the fragment cluster is essentially of the ion−dipole type.

A rough estimate of the potential energy ($V = -D_P$) of the electrostatic interaction between the cyanomethyl radical and the halide ions can be obtained from the following equation

$$V = \frac{N_A e\mu}{4\pi\epsilon_0 a_1}\left(\frac{1}{a_X + (3/2)a_1} - \frac{1}{a_X + (1/2)a_1}\right) \tag{19}$$

where a_1 and a_X are the radii of the radical and the halide ion, respectively, N_A is the Avogadro number, μ is the dipole moment of the radical, and ϵ_0 is the vacuum permittivity. In deriving eq 19, which expresses the interaction energy as the sum of an attractive and a repulsive term, the dipole was considered to be aligned and in close contact with the negative charge, taking the sum of the radii of the two fragments as the distance of their closest approach. A further assumption in eq 19 is that the negative and positive charges of the dipole are at a distance of $0.5a_1$ from the center of the dipole. The dipole moment of $^\bullet CH_2CN$ is 3.99 D,[30] whereas its radius was taken to be approximately that of CH_3CN ($a = 2.76$ Å). The calculated interaction energies (D_P^{calcd}) are 14.5, 13.5, and 12.2 kcal mol^{-1} for Cl^-, Br^-, and I^-, respectively. Note that the interaction energies were calculated in the vacuum, whereas in solution the fragments in the solvent cage give rise to interactions with solvent molecules and are hence partially solvated. Thus, the interaction energies in solution are expected to be considerably smaller than the D_P^{calcd} values calculated from eq 19. Figure 4 shows a correlation between D_P^{calcd} and the experimental interaction energies. It can be seen that the experimental D_P values are much smaller than the calculated interaction energies while both decrease with increasing a_X. The considerable decrease of D_P in solution with respect to its values in the vacuum is due to the solvation of X^- by the dipolar solvent. A remarkable solvent effect on the stability of ion radical pairs formed upon dissociative ET to alkyl halides has been recently

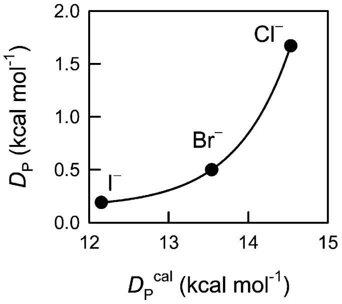

Figure 4. Correlation of the experimental interaction energies in the solvent cage (D_P) with the D_P^{calcd} values calculated from eq 19. The solid line was drawn to show the trend of the data.

reported.[6c] The interaction energies in solution decrease with a_X more rapidly than the D_P^{calcd} values. Also, this effect should be related to the solvating role of the solvent molecules surrounding the fragment cluster. In fact, the same trend obtained in this work has been shown for the heterogeneous reduction of haloacetonitriles by comparing the experimental interaction energies with D_P^{calcd} values obtained by quantum chemical calculations in the gas phase.[7]

The values of D_P determined in this work may be compared with those previously measured in the heterogeneous case,[7] but direct comparison is not possible because slightly different parameters have been used in the two studies. The heterogeneous data were therefore re-elaborated as previously described by using the D_{RX} and $E^\circ_{RX/R^\bullet+X^-}$ values reported here. The following interaction energies were obtained: $D_P = 2.35$, 1.26, and 0.50 kcal mol^{-1} for X = Cl, Br, and I, respectively. As can be seen, D_P values measured in the heterogeneous process are always higher than those determined for the corresponding homogeneous one. In the case of homogeneous dissociative ET, the donor molecule is also present in the solvent cage in close proximity to the fragment cluster. It is likely that the donor molecule exercises some steric effect on the formation of the ion radical cluster, perhaps with some distortion of the optimal geometry of the latter.

