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Sticky Dissociative Electron Transfer to Polychloroacetamides. In-Cage Ion−Dipole Interaction Control through the Dipole Moment and Intramolecular Hydrogen Bond

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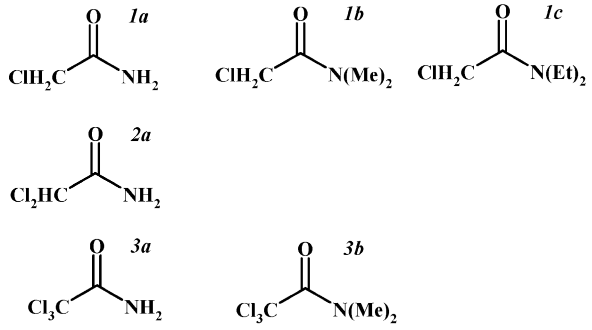
The reductive cleavage of chloro- and polychloroacetamides in *N*,*N*-dimethylformamide gives new insights into the nature of the in-cage ion radical cluster formed upon dissociative electron transfer. Within the family of compounds investigated, the electrochemical reduction leads to the successive expulsion of chloride ions. At each stage the electron transfer is concerted with the breaking of the C−Cl bond and acts as the rate-determining step. The reduction further leads to the formation of the corresponding carbanion with the injection of a second electron, which is in turn protonated by a weak acid added to the solution. From the joint use of cyclic voltammetric data, the sticky dissociative electron-transfer model and quantum ab initio calculations, the interaction energies within the cluster fragments ($^{\bullet}$R, Cl$^-$) resulting from the first electron transfer to the parent RCl molecule are obtained. It is shown that the stability of these adducts, which should be viewed as an essentially electrostatic radical-ion pair, is mainly controlled by the intensity of the dipole moment of the remaining radical part and may eventually be strengthened by the formation of an intramolecular hydrogen bond, as is the case with 2-chloroacetamide.

Introduction

The properties of molecules may be manipulated by injection or removal of an electron leading to structural changes that could be as substantial as bond cleavage or bond formation. Such electron transfers can be triggered in various ways, electrochemically,[1,2] photochemically,[3] by homogeneous electron donors or acceptors,[1,4,5] or by means of pulse radiolysis.[6] The fact that so many chemical reactions can follow or accompany electron transfer is the basis of the synthetic value of electron-transfer chemistry. Questions dealing with the fundamentals of chemical reactivity are also raised in this field such as the concerted or sequential character of electron transfer and accompanying chemical events.

Electron-transfer chemistry also irrigates more applied fields, for example the area of sensors and biosensors, which both involve the transduction of the presence of a molecule into an electrochemical signal. Another, more prospective field, concerns molecular electronics, where the understanding of the structural changes coupled to charge transfer will be central in the design and working of devices including redox centers connected by molecular wires. In a different vein, a large body of work has been recently devoted to the study of the degradation mechanisms of common chlorinated and polychlorinated solvent and to the nature of the ensuing products in various environmental situations, since these compounds represent one of the main groups of environmental pollutants present in soils and underground waters of many industrial sites.[7] The results so far obtained in this domain stressed the importance of a more systematic analysis of reaction mechanisms coupling charge transfer to a strong molecular modification, namely a bond cleavage, and of a structure−reactivity relationship, that will lead to predictive rules. Following our recent results concerning the electrochemical reduction of polychloromethanes, polychloroethanes and polychloroethenes,[8] the first objective of the work presented here was to pursue these investigations by deciphering the exact mechanisms by which a family of chloro- and polychloroacetamides, which are widely used as pesticides and herbicides,[9] are dechlorinated (Chart 1). For this purpose we studied the heterogeneous reduction at glassy carbon electrodes in *N*,*N*-dimethylformamide (DMF) of 2-chloroacetamide (***1a***), 2-chloro-*N*,*N*-dimethylacetamide (***1b***), 2-chloro-*N*,*N*-diethylacetamide (***1c***), 2,2-dichloroacetamide (***2a***), 2,2,2-trichloracetamide (***3a***) and 2,2,2,-trichloro-*N*,*N*-dimethylacetamide (***3b***).

