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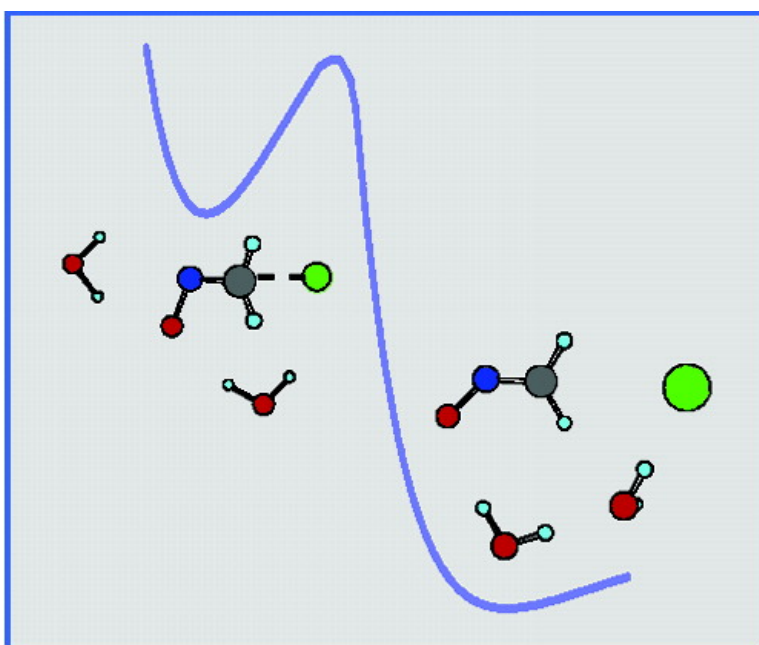# Stepwise and Concerted Electron-Transfer/Bond Breaking Reactions. Solvent Control of the Existence of Unstable Ion Radicals and of the Activation Barriers of Their Heterolytic Cleavage

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Stepwise and Concerted Electron-Transfer/Bond Breaking Reactions. Solvent Control of the Existence of Unstable π Ion Radicals and of the Activation Barriers of Their Heterolytic Cleavage

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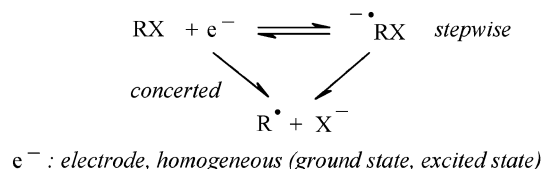
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Abstract: Available data from various sources seem to indicate an important role of solvation in the cleavage rates of intermediate π ion radicals, in the passage from concerted to stepwise electron-transfer/bond breaking reaction pathways and even in the very existence of π ion radicals. After preliminary computations treating the solvent as dielectric continuum, these expectations are examined with the help of a simple model system involving the anion radical of $ONCH_2Cl$ and two molecules of water, which allows the application of advanced computational techniques and a treatment of these solvent effects that emphasizes the role of solvent molecules that sit close to the charge centers of the molecule. A π ion radical minimum indeed appears upon introduction of the two water molecules, and cleavage is accompanied by their displacement toward the leaving anion, thus offering a qualitative mimicry of the experimental observations.

Introduction

The coupling between electron transfer and bond breaking may competitively involve a concerted and a stepwise pathway as sketched in Scheme 1 and, in terms of potential energy

Scheme 1

$$RX + e^- \rightleftharpoons {}^{-\bullet}RX \quad \textit{stepwise}$$

$$\textit{concerted} \searrow \quad \swarrow$$

$$R^\bullet + X^-$$

e^- : electrode, homogeneous (ground state, excited state)

profiles, in Figure 1.[1,2] If the intermediate anion radical "does not exist", that is, live less than a vibration, the concerted
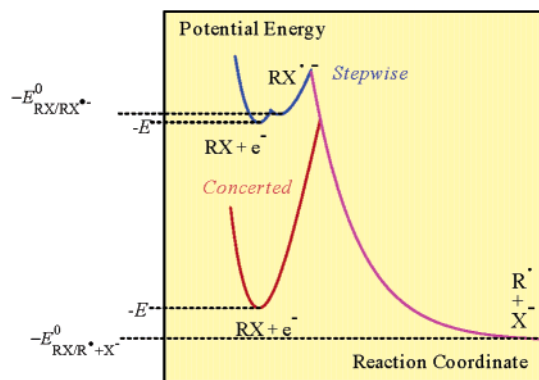

Figure 1. Potential energy profiles for the concerted and stepwise pathways according to Scheme 1. The E^0's are the standard potentials of the subscript couples. E is the electrode potential or the standard potential of the homogeneous donor.