Determination of the Reduction Potential of $^\bullet$CH$_2$CN. Analysis of the competition between the two reactions of $^\bullet$CH$_2$CN with D$^{\bullet-}$ (eqs 10 and 11) allows determination of the standard reduction potential of the cyanomethyl radical. Equation 11 is a very fast radical−radical coupling, with a rate constant close to the diffusion limit and practically independent of the difference between the E° values of the $^\bullet$CH$_2$CN/$^-$CH$_2$CN and D/D$^{\bullet-}$ couples. Values of k_c of the order of 10^9 M^{-1} s^{-1} have been reported for the coupling between alkyl radicals and aromatic radical anions,[31] and thus we will use this value for all coupling reactions between $^\bullet$CH$_2$CN and D$^{\bullet-}$. The rate constant k_{et} of eq 10, which is an outer-sphere ET, is given by eq 20, according to the Marcus theory of electron transfer.[32]

$$k_{et} = \cfrac{k_d}{1 + \cfrac{k_d}{K_d Z}\exp\left[\cfrac{\lambda}{4RT}\left(1 + \cfrac{F(E^\circ_{D/D^{\bullet-}} - E^\circ_{R^\bullet/R^-})}{\lambda}\right)^2\right] + \exp\left(\cfrac{F(E^\circ_{D/D^{\bullet-}} - E^\circ_{R^\bullet/R^-})}{RT}\right)} \qquad (20)$$

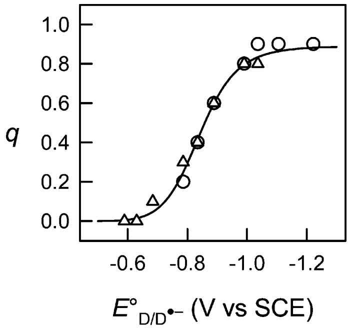

Figure 5. Variation of the competition parameter q as a function of the standard potential of the mediators. The solid line is the best fitting of the experimental data for BrCH$_2$CN (○) or ICH$_2$CN (△) to eq 21.

where k_d is the diffusion-limited rate constant and K_d is the equilibrium constant for the formation of the encounter complex. Both K_d and k_d depend on the dimensions of the molecules involved in the ET.[33] When at least one of the reagents is uncharged, the stability constant of the encounter complex can be calculated from the expression $K_d = 4\pi N_A \sigma^3/3000$, where σ (in centimeters) is the distance of closest approach between the reagents, which can be taken as the sum of their radii. Using $a_D = 3.7$ Å for the donors and assuming the radius of CH$_3$CN ($a = 2.76$ Å) for $^\bullet$CH$_2$CN, we find that $\sigma = 6.46$ Å, which leads to a K_d value of 0.68 M^{-1}. k_d can be calculated from the viscosity η of the medium according to the expression $k_d = 8RT/3\eta$, which leads to $k_d = 8.3 \times 10^9$ M^{-1} s^{-1} at 25 °C in DMF.

Substituting k_{et} in the expression for q (eq 14) and rearranging yields:

$$q = \cfrac{1}{1 + \cfrac{k_c}{k_d}\left\{1 + \cfrac{k_d}{K_d Z}\exp\left[\cfrac{\lambda}{4RT}\left(1 + \cfrac{F(E^\circ_{D/D^{\bullet-}} - E^\circ_{R^\bullet/R^-})}{\lambda}\right)^2\right] + \exp\left(\cfrac{F(E^\circ_{D/D^{\bullet-}} - E^\circ_{R^\bullet/R^-})}{RT}\right)\right\}} \qquad (21)$$