CHART 1



When charge transfer is coupled to a bond cleavage reaction, the two events may occur concertedly (concerted dissociative electron transfer, CDET) or in two successive steps, the electron transfer then leading to a frangible species that cleaves in a distinct and purely chemical step endowed with an activation barrier (sequential dissociative electron transfer, SDET).[1,2] Sequential cleavage of ion radicals may occur in a homolytic

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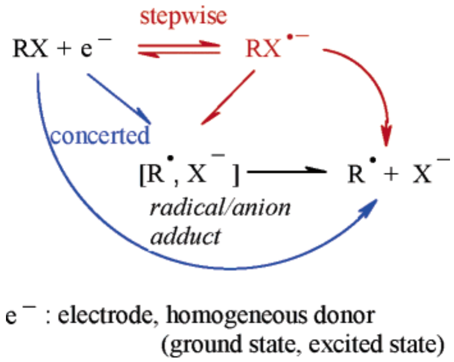
SCHEME 1



or heterolytic manner, and in both cases the cleavage amounts to an intramolecular dissociative electron-transfer reaction.[1,5,6,10−12]

The two pathways (CDET vs SDET), well identified and illustrated on both the experimental (homogeneous and heterogeneous (electrochemical) thermal reactions, homogeneous photoinduced reactions) and theoretical sides, are sketched in Scheme 1. After the cleavage has taken place, another energy minimum is represented in Scheme 1 and in the potential energy diagram of Figure 1, corresponding to an ion-radical adduct which may or may not survive in a polar solvent. When existing, this adduct, resulting from a charge-dipole attractive interaction between the cage fragments before they diffuse out, may be viewed alternatively as a σ^* anion radical or as forming a weak three-electron bond. If such interactions are expected to decrease or even to vanish in polar liquid, several recent experimental studies have confirmed their existence, at least when a partial positive charge is induced on the remaining radical part, thanks to the presence of a strong electron-withdrawing substituent.[13]

This is, for example, the case during the electrochemical dehalogenation of carbon tetrachloride and 4-cyanobenzyl chloride. Albeit small in magnitude (typically a few tens of meV), these interactions may strongly affect the dynamics of the dissociative charge transfer to the parent molecule. This enhanced reactivity has been modeled through a modification of the dissociative electron-transfer theory (CDET) taking into account the formation of a weakly attractive cluster en route to the products $R^\bullet$ and X^- when starting from the parent RX. Potential energy curves describing both reactant and products are modeled by Morse curves and lead to a quadratic activation (activation free energy: $\Delta G^{\ddagger}$)—driving force (standard free energy: ΔG°) relationship as given in eq 1

$$\Delta G^{\ddagger} = \frac{(\sqrt{D_{RX}} - \sqrt{D_{R^\bullet,X^-}})^2 + \lambda_0}{4} \times \left(1 + \frac{\Delta G^\circ - D_{R^\bullet,X^-}}{(\sqrt{D_{RX}} - \sqrt{D_{R^\bullet,X^-}})^2 + \lambda_0}\right)^2 \qquad (1)$$

where λ_0 is the solvent reorganization energy, D_{RX} is the bond dissociation of the reactant RX and $D_{R^\bullet,X^-}$ is the interaction energy within the ion-radical pair.[13] The interference of this last term through its square root makes it potentially important. If the sticky interaction amounts to ca. 1% of D_{RX}, then a decrease of about 15% of the intrinsic barrier will ensue, thus accelerating the reaction to an experimentally detectable amount. Several recent experimental works have indeed confirmed the reality of such interactions and the applicability of the model. These examples mostly concerned heterogeneous reactions,[8,13,14] but two homogeneous electron-transfer examples have also been found.[15]

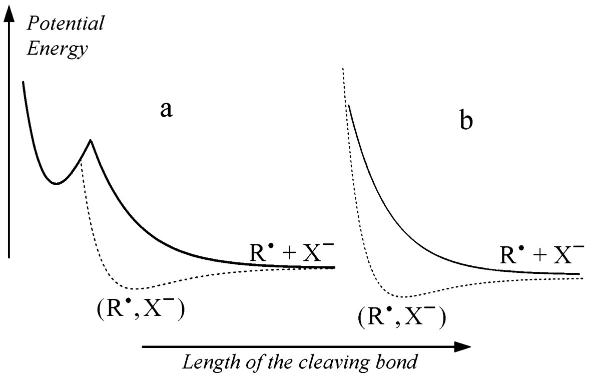


Figure 1. Energy as function of the intramolecular reorganization for the cleaving system RX + 1e⁻, with (dotted line) and without (full line) interaction between the fragments, along a sequential (left, a) and a fully concerted (right, b) pathway.