pathway is necessarily followed. If the intermediate exists, the stepwise pathway is not necessarily followed. The reaction proceeds through the most energetically favorable paths as sketched in Figure 1. The competition between the two routes hinges on structural factors that are related to the three terms in the expression of the standard free energy for the cleavage of the intermediate anion radical (eq 1):

$$\Delta G^0_{{}^{-\bullet}RX \to R^\bullet + X^-} = D_{RX \to R^\bullet + X^\bullet} - T\Delta S_{RX \to R^\bullet + X^\bullet} + E^0_{RX/{}^{-\bullet}RX} - E^0_{X^\bullet/X^-} \quad (1)$$

where $D_{RX \to R^\bullet + X^\bullet}$ is the RX bond dissociation energy, $\Delta S_{RX \to R^\bullet + X^\bullet}$ is the corresponding entropy change, and $E^0_{RX/{}^{-\bullet}RX}$, $E^0_{X^\bullet/X^-}$ is the
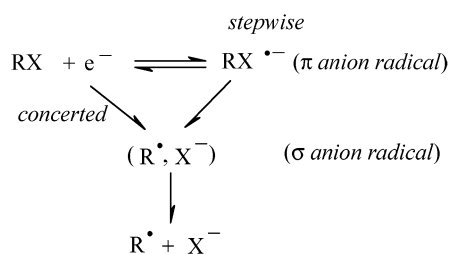
(1) (a) For reviews see refs 1b–f. For additional key references, see refs 1g–m. (b) Savéant, J.-M. Single Electron Transfer and Nucleophilic Substitution. In *Advances in Physical Organic Chemistry*; Bethel, D., Ed.; Academic Press: New York, 1990; Vol. 26, pp 1–130. (c) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455. (d) Savéant, J.-M. Electron Transfer, Bond Breaking and Bond Formation. In *Advances in Physical Organic Chemistry*; Tidwell, T. T., Ed.; Academic Press: New York, 2000; Vol. 35, pp 117–192. (e) Maran, F.; Wayner, D. D. M.; Workentin, M. S. In *Advances in Physical Organic Chemistry*; Tidwell, T. T., Ed.; Academic Press: New York, 2001; Vol. 36, pp 85–116. (f) Rossi, R. A.; Pierini, A. B.; Penenory, A. B. *Chem. Rev.* **2003**, *103*, 71. (g) Maslak, P.; Vallombroso, T. M.; Chapmann, W. H.; Narvaez, J. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 73. (h) Maslak, P.; Chapmann, W. H.; Vallombroso, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12373. (i) Maslak, P.; Narvaez, J. N.; Vallombroso, T. M.; Watson, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12380. (j) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 65362. (k) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 1844. (l) Tanko, J. M.; Drumright, R. E.; Suleman, N. K.; Brammer, L. E., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 1795. (m) Tanko, J. M.; Phillips, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 6078.
(2) Throughout the article we take as example the reduction of a neutral molecule leading to an anion radical. All the developments also apply for the oxidation of a neutral molecule leading to a cation radical.

standard potentials of the subscript couples, energies in eV, potentials in V. The more negative $\Delta G^0_{RX^{\bullet-}\rightarrow R^{\bullet}+X^-}$, the more favorable the concerted pathway, and vice versa. The outcome of the competition also depends of the driving force offered by the electron donor. As represented in Figure 1 by a vertical upward translation of the reactant curve, a strong reducing power favors the stepwise route and vice versa. Thus in borderline situations, the system passes from one mechanism to the other upon variation of the electrode potential or of the standard potential of the homogeneous electron donor,[3] possibly making systems that are concerted in electrochemistry become stepwise in a photoinduced electron-transfer reaction.[4]

The classical Hush−Marcus model of outersphere electron transfer[5] is applicable to the electron-transfer step of the stepwise reaction, while Morse curve models can be used for the concerted pathway[6] and for the cleavage of the intermediate anion radical in the stepwise case.[7] All three reactions are characterized by a quadratic activation/driving force relationship. In each case, the intrinsic barrier may be expressed by means of parameters involving the reactant and product states, its main component being the bond dissociation energy for the two bond-breaking reactions. The anion radical cleavage may be heterolytic (as shown in Scheme 1 and eq 1) or homolytic ($^{-\bullet}RX \rightarrow R^- + X^{\bullet}$).[1,8] In the heterolytic case,[1d,7,9] as well as in the homolytic case,[10] it can be viewed as an intramolecular dissociative electron-transfer reaction.