The dependence of q on $E^\circ_{D/D^{\bullet-}}$ is shown in Figure 4, where data from BrCH$_2$CN and ICH$_2$CN are reported. The q values derived from ClCH$_2$CN fall in the plateau zone of Figure 4, where q becomes independent of $E^\circ_{D/D^{\bullet-}}$, and were thus omitted because of their limited importance in this analysis. It is interesting to note that the two series of q values obtained from the homogeneous reduction of BrCH$_2$CN and ICH$_2$CN lie on the same curve and are essentially indistinguishable. The data were fit to eq 21 to obtain $E^\circ_{R^\bullet/R^-}$ and the reorganization energy λ. The best fitting curve is shown in Figure 5 (solid line), and the values extracted from the regression are $E^\circ_{R^\bullet/R^-} = -0.69 \pm 0.06$ V vs SCE and $\lambda = 19.2 \pm 2.4$ kcal mol^{-1}. The self-exchange reorganization energy of the cyanomethyl radical $\lambda_{R^\bullet/R^-}$ can be estimated from the experimental λ value by using the Marcus cross-relation $\lambda = 1/2[\lambda_{R^\bullet/R^-} + \lambda_{D/D^{\bullet-}}]$, where $\lambda_{D/D^{\bullet-}}$ is the self-exchange reorganization energy of the electron donor. The reorganization energy is the sum of two terms, λ_o and λ_i, the contribution from the changes in bond lengths and angles in the molecule. Since the radical anions D$^{\bullet-}$ of the donor molecules used in this work are highly delocalized, we neglect λ_i and assume $\lambda_{D/D^{\bullet-}}$ to be equal to λ_o, which can be calculated from eq 18. By using $a = a_D = 3.7$ Å in eq 18, $\lambda_{D/D^{\bullet-}}$ is found to be 12.8 ± 1.2 kcal mol^{-1}. This leads to a total reorganization energy $\lambda = 25.6 \pm 2.7$ kcal mol^{-1} for the $^\bullet$CH$_2$CN/$^-$CH$_2$CN couple. Estimation of λ_o ($^\bullet$CH$_2$CN/$^-$CH$_2$CN) from eq 18 gives a value of 17.2 ± 1.2 kcal mol^{-1}, which leads to λ_i value of 8.4 ± 1 kcal mol^{-1}. It is noteworthy that λ_i in the electron exchange between $^\bullet$CH$_2$CN and $^-$CH$_2$CN is quite high and constitutes ca. 33% of the total reorganization energy. This suggests that there is a significant difference between the geometrical structures of the cyanomethyl radical and the cyanomethide ion. This conclusion is in agreement with literature reports on the structures of the two species.[14,30,34,35] In fact, the molecular structure of $^{\bullet}CH_2CN$ and $^{-}CH_2CN$ has been the subject of several studies, both experimental[14,34] and theoretical,[30,35] and it has been shown that the cyanomethyl radical is a planar, symmetric species, while the cyanomethide ion is slightly pyramidal.

Conclusions

The results of our study on the homogeneous reduction of haloacetonitriles by electrogenerated organic radical anions allow the following conclusions.

(i) Homogeneous reduction of all three haloacetonitriles follows a concerted dissociative electron transfer mechanism with the formation of interacting caged fragments. The nature of the interaction appears to be of the electrostatic type as judged by the small values of the interaction energies determined by application of the "sticky" model of the dissociative ET theory. The interaction energies decrease rapidly as the radius of the leaving halide ion increases, again underscoring the electrostatic character of the interaction.

(ii) Comparison between the homogeneous and heterogeneous reductive cleavages of haloacetonitriles shows that higher interaction energies D_P are obtained for the heterogeneous process. The stability of the ion radical pair is affected by the mode of electron injection into XCH_2CN, electron transfer from an inert electrode resulting in a more stable fragment cluster than reduction by a species in solution. In the homogeneous process, the donor molecule remains in the proximity of the ion radical pair and probably exercises some steric effect on the cluster. Thus, a slightly more elongated fragment cluster is formed in the homogeneous process than in the heterogeneous one.

(iii) Analysis of the two competing reactions between $^{\bullet}CH_2CN$ and $D^{\bullet -}$ allowed the determination of both the standard potential and the self-exchange reorganization energy of the $^{\bullet}CH_2CN/^{-}CH_2CN$ couple. It is found that there is a significant contribution (ca. 33%) of internal reorganization to the total reorganization energy. The internal reorganization arises from variations of structural configuration required in the passage from flat cyanomethyl radical to a slightly pyramidal cyanomethide ion and vice versa.

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