The pieces of evidence on hand so far were obtained by looking at the systematic modulation of the charge-transfer kinetics among various families of compounds and at the ensuing modulation of in-cage cluster interaction energies. The existence of these interactions in a polar condensed medium were thus probed and illustrated first by varying the nature of the solvent molecules surrounding the substrates, then by keeping the remaining radical constant while changing the leaving anion and finally by keeping the leaving anion constant while changing the nature of the remaining radical. It has been shown that upon electrochemical reduction of 4-cyanobenzyl chloride, the interaction energy within the ($^\bullet CH_2PhCN$, Cl^-) pair decreases with solvent polarity (from 135 meV in 1,2-dichloroethane to 40 meV in formamide), in line with an increasing solvation ability toward the leaving chloride anion.[13b] In another family of three haloacetonitriles ($NCCH_2X$; X = Cl, Br, I), for which ion-radical pairs in DMF survive, the interaction rapidly decreases from Cl to Br and I thus showing a decreasing correlation with the halide radius.[14] Keeping the leaving group identical, it has been demonstrated that the intensity of the interaction decreases as the polar character of the remaining radical decreases: comparison within a family of polychloromethanes and polychloroethanes indeed indicate the following order of cluster interaction energies upon departure of a chloride anion, Cl_3C-CCl_3 ($D_{R^\bullet,Cl^-} \approx 190$ meV) > CCl_4 > $CHCl_3$, $Cl_2HC-CCl_3$ > CH_2Cl_2, $Cl_2HC-CHCl_2$, $ClH_2C-CHCl_2$ ($D_{R^\bullet,Cl^-} = 75$ meV), in line with the expected inductive effects.[8] The examples so far explored clearly indicate the formation of an electrostatic, endothermically cleaving ion-radical pair, which should be regarded as a σ-ion radical strongly influenced by the nature of the solvent.[13b,16] Additional experimental examples would be welcome to get more insights into the dynamics of the cleavage reaction, but it would also be valuable to explore the influence of intramolecular factors different from the electrophilicity of the remaining radical and from the nature of the leaving group on the interaction. Such effects may occur under the form of intramolecular hydrogen bonds. In the family of chloroacetamides investigated here, if one considers for example the 2-chloroacetamide derivative (***1a***), the hydrogen atoms borne by the nitrogen bear a partial positive charge and may interact with a negatively charged fragment. Consequently, the leaving Cl^- produced upon electrochemical dechlorination may interact with the acetamide radical more strongly than it does with *N*,*N*-dimethylacetamide radical (obtained from **1b** reductive dechlorination) in which the hydrogen atoms in the methyl groups are much less positively charged. This effect,

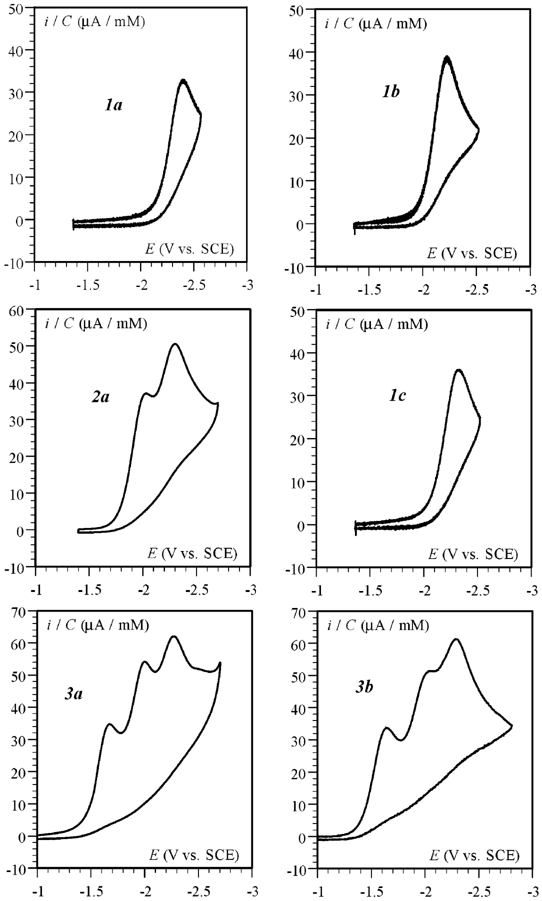


Figure 2. Cyclic voltammetry on a GC electrode, in DMF + 0.1 M NEt_4BF_4 + PhOH (1 eq with ***1a***, ***1b*** and ***1c***; 2 eq with ***2a***; 3 eq with ***3a*** and ***3b***). Scan rate: 0.2 V/s. Temperature: 25 °C. On the vertical axis, the current is normalized versus concentration.

induced by the molecular structure, may lead to the tuning of the cleavage dynamics in the series. Searching for such effects, their possible role and influence in the reaction dynamics was the second objective of our study. For this purpose, we will take advantage of the synergistic use of a sticky dissociative electron-transfer model and of quantum ab initio calculations in the interpretation of the experimental data.