These mechanism analyses have been recently improved by consideration of the interactions that may exist between the cage fragments resulting from cleavage, leading to what can be alternatively called a σ ion radical (Scheme 2).[11a] There are

Scheme 2

$$RX + e^- \rightleftharpoons RX^{\bullet-} \quad (\pi\ anion\ radical)$$

stepwise

concerted

$$(R^{\bullet}, X^-) \quad (\sigma\ anion\ radical)$$

$$R^{\bullet} + X^-$$

definite clues that these adducts may survive in polar solvents, although considerably weakened as compared to their gas-phase
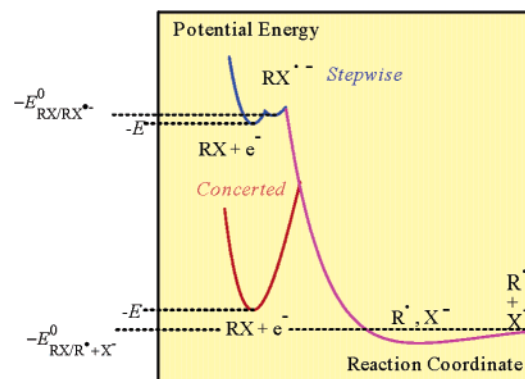

Figure 2. Potential energy profiles for the concerted and stepwise pathways involving the formation of a σ ion radical according to Scheme 2. The E^0's are the standard potentials of the subscript couples. E is the electrode potential or the standard potential of the homogeneous donor.

counterparts.[11b] The corresponding potential energy profiles are as shown in Figure 2. Quadratic activation/driving force relationships are still found but with diminished contributions of the bond-dissociation energies.[11a,12] The stability of the σ anion radical adduct varies with the nature of the solvent. It decreases as the leaving group solvating power of the solvent increases.[11b]

In the context just recalled, the purpose of the present article is to discuss the influence of the solvent, not only on the cleavage rate of the intermediate π ion radical but also on the concerted vs stepwise dichotomy and on the very existence of the intermediate ion radical. In the first section, we gather and discuss experimental clues found in the literature of such roles of the solvent as well as preliminary quantum chemical calculations concerning some of these experimental systems. In the next section, a more precise investigation of these questions is carried out on a simple model system, namely the anion radical of $ONCH_2Cl$ in the presence of two water molecules representing the effect of the solvent, thus allowing the application of higher level computational techniques.

Experimental Clues. Preliminary Computations

We discuss below the behavior of selected systems that give precious indications about the possible role of the solvent in electron-transfer/bond breaking reactions.

Solvent Reorganization in the Cleavage of α-Substituted Acetophenones Anion Radicals. An example is provided by the electrochemical reduction of a series of α- and ring-substituted acetophenones (Chart 1) in acetonitrile.[13] They all follow a stepwise mechanism. The rate constants for the cleavage of the anion radicals correlate with the driving force along a common quadratic law, thus indicating that the intrinsic barrier is quite substantial and approximately the same for all

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(10) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 105.

(11) (a) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2000**, *122*, 9829. (b) Pause, L.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 11908.

(12) In both cases, the bond dissociation energies, noted D, are replaced by $(\sqrt{D} - \sqrt{D_{R^{\bullet},X^-\rightarrow R^{\bullet}+X^-}})^2$, leading to a substantial lowering of the barrier even for small values of $D_{R^{\bullet},X^-\rightarrow R^{\bullet}+X^-}$.

(13) Andrieux, C. P.; Savéant, J.-M.; Tallec, A.; Tardivel, R.; Tardy, C. *J. Am. Chem. Soc.* **1996**, *118*, 9788.

Chart 1

Chart 2
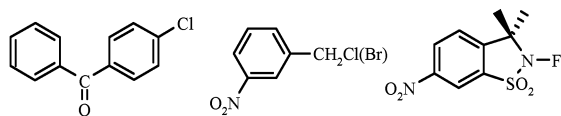
compounds (∼0.7 eV) although very different leaving and remaining groups are involved. An estimate of the intramolecular contribution to the intrinsic barrier shows that it is small, leading to the conclusion that the main contribution is that of the solvent reorganization that attends the shift of the negative charge from the carbonyl oxygen of the radical anion to the leaving anion upon cleavage.

Effect of Water Addition on the Cleavage Rate of Anion Radicals in Acetonitrile. Another manifestation of the importance of solvation as a factor controlling the rate of cleavage of anion radicals can be found in experiments carried out in acetonitrile where the effect of water addition has been investigated[14] for the anion radicals of the three compounds shown in Chart 2. In all cases, the addition of water slows down the cleavage of the anion radical, in parallel with a positive shift of the standard potential for its formation. In pure water, the cleavage of the anion radicals of 3-nitro benzyl chloride and bromide becomes accordingly very slow.[9c]

Reductive Cleavage of Nitro and Cyanobenzyl Halides. The preceding two series of examples provide evidence that polar solvents tend to stabilize π ion radicals. We may thus infer that a strong solvation should tend to favor the stepwise mechanism at the expense of the concerted mechanism. At this stage, it is thus worthwhile having a closer look at the compared behaviors of 3- and 4-nitro and cyanobenzyl halides.

The experimental data regarding the reductive cleavage of these compounds are summarized in Table 1.

