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Theoretical study of electron transfer to neopentyl chloride and phenyl-substituted derivatives: existence of radical anions as intermediates†

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ABSTRACT: Aliphatic halides such as neopentyl, bicycloalkyl and polycycloalkyl halides can be substituted by mechanisms that involve electron transfer (ET) steps. The homogeneous or heterogeneous ET to these compounds follows a concerted dissociative pathway, that is, the C–halogen bond cleaves as the electron is being transferred. The ET to alkyl halides substituted by π-electron acceptors, on the other hand, may follow a stepwise mechanism with radical anions as intermediates. Both mechanistic pathways are analyzed on the basis of AM1, B3LYP and MP2 calculations for neopentyl chloride (**6**) and its phenyl- and benzyl-substituted derivatives 1-chloro-2-methyl-2-phenylpropane (neophyl chloride, **7**) and 1-chloro-2,2-dimethyl-3-phenylpropane (**8**). The solvent effect was evaluated with Tomasi's continuum polarized model. While relatively stable π radical anions appear as intermediates on the AM1 potential surfaces of **7** and **8**, B3LYP and MP2 favor a concerted dissociative pathway for these compounds. Based on the B3LYP and MP2 results, it can be concluded that the driving force for the dissociative ET to the three compounds depends mainly on their C—C1 bond dissociation. The strength of the C—C1 bond is similar for **6** and **8** and lower for **7**. The difference in the C—C1 bond strength of **7** and **8** is ascribed to differences in the stabilizing effect of the phenyl substituent, through a bridge of variable length, and also to the stability of the radical formed in the cleavage. The theoretical results obtained are of help in the interpretation of the relative experimental reactivity previously obtained for the family. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: concerted-dissociative electron transfer; stepwise electron transfer; neopentyl halides and stabilized derivatives; radical anions; B3LYP; MP2; AM1

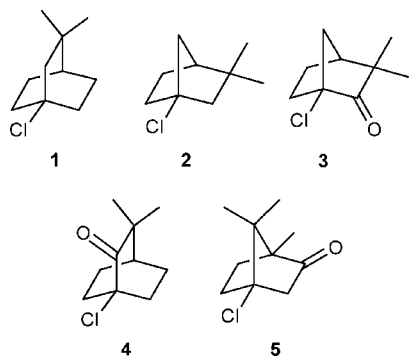
INTRODUCTION

Aliphatic halides which, owing to electronic, steric or strain factors, do not react with nucleophiles under classical polar nucleophilic substitutions can be substituted by processes that involve electron transfer (ET) steps.[1] Neopentyl, cycloalkyl, bicycloalkyl and polycycloalkyl halides are some of the compounds known to react by this means, the bromo and iodo compounds being more reactive than the chloro derivatives. As is known, the C—X bond frangibility follows the order I >Br >Cl, in agreement with the order of their reduction potentials (for reviews on aliphatic $S_{RN}1$ reactions, see Ref. 1).

The ET to these aliphatic halides follows a concerted dissociative mechanism, that is, the carbon–halogen (C—X) bond breaks as the electron is being transferred [Eqn. (1)],[2] the donor being an electrode, a charged nucleophile, radical anions of aromatic hydrocarbons, etc.

$$RX + e^- \longrightarrow R^{\cdot} + X^- \qquad (1)$$

In some cases and for a given halogen, the reactivity can be increased by the presence of good π-electron acceptors as substituents. For example, it has been shown that 3,3-dimethylbicyclo[2.2.2]oct-1-yl (**1**) and bicyclo[2.2.1]



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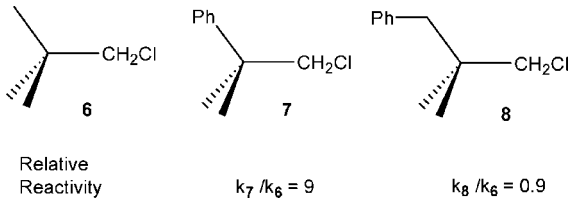
hepta-1-yl chlorides (**2**) do not react with Ph_2P^- ions under irradiation, whereas the 2- and 3-oxo derivatives **3–5** react under the same experimental conditions.[3]

In the neopentyl family, 1-chloro-2-methyl-2-phenyl propane (**7**) (neophyl chloride) has been shown to be nine times more reactive than neopentyl chloride (**6**) toward Ph_2P^- ions.[4] However, 1-chloro-2,2-dimethyl-3-phenyl propane (**8**) has a reactivity similar to **6**.[4]