Results

Heterogeneous Reductive Cleavage of Chloro- and Polychloroacetamides. Typical cyclic voltamograms of the six acetamide derivatives studied, obtained in DMF at low scan rate on a glassy carbon (GC) electrode, are shown in Figure 2. In all cases, the number of waves equals the number of chlorine atoms borne by the parent molecule. All the waves are bielectronic, provided that a small amount of acid is added to the solution. This also ensures that no secondary father-son reaction between the bases generated upon the reductive process and the starting compound occurs. In the case of 2-chloroacetamide (***1a***), the voltamograms exhibit a single irreversible wave, corresponding to the cleavage of the C−Cl bond. The acetamide radical formed upon charge transfer accepts a second electron since it is intrinsically more easily reducible than the starting neutral, and the carbanion is protonated from the added phenol, thus leading to a two-electron wave. The stoichiometry of the wave was inferred from comparison with the fully reversible wave of a standard redox compound (benzoquinone), for which the following equation applies[17]

$$i_{\mathrm{p}}^{\mathrm{1e,rev}} = 0.446 \times FSC^0\sqrt{D_{\mathrm{standard}}}\sqrt{\frac{Fv}{RT}}$$

while in the case of the acetamide the overall number of electrons n is given by

$$i_{\mathrm{p}}^{\mathrm{ne,irr}} = n \times 0.496 \times FSC^0\sqrt{D_{\mathrm{substrate}}}\sqrt{\frac{\alpha Fv}{RT}}$$

where i_p is the peak current, S is the electrode surface area, C^0 is the bulk concentration, D is the diffusion coefficient, and v is the scan rate. The transfer coefficient, α, was obtained from the peak-width, $E_{p/2} - E_p$:

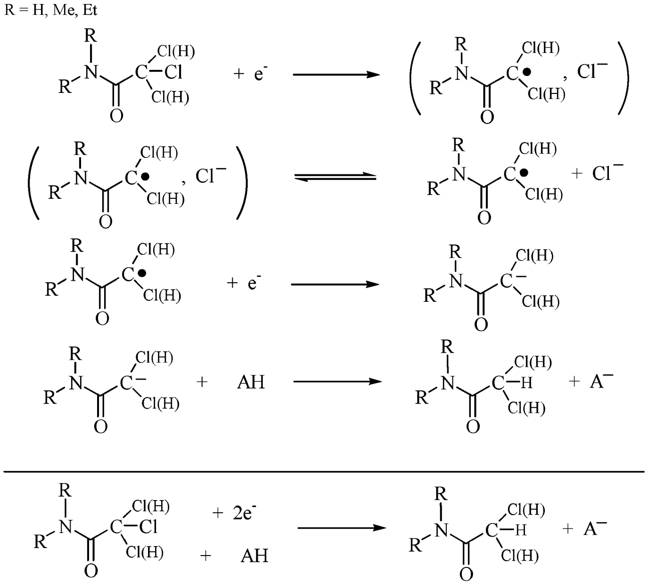
$$\alpha = 1.856\frac{RT}{F}\Big/(E_{\mathrm{p/2}} - E_{\mathrm{p}}) \qquad (2)$$

The kinetics of the reduction is under the control of the electron transfer, as indicated by the small values of α, which is below 0.35 at all scan rates. The smallness of the transfer coefficient also strongly suggests that charge transfer and bond breaking are in fact concerted (CDET).[1] Moreover, there is no second wave before the discharge of the supporting electrolyte, meaning that the acetamide resulting from cleavage is not reduced in the available potential window (this point was further checked with an authentic sample of acetamide). Since the standard redox potential of this latter compound should be close to that of the chlorinated substrate, a sequential reduction process (SDET) would have implied an α value greater than 0.5, thus providing an additional clue that the CDET mechanism is indeed followed.[18] With the two other monochloroacetamides ***1b*** and ***1c***, the voltamograms are very similar in shape and location to those observed with ***1a***. In both cases, the wave is bielectronic and is just slightly more positive than with ***1a***. The dynamics of the reduction process is again controlled by the electron-transfer step, and for the same reasons evoked with ***1a***, a CDET pathway is followed.

With 2,2-dichloroacetamide (***2a***), two successive irreversible two-electron waves are obtained. The second of these is the same as the single wave observed with ***1a***, thus showing that the reduction product of ***2a*** is indeed the monochloroacetamide ***1a***. As expected along the same lines, the voltamograms for the two trichloroacetamides ***3a*** and ***3b*** exhibit three irreversible bielectronic waves, due to the successive cleavage of the three C−Cl bonds. In all cases charge transfer kinetically determines the first cleavage step. The symmetry factor α for all polychloroacetamides (***2a***, ***3a***, and ***3b***) ranges between 0.30 and 0.36, strongly suggesting that a CDET reaction is followed with all three molecules. The general reaction sequence for the various substrates is summarized in Scheme 2.