With the two nitro compounds, a stepwise mechanism is followed both in DMF and in water. As expected, the cleavage rate constant diminishes from DMF to water. The decrease is much more important for the para- than for the meta-derivative. It is interesting to see whether these experimental trends are reproduced by quantum mechanical calculations. Figure 3 shows the potential energy profiles of the corresponding anion radicals obtained from B3LYP/6-31G* density functional calculations in the gas phase as well as the effect of solvation simulated by the COSMO dielectric continuum method (see Methodology for Quantum Chemical Calculations section) for two values of the dielectric constant, 36.6 and 78.4, aiming at simulating DMF and water, respectively.

The profile for the meta-isomer in the gas phase corresponds to a stepwise mechanism with successive formation of a π anion

(14) Andrieux, C. P.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 9340.

Table 1. Characteristics of the One-Electron Reductive Cleavage of Nitro and Cyanobenzyl Halides

compound	solvent	technique	mechanism [a]	ref.
	DMF	CV [b]	stepwise (15 [e])	14
	H_2O	PR [c]	stepwise (<5)	9c
	DMF	CV	stepwise (8×10^6)	15
	H_2O	PR	stepwise (8×10^3)	9d
	DMF	CV	concerted	4
		PET [d]	concerted	4
	H_2O	PR	stepwise ($>3 \times 10^7$)	9b
	DMF	CV	concerted	15
	H_2O	PR	stepwise ($>6 \times 10^7$)	9b
	DMF	CV	concerted	15
	H_2O	PR	stepwise (10^7)	9b

[a] Between parentheses: cleavage rate constant in s^{-1} in the stepwise case. [b] Cyclic voltammetry. [c] Pulse radiolysis. [d] Photoinduced electron transfer. [e] Decreases to 1.5 s^{-1} upon addition of 1 mol L^{-1} H_2O.

radical and a σ anion radical as attested by the appearance of two successive minima on the profile. Upon solvation, the first minimum becomes deeper, while the second disappears. With the para-isomer, the first minimum is hardly visible in the gas phase, being reduced to a small shoulder on the rising part of the σ anion radical curve. A distinct albeit small π anion radical minimum appears upon solvation, while the σ anion radical minimum disappears. The general experimental trends as to the role of the solvent and the comparison between the meta- and para-isomers are thus qualitatively reproduced by the calculations. However, the barriers for the cleavage of the π anion radicals are much too small to match the experimental data. Also, the larger sensitivity of the para-isomer to the solvent effect as compared to the meta-isomer is poorly reproduced by the calculations. Last, but not least, there is practically no change in the profiles when passing from $\epsilon = 36.6$ to $\epsilon = 78.4$ in contrast with the strong slowing down of the cleavage from DMF to water. The similarity of the solvation energies in water and DMF derives from the fact that a change of dielectric constant from 78.4 to 36.6 is not expected to change significantly the predominant electrostatic term.

Coming now to the cyanobenzyl halides, the general tendency is that the cleavage is faster than with the nitro derivatives, so fast that the reaction eventually becomes concerted (Table 1). There is a thermodynamical reason for this acceleration, namely that the standard potential $E^0_{RX/{}^{\bullet}RX}$ is more negative in the first case than in the second (because CN is a weaker electron-withdrawing group than NO_2), thus offering more driving force to cleavage (eq 1), which is likely to be amplified by a decrease of the intrinsic barrier.

All three cyanobenzyl derivatives follow a concerted mechanism in electrochemistry, with DMF as solvent, under the standard conditions of cyclic voltammetry. With 4-cyanobenzyl chloride this is also the case even for photoinduced electron
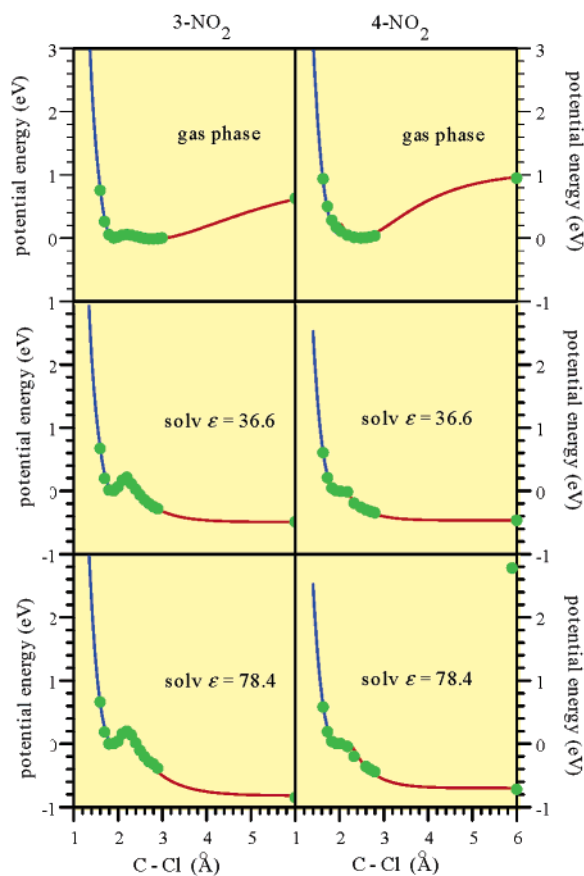
Figure 3. Potential energy profiles (from B3LYP/6-31G* calculations) for the cleavage of 3- and 4-nitrobenzyl chloride anion radicals in the gas phase (top) and in a solvent (middle and bottom) (from COSMO solvation calculations with a dielectric constant of 36.6 and 78.4, respectively). Full lines: best fitting Morse or dissociative Morse curves.

Figure 4. Potential energy profiles (from B3LYP/6-31G* calculations) for the cleavage of 4-cyanobenzyl chloride anion radical in the gas phase (top) and in a solvent (middle and bottom) (from COSMO solvation calculations with a dielectric constant of 36.6 and 78.4, respectively). Full lines: best fitting Morse or dissociative Morse curves.

transfer, in the same solvent, for a reducing power of the electron donor excited state measured by a standard potential of ca. -3 V vs SCE, while the potential window for cyclic voltammetry ranges from ca. -1.7 to -2 V vs SCE. The fact that a stepwise mechanism, with a very fast cleavage step, was observed in pulse radiolysis is therefore related to the use of water as a solvent. The same conclusion appears to also hold for the two other cyanobenzyl halides.

The same type of calculations as performed with the nitro derivatives produced the results displayed in Figures 4 and 5. As with the nitro compounds, the σ anion radical minimum vanishes upon solvation. In the gas phase, there is no π anion radical minimum even with 3-cyanobenzyl bromide, only an almost undetectable inflection in the rising part of the σ anion radical curve. The inflection is somewhat more apparent upon solvation. It has about the same importance for $\epsilon = 36.6$ and $\epsilon = 78.4$. The same is true with 4-cyanobenzyl chloride and bromide, actually even truer in the sense that the inflections representing the tendency to form the π anion radical are even less marked. As with the nitro derivatives, the calculations give a correct general picture of the effect of the solvent, but underestimate the role of the solvent in the stabilization of the π anion radical intermediate. The situation is in fact worse than with the nitro derivatives, since the underestimation of the solvent effect has a mechanistic consequence, namely that the concerted/stepwise transition is misplaced. Another obvious drawback of the calculations is the fact that the profiles are
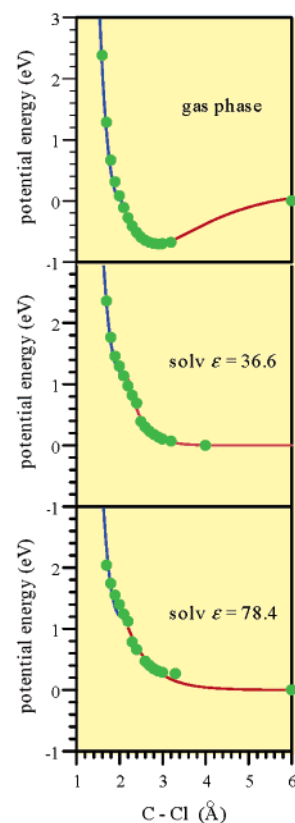
practically the same with $\epsilon = 36.6$ and $\epsilon = 78.4$, in contrast with experimental observations.

A Simplified Model System

The overestimation of the cleavage rates depicted in the preceding section may be assigned to two sources. One could be the inaccuracy of DFT techniques in the depiction of bond cleavage in open shell species. The other may be the imprecision, or even the inappropriateness, of dielectric continuum approaches of solvation in the present cases where microsolvation[16] of small domains of the molecules (nitro or cyano groups and leaving anion) is likely to play a prominent role. This last suspicion is reinforced by the lack of sensitivity of the calculated potential energy profiles to a change of the dielectric constant aiming to mimic the passage from DMF to water.

To get further insights into the problem, we therefore selected a simplified system consisting in the anion radical of ONCH$_2$-Cl plus two water molecules. This allowed us to raise the quality of computations to the QCISD(T)/6-31G* level based on QCISD/6-31G* or B3LYP/6-31G* optimized geometries (see Methodology for Quantum Chemical Calculations section) and to investigate the microsolvation aspects of the problem, even