Analysis of Cleavage Dynamics through the Application of the Sticky Dissociative Electron-Transfer Model. Coming now to the quantitative analysis of the cleavage reaction dynamics of the first C−Cl bond, we may apply the dissociative electron-transfer model, which allows for the existence of attractive interactions in the clustered products.[1a,13] As recalled in the Introduction, a quadratic activation-driving force relationship applies in such a case (eq 1), and the introduction of a parameter $D_{R^\bullet,X^-}$ that represents the interaction energy within the radical-ion pair has the effect of decreasing the intrinsic barrier and consequently of increasing the reaction rate. Briefly, the relation between the activation free energy, $\Delta G^\ddagger$, and the standard free energy, ΔG°, is obtained from the intersection of

SCHEME 2



the free energy of the reactant and product systems, G_R and G_P, respectively

$$G_R = D_{RX}Y^2 + \lambda_0(Y)X^2 \tag{3}$$

$$G_P = \Delta G^\circ - D_{R^\bullet,X^-} + D_{RX}\left(1 - \sqrt{\frac{D_{R^\bullet,X^-}}{D_{RX}}} - Y\right)^2 + \lambda_0(Y)(1 - X)^2 \tag{4}$$

which are both a function of two reaction coordinates X and Y. X is a nominal charge borne by the molecule, varying from 0 to 1, serving as an index for solvent reorganization. Y stands for bond breaking, being expressed, in the framework of a Morse curve approximation, by

$$Y = 1 - \exp[-\beta(y - y_{RX})]$$

with

$$\beta = \nu(2\pi^2\mu/D_{RX})^{1/2}$$

where y is the bond length, y_{RX} is the equilibrium value of y in the reactant system, ν is the frequency of the cleaving bond, μ is the reduced mass, and D_{RX} is the bond dissociation energy of the starting molecule. $\lambda_0(Y)$, the solvent reorganization energy, which is a priori a function of the elongation coordinate Y varies between a "reactant value" $3/a_{RX}$ (where a_{RX} is the equivalent hard sphere radius for the reactant) and a "product value", $3/a_{Cl^-}$, corresponding to chloride solvation (a_{Cl^-}, the ionic radius of Cl^- equals 1.81 Å).[8]

The standard free energy of the reaction leading to complete dissociation (E: electrode potential, $E^0_{RX/R^\bullet+X^-}$: standard potential of the $RX/R^\bullet + X^-$ couple) is given by

$$\Delta G^\circ = E - E^0_{RX/R^\bullet+X^-} = E + D_{RX} - T\Delta S^\circ - E^0_{X^\bullet/X^-} \tag{5}$$

where ΔS° is the bond dissociation entropy and $E^0_{X^\bullet/X^-}$ is the standard potential of the $X^\bullet/X^-$ couple.

The transition state (quantity marked with $\neq$) is characterized as the intersection minimum of reactant and product surfaces. This intersection is defined by $G_R{}^\ddagger = G_P{}^\ddagger$ and $(\partial G_R/\partial X)/(\partial G_P/\partial X) = (\partial G_R/\partial Y)/(\partial G_P/\partial Y)$ thus leading to the set of the three following equations

$$\Delta G^\ddagger = G_R{}^\ddagger - G_R(X = 0, Y = 0) = D_{RX}Y^{\ddagger 2} + \lambda_0{}^\ddagger X^{\ddagger 2} \tag{6}$$

$$Y^\ddagger = \left(1 - \sqrt{\frac{D_{R^\bullet,X^-}}{D_{RX}}}\right)X^\ddagger \tag{7}$$

$$\Delta G^\circ = D_{R^\bullet,X^-} + \left\{D_{RX}\left(1 - \sqrt{\frac{D_{R^\bullet,X^-}}{D_{RX}}}\right)^2 + \lambda_0{}^\ddagger\right\}(2X^\ddagger - 1) \tag{8}$$

In deriving the free energies from eqs 3 and 4, $\lambda_0(Y)$ was kept constant. It indeed appears in practice that the solvent reorganization energy at the transition state can be considered as approximately constant over the whole range of driving forces investigated (see data in Table 1), even if the density of electric charges on the molecule represented by $X^\ddagger$ and the elongation coordinate $Y^\ddagger$ vary when the driving force is modulated, as it can be seen from eqs 7 and 8.

We use these equations to test the applicability of the model to the compounds investigated and to determine the interaction energies in the fragment cluster. The experimental data for the plots $\Delta G^\ddagger$ vs ΔG° were obtained from the shape and location of the voltammetric waves. Derivation of the activation free energy at the peak potential was done according to[20]

$$\Delta G_{peak} = \frac{RT}{F}\left\{\ln\left(Z^{el}\sqrt{\frac{RT}{\alpha F v D}}\right) - 0.78\right\} \tag{9}$$

where v is the scan rate and D is the diffusion coefficient (taken as equal to 10^{-5} cm^2 s^{-1} in average). α is the transfer coefficient and is extracted from peak-width through eq 2. The preexponential factor is taken as equal to the electrochemical collision frequency

$$Z^{el} = (\sqrt{RT/2\pi M}) \tag{10}$$

where M is the molar mass. The experimental standard free energies at the peak were estimated through eq 5 by taking $E = E_{peak}$.