(15) Andrieux, C. P.; Le Gorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892.
(16) (a) Sicinska, D.; Paneth, P.; Truhlar, D. G. *J. Phys. Chem. B* **2002**, *106*, 2708. (b) Barthel, E. R.; Martini, I. B.; Schwartz, B. J. *J. Phys. Chem. B* **2001**, *105*, 12230.
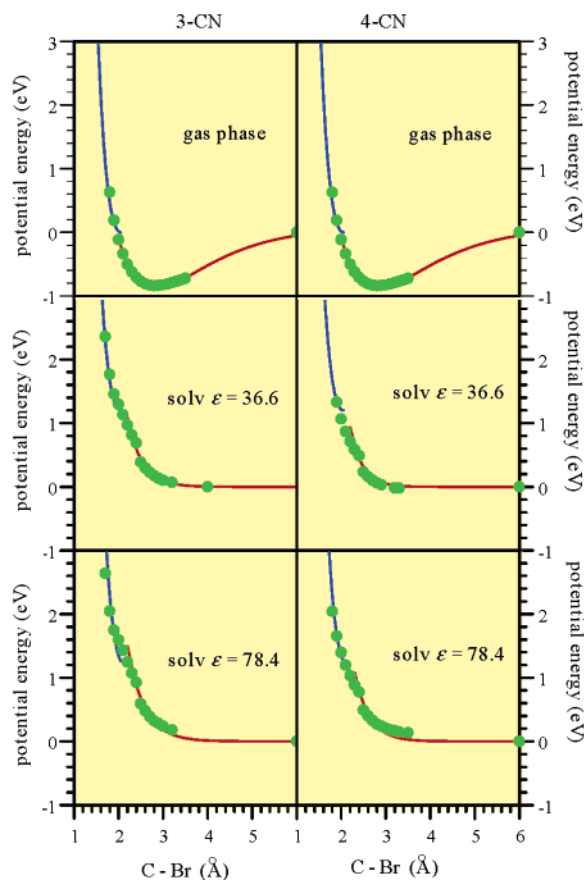
Figure 5. Potential energy profiles (from B3LYP/6-31G* calculations) for the cleavage of 3- and 4-cyanobenzyl bromide anion radicals in the gas phase (top) and in a solvent (middle and bottom) (from COSMO solvation calculations with a dielectric constant of 36.6 and 78.4, respectively). Full lines: best fitting Morse or dissociative Morse curves.

Figure 6. Potential energy profiles (from QCISD(T)/6-31G* calculations) for the cleavage of $ONCH_2Cl$ anion radical in the gas phase (top) and in a solvent (middle and bottom) (from IPCM solvation calculations with a dielectric constant of 36.6 and 78.4, respectively). Full lines: best fitting Morse or dissociative Morse curves.

though in a very simplified manner aiming at uncovering qualitative trends rather than reproducing a real situation.

The potential energy profile of $ONCH_2Cl + e^-$ in the gas phase, computed under the conditions defined above, is shown in Figure 6. Application of a dielectric continuum estimation of solvation with dielectric constants representing DMF and water respectively leads to the other two profiles shown in Figure 6. It is interesting to note that the results are very similar to those obtained from B3LYP/6-31G* calculations. It follows that the $ONCH_2Cl$ system stands somewhere between the 4-nitro (Figure 3, right) and 4-cyano (Figure 4) benzyl chloride. It also appears that the calculation technique is not responsible for the lack of a clear energy minimum corresponding to a definite π anion radical minimum on the potential energy profiles. We therefore suspect instead dielectric continuum estimates of solvation to undervalue the solvation stabilization of the π anion radical and, incidentally, to overvalue the solvation destabilization of the σ anion radical. As before, the profiles are practically the same for $\epsilon = 36.6$ and $\epsilon = 78.4$.

We thus turn now to the results obtained with the $ONCH_2$-$Cl + e^- + 2 H_2O$ system. Both water molecules are placed near the NO moiety and then let free to move. Two relevant minima (Figure 7, bottom), fully characterized as such by means of frequency calculations, are found on the energy surface. One is found at short C—Cl distance (2.40 Å). In this structure, the interaction between the oxygen of the NO group and the closest
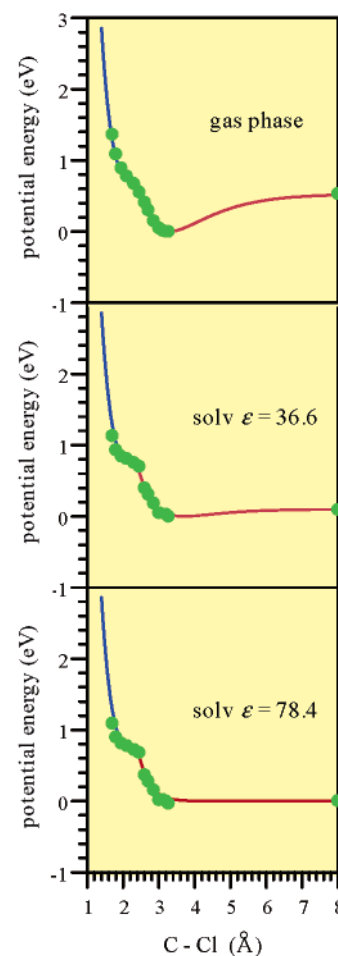
water molecule is strong (distance $_{(HO)}H\cdots O_{(NCH_2Cl^{\bullet-})} = 1.86$ Å). The interaction between the Cl atom and the other water molecule is weak (distance $_{(HO)}H\cdots Cl_{(CH_2NO^{\bullet-})} = 2.52$ Å). This water molecule also interacts with the oxygen of the NO group. The other minimum is found at long C—Cl distance (3.30 Å). In this structure, the interaction between the oxygen of the NO group and the closest water molecule is weakened (the distance is increased to 2.21 Å), while the interaction between the Cl atom and the second water molecule is strengthened (the distance is decreased to 2.15 Å). Although the role of the water molecule that stands closest to either the oxygen of the NO or the leaving Cl^- is predominant, we also see a displacement of the other water molecule in the same direction. In total, there is a global displacement of the two water molecules representing the solvent from oxygen of the NO or the leaving Cl^- as the intramolecular dissociative electron transfer takes place. The minimum at short C—Cl distance is too shallow to allow the localization of a transition state and the calculation of an intrinsic reaction coordinate connecting both minima. However, it can be seen that analysis of the cleavage reaction path requires considering not only the stretching of the cleaving bond but also the translocation of the water molecules. We may consider, as a first approximation, that the two main ingredients of the reaction coordinate are the C—Cl distance and the dihedral angle,
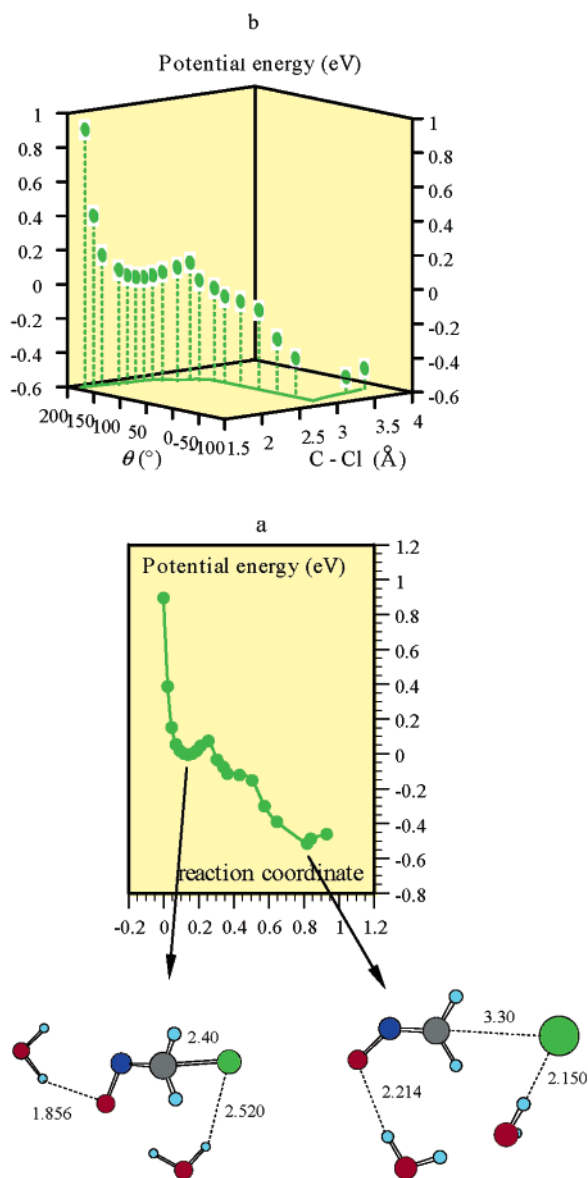
Figure 7. Potential energy profiles (from QCISD(T)/6-31G* calculations) for cleavage of ONCH$_2$Cl anion radical in the presence of two water molecules. (a) Potential energy vs reaction coordinate, z (defined in the text). (b) Potential energy profile as a function of C−Cl distance and θ, the C, N, O, H$_{(OH)}$ dihedral angle showing the reaction pathway as projection on the horizontal plane. Bottom: structures at each potential energy minimum.

θ, formed by the C, N, O, and H (from the upper water molecule in the bottom of Figure 7) atoms. It is indeed the displacement of this water molecule that best represents the solvent reorganization attending the intramolecular dissociative electron-transfer process. A three-dimensional representation of the cleavage reaction pathway as a function of these two coordinates is shown in Figure 7b. The reaction pathway may be depicted in terms of two normalized coordinates, x and y, defined as:

$$x = \frac{\theta_{max} - \theta}{\theta_{max} - \theta_{min}} \quad \text{and} \quad y = \frac{(C-Cl) - (C-Cl)_{min}}{(C-Cl)_{max} - (C-Cl)_{min}}$$

where $\theta_{max} = 180.44°$, $\theta_{min} = 75.21°$, $(C-Cl)_{max} = 3.7$ Å, and $(C-Cl)_{min} = 1.6$ Å. An approximate reaction coordinate, z, may thus be introduced ($dz = \sqrt{dx^2 + dy^2}$ and normalization),

leading to the potential energy profile depicted by Figure 7a. Comparison of these results obtained with those pertaining to the sole consideration of intramolecular effects (Figure 6 top) clearly shows the essential role of the solvent molecules in the very existence of the anion radical, particularly those that are located in the vicinity of the NO group that bears the first residence orbital of the unpaired electron on one hand and those that stand around the leaving Cl$^-$.