In these determinations, the bond dissociation entropies and the bond dissociation energies of the neutrals were calculated by quantum chemical calculations, by means of a DFT calculation method particularly suited to the estimation of BDEs for chloro and polychloro compounds (see the Quantum Chemical Calculations section). Error bars were further put on $D_{R^\bullet,X^-}$ values, and ensuing errors were estimated through

$$\Delta D_{R^\bullet,X^-} \approx \frac{3 - \sqrt{D_{R^\bullet,X^-}/D_{RX}}}{1 + \sqrt{D_{RX}/D_{R^\bullet,X^-}}}\Delta D_{RX}$$

The $\Delta G^\ddagger_{peak}/\Delta G^\circ_{peak}$ plots were fitted with modeling curves generated from eqs 6−8. After choosing a test value for $D_{R^\bullet,X^-}$ and a starting guess value for $\lambda_0^\ddagger$ between its reactant and product boundaries, application of eqs 6, 7, and 8 leads to a set of values for $\Delta G^\ddagger$, ΔG°, and $\lambda_0^\ddagger$ in a rapidly converging procedure. Then $D_{R^\bullet,X^-}$ was varied, and the procedure was repeated, until a good agreement was reached with experimental data over the whole range of driving force. The results are shown in Figure 3 and gathered in Table 1. One can see there is a good agreement between the theoretical predictions and the experimental data points, thus validating the 'sticky' CDET

TABLE 1: Parameters for the Application of the 'Sticky' CDET Model to Chloro- and Polychloroacetamides

compd	Z_{el}[a] (cm/s)	α	E_{peak}[b] (V vs SCE)	$T\Delta S^{\circ}$[c] (eV)	$E^{0}_{RX/R^{\bullet}+X^{-}}$[d] (V vs SCE)	$\lambda_0^{\ddagger}$[e] (eV)	D_{RX}[f] (eV)	$D_{R^{\bullet},X^{-}}$[g] (eV)
1a	6497	0.29−0.30	−2.425	0.33_5	−1.356	1.17	3.50 ± 0.05	0.150 ± 0.025
1b	5689	0.27−0.32	−2.275	0.30	−1.231	0.97	3.34 ± 0.05	0.100 ± 0.020
1c	5136	0.28−0.34	−2.325	0.33_5	−1.213	0.97	3.36 ± 0.05	0.085 ± 0.020
2a	5513	0.34−0.36	−2.102	0.33	−1.033	1.03	3.18 ± 0.05	0.090 ± 0.020
3a	4928	0.34−0.36	−1.745	0.34	−0.628	1.07	2.78 ± 0.04	0.040 ± 0.015
3b	4552	0.28−0.31	−1.610	0.35	−0.700	0.92	2.86 ± 0.04	0.080 ± 0.015

[a] Heterogeneous collision factor (see text). [b] At 0.1 V/s. [c] Standard entropic term of the reaction $RX \rightarrow R^{\bullet} + X^{\bullet}$ at the temperature of the experiment.[19] [d] Dissociative standard potential from eq 5. [e] Averaged solvent reorganization energy at the transition state (for each compound, variations do not exceed 3% in the covered range of driving forces). [f] Substrate bond dissociation energy. [g] Ion-radical interaction energy.

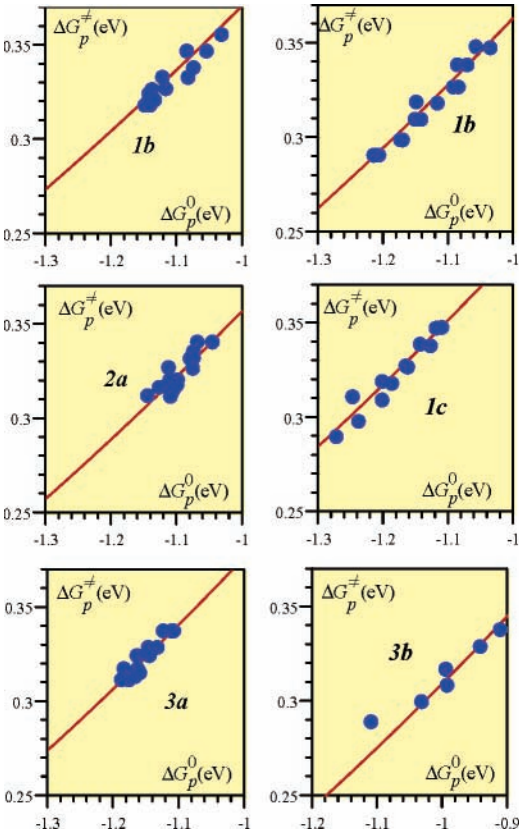


Figure 3. Activation−driving force plots obtained from the variation of the peak potential with the scan rate using eqs 5 and 9 (blue dots) and from the application of eqs 6−8 (parameter values from Table 1) for all six acetamide derivatives.

mechanism and the values found for the interaction energies between the caged fragments.

Discussion

With all six compounds, the analysis of the data shows that there is formation of a fragment cluster upon dissociative charge transfer. The interaction energies in the radical-ion pairs are measurable despite the polar character of the solvent and are in the range of the values previously obtained with polychloromethanes and polychloroethanes, as well as with 4-cyanobenzyl chloride. The fact the acetamide radicals formed upon cleavage are polarized together with the magnitude of the sticky interactions reinforce the idea that such adducts should be viewed as being mainly electrostatic radical-ion pairs rather than covalently bound molecules. In the polychloroalkyl series, it was shown that the interaction increases with the number of chlorine atoms borne by the molecule, parallel to the electrophilicity of the remaining radical.[8] The following order of clustering energies was obtained, in line with the expected inductive effect: $Cl_3C-CCl_3 > CCl_4 > CHCl_3$, $Cl_2HC-CCl_3 > CH_2Cl_2$, $Cl_2HC-CHCl_2$, $ClH_2C-CHCl_2$. Such an observation also holds true in a polychloroacetonitrile series. However, at variance with these previous findings, it is observed that in the series ***1a***, ***2a***, ***3a***, the sticky interaction decreases with the number of chlorine atoms borne by the carbon bearing the leaving group in the parent molecules, with values of $D_{R^{\bullet},X^{-}}$ equal to 150, 90 and 40 meV, respectively. The same observation holds true when passing from ***1b*** to ***3b***, since the interaction energy drops from 100 to 80 meV. Despite the small differences between these values, the accuracy on the determination of the interaction energies (see Table 1) shows that these trends are meaningful.

To understand these variations, we looked at the gas-phase clusters formed between $^{\bullet}R$ and Cl^{-} upon electron-transfer calculated at the same level as the computed bond-dissociation energies (see the Quantum Chemical Calculations section). Even if the surrounding polar solvent molecules may alter the structure of these σ-ion radicals, in particular the C−Cl bond cleaving distance and the chlorine atom location, such calculations may give important clues on the pairing structures as a function of the number of chlorine atoms on the parent molecule and of the substituent borne by the nitrogen atom of the amide group. Briefly, the clusters were identified as minima on the potential energy surfaces associated with the reductive cleavage of the substrates ($RCl + 1e^{-}$) and the negative charge appears to be mainly borne by the chloride leaving anion. The minima corresponding to the one-electron reduction of substrates ***1a***, ***1b***, ***2a***, ***3a***, and ***3b*** are all sketched in Figure 4. The dipole moments (μ) of the acetamide radicals were also computed from their optimized geometries and are given along with the cluster configurations in Figure 4 (acetamide radicals resulting from complete dissociation and acetamide moieties inside clusters almost have the same geometrical features).

We look first at the effect of the substituent borne by the nitrogen atom. Comparing the minima obtained for the reduction of ***1a*** and ***1b***, the main difference does not arise from difference in the polar character of the remaining radical but rather from the fact that upon Cl^{-} leaving in 2-chloroacetamide, an intracluster hydrogen bond formed between Cl^{-} and one of the two hydrogen atoms borne by the nitrogen, strengthens the sticky interaction, which consequently increases from almost 100 meV up to 150 meV, thus giving an additional stability of about 5 kJ/mol to the caged fragments, a magnitude that seems reasonable for this type of interaction. When passing from ***1b*** to ***1c*** (cluster not shown), the sticky interaction just slightly decreases, which is likely the consequence of a looser structure at the cluster level, due to the presence of the more bulky ethyl groups attached to the nitrogen atom.

We may discuss now the effect of the number of chlorine atoms present on the parent molecule. On going from ***1b*** to ***3b***, one can see that the polarity of the radical moiety within the cluster is reduced, and at the same time a looser structure at

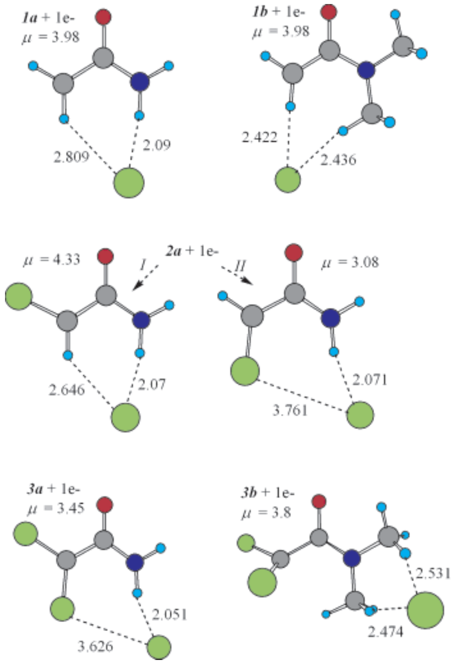


Figure 4. Gas-phase ion-radical clusters ($^•$R, Cl$^-$) formed upon the reduction of chloroacetamides ***1a***, ***1b***, ***2a***, ***3a***, and ***3b***, at the B3P86/6-311++G(2df,p) level of calculation (interatomic distances in Å, dipole moments, μ, in D).