It thus appears that the existence of a π^* anion radical in conjugated (benzyl-type) molecules requires the concomitant fulfillment of two conditions, namely, the presence of a group bearing an orbital susceptible to host the unpaired electron and the short distance solvation of the partial charge thus created.

Methodology for Quantum Chemical Calculations

All the calculations were performed with the Gaussian 98 series of programs.[17] Minimum energy structures were fully optimized. Frequency calculations were made to verify that the structures were minima (no imaginary frequencies). Energy profiles were obtained at fixed values of C−Cl or C−Br distance. The B3LYP method was used for the density functional theory approach. An ab initio approach taking into account electron correlation was also used to described the simple model system ONCH$_2$Cl + e$^-$ (geometry optimization at QCISD level and single point calculation at QCISD(T)) and the ONCH$_2$-Cl + e$^-$ + 2 H$_2$O system (single point calculations at QCISD-(T) level on B3LYP optimized geometries). To check the reliability of this single-reference QCISD method, the T1 diagnostic was calculated.[18] A value of 0.032 was found, smaller enough to trust single-reference calculations. Comparison of single point calculations obtained for the ONCH$_2$Cl + e$^-$ system at the QCISD(T) level on geometries optimized either at QCISD or B3LYP levels shows no difference.

Solvation free energies were computed on the gas-phase optimized geometries according to the Self-Consistent Reaction Field method using the COSMO model[19] for substituted benzyl halide anion radicals and the IPCM model[20] for the ONCH$_2$Cl anion radical system.

The 6-31G* basis set was used. All investigated anion radicals are stable to electron loss even at short C−Cl or C−Br distances. This is confirmed by the fact that 6-31G* and 6-31+G* basis sets lead to the same results.

Concluding Remarks

In summary, analysis of available experimental data from various sources, particularly those pertaining to the one-electron reductive cleavage of nitro and cyano-substituted benzyl chlorides, suggests that not only the cleavage of π anion radicals

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may be slow by a solvent effect and not only the solvent may be responsible for the passage from a stepwise to a concerted mechanism of the reductive cleavage reaction but also that the very existence of π anion radicals may hinge on interactions with the solvent. In terms of trends, the expectations are confirmed by preliminary calculations on these benzylic derivatives using a DFT technique and treating solvation by a dielectric continuum method. It appears, however, that this approach underestimates these solvent effects. Analysis of a simplified system, namely $ONCH_2Cl + e^- + 2\ H_2O$, allows both the improvement of the calculation level and a treatment of these solvent effects that emphasizes the role of solvent molecules that sit close to the charge centers of the molecule. It then appears that the presence of the electron first residence group and its interaction with the solvent play a synergistic role in the very existence of a π^* anion radical. Bond stretching and solvent reorganization jointly govern the cleavage activation barrier. Even though the representation of the solvent by only two water molecules is certainly simplistic at the quantitative level, the mechanism of solvent reorganization attending bond cleavage is clearly pictured in qualitative terms by the decrease of the interaction between one water molecule and the oxygen of the NO group and the concomitant increase of the interaction between the second water molecule and the leaving chloride ion. In a real solvent, one of the water molecules that interacts

with the oxygen atom in the anion radical is, of course, not going to travel all the way to the vicinity of the leaving chloride ion. Transposing the two-water molecules picture to a real solvent rather points to the notion that, upon electron transfer, the interactions of the surrounding solvent molecules with the negative charge on the oxygen atom weaken at the benefit of the interactions between the solvent molecules surrounding the chlorine atom with the charge borne by this atom. Although the representation of the polar solvent by water molecules is more suited to the case of protic solvents, the conclusions reached with this system are likely to extend to the case of other polar solvents, including nonprotic solvents, at the qualitative level. Indeed, whatever the type of interaction of solvent molecules with the negative charges, H-bonding or dipolar, they should induce solvent molecules to execute a similar reorganization movement.

Also, the stabilization of the anion radical in a real solvent should be larger than that found here with only two water molecules. A larger stabilization, logically accompanied by a larger cleavage barrier, due to a larger solvent reorganization, would allow addressing the dynamics of the reaction in more realistic terms than in the present case, where the barrier remains too small for a transition state approach to be meaningful.