the level of the cluster is found, which may be ascribed to repulsive interactions between the two chlorine atoms and the leaving chloride anion, thus leading to a smaller value of $D_{R^•,X^-}$. As mentioned earlier, a striking feature is the decrease of the interaction energies along the series ***1a***, ***2a***, ***3a***. Ion-radical clusters are almost planar (Figure 4) for all three substrates, and the weakest interaction is found with ***3a*** and amounts to only 40 meV. With this latter derivative, the dipole moment of the remaining radical is the weakest of all six acetamides, and the cluster configuration suggests that repulsive interactions between the leaving anion and the chlorine atoms are maximized, thus leading to less stable caged fragments, despite the fact that like with ***1a***, an intramolecular hydrogen bond may stabilize the interacting fragments. The case of ***2a*** is somehow unique since two distinct clusters are found on the potential energy surface en route to dissociation (Figure 4, pairs *I* and *II*). The more stable cluster (pair *I*) has a similar structure to the one calculated for the reduction of ***1a***, with a strong dipole moment of the radical part and an intramolecular hydrogen bond between the chloride and a partially negatively charged hydrogen atom. A less stable cluster was also found (pair *II*), whose characteristics are close to the pair found for the reduction of ***3a***, with a reduced polar character of the radical part and repulsive interaction between the chlorine and the chloride. The experimentally measured ion-radical interaction energy amounts to 100 meV and may reflect an averaged value due to the formation of both clusters, the pair *I* being statistically favored since it should be formed more easily on kinetic grounds.

Conclusion

Electrochemical reduction of chloro- and polychloroacetamides leads to full dechlorination in successive and separated steps each corresponding to the cleavage of one C−Cl bond. Each of these steps was characterized as a concerted dissociative electron transfer followed by further reduction of the remaining radical which is protonated by any trace of acid present in the reaction medium. These sequences thus yield to acetamides. The dynamics of the concerted charge-transfer/bond-breaking reaction was analyzed through the sticky concerted dissociative electron-transfer model. In all cases, ion-radical interaction in the product cluster resulting from cleavage are quite significant and are associated with a large decrease of the contribution of intramolecular reorganization to the intrinsic barrier. These interactions are jointly controlled by the electrophilicity of the intermediate radical, the more-or-less loose structure inside the fragment cluster, eventual repulsive interactions between the leaving chloride and the remaining chlorines, and finally by an intramolecular hydrogen bond that may give an additional stability to the pair, as is observed with 2-chloracetamide where the sticky interaction is largest.

Experimental Section

Chemicals. *N*,*N*-Dimethylformamide (Fluka, >99.5%, stored on molecular sieves and under argon atmosphere), the supporting electrolyte NEt_4BF_4 (Fluka, puriss), 2-chloroacetamide (Aldrich), 2-chloro-*N*,*N*-dimethylacetamide (Merck > 98%), 2-chloro-*N*,*N*-diethylacetamide (Merck > 98%), 2,2-dichloroacetamide (Aldrich > 98%), 2,2,2-trichloracetamide (Aldrich > 98%) and 2,2,2,-trichloro-*N*,*N*-dimethylacetamide (Frinton Lab) were used as received.

Instrumentation. The working electrode was a 3-mm diameter glassy carbon electrode disk (Tokai) carefully polished and ultrasonically rinsed in absolute ethanol before use. The counter electrode was a platinum wire and the reference electrode an aqueous SCE electrode. The potentiostat, equipped with positive feedback compensation and current measurer, used at low or moderate scan rates, was the same as previously described.[21] All experiments have been done at 25 °C, the double-wall jacketed cell being thermostated by circulation of water.

Quantum Chemical Calculations

All the calculations were performed with the Gaussian 98 series of programs.[22] The DFT (B3P86) method and the 6-311++G(2df,p) basis set were used, in particular for calculation of bond-dissociation energies.[23] Minimum energy structures were fully optimized. Frequency calculations were made to verify that the structures were minima (no imaginary frequencies) and to evaluate thermodynamical functions.

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(19) The standard values calculated in gas phase have to be corrected for the change in the standard state when passing from the gas to the liquid phase (1 atm and 1 mol/L respectively) which amounts to decreasing each of the values obtained by R/F ln(22.4), i.e., 0.268 meV/(mol K).

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