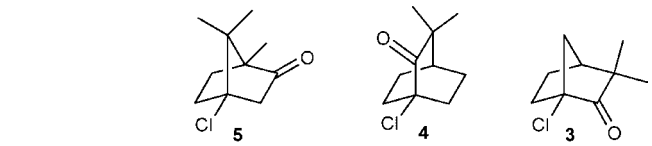
Different proposals can be taken into consideration in relation to the mechanism of ET to the π-substituted compounds. It is possible that the reaction does not follow a dissociative concerted step but a stepwise mechanism with formation of π radical anions (RAs) as intermediates, the unpaired electron being initially located in the π acceptor group, the cleavage of the C—X bond taking place through an intramolecular ET reaction (*intra*-ET) from the π acceptor to the breaking bond [Eqn. (2)].

$$\text{Ac}\pi\text{-Bridge-CH}_2\text{X} + \text{Nu}^- \xrightarrow{\text{ET}} (\text{Ac}\pi)^{\cdot}\text{-Bridge-CH}_2\text{X} \xrightarrow{intra-\text{ET}} \text{Ac}\pi\text{-Bridge-CH}_2^{\cdot} + \text{X}^- \qquad (2)$$

Under these conditions, the higher reactivity of the π-substituted halides could be interpreted in terms of the more positive reduction potential with respect to the unsubstituted derivatives, whenever an efficient *intra*-ET is in play. For example, in terms of the LUMOs energy, which can be taken as an estimation of the electron affinity of the compounds, the LUMOs of the oxo bicyclic compounds **3–5** belong to the carbonyl group and have a lower energy than the LUMO of the unsubstituted analogues. In agreement with the LUMOs predictions, **4** was found to be 700 times more reactive than 1-chloroadamantane (higher σ^* C—X LUMO), and only 0.40 times less reactive than 1-bromoadamantane (similar σ^* C—X LUMO energy).[3b]

The relative reactivity of **5** is similar to that of **4** and lower than that of **3**. This reactivity order is in agreement with the energy value of the C=O π^* LUMO but not with that of the C—Cl σ^* MO of the compounds (Chart 1).[3a] In this system an efficient *intra*-ET from the π C=O radical anion to the C—Cl bond has been proposed for the different positions of the carbonyl group on the bridge.[3]

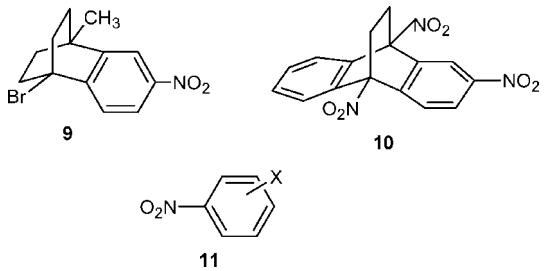
The *intra*-ET depends on, among other factors, the number of σ-bonds between the π and σ acceptor groups, their relative orientation and their spatial proximity. For example, the radical anion of the rigid bicyclooctane **9** fragments at a considerable low rate (9.3×10^{-3} s^{-1}).[5] In this compound, the rigid bicyclic structure precludes



	5	4	3
Rel. Reactivity	1.0	1.1	2.8
π^* C=O (eV)	0.713	0.723	0.678
σ^* C-Cl (eV)	1.20	1.16	1.30

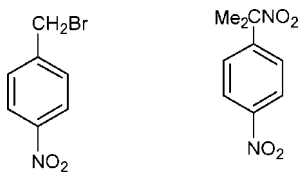
Chart 1

overlap between the π^* MO, where the unpaired electron initially locates, and the σ^* C—Br MO, to which it has to be transferred to afford the dissociation of the C—Br bond.[5] Another example is the radical anion of compound **10**, which does not react with p-$MeC_6H_6S^-$ under ET conditions.[6]



Similarly, in the aromatic family, the fragmentation of the radical anions p-[7–9] and m-bromo-,[10] p-[7,8] and m-chloronitrobenzenes[10] (**11**), in which the π and σ C—X systems are orthogonal, occurs at considerably low rates ($\sim 10^{-2}$ s^{-1} or lower).[8] These compounds are usually unreactive toward nucleophiles under ET conditions. The relative order of the thermal and photochemical fragmentation of radical anions of type **11** has been explained satisfactorily through AM1 calculations.[11]

Another possibility is for both groups to interact (overlap) through a flexible bridge. Even though radical anions may be formed, mainly in the case of highly stabilized π systems, the intermediates may have a mixed π–σ electronic nature (i.e. the SOMO involves both the aromatic system and the σ^* bond) and they will fragment at a higher rate than the rigid analogues. For example, the fragmentation rate constant of the radical anion of p-$O_2NC_6H_4CH_2Br$ (**12**) is estimated to be $\geq 7.9 \times 10^8$ s^{-1} (MeCN),[12] and **13**, the benzylic analog of **10**, reacts with p-$MeC_6H_4S^-$ ions by ET.[13]



The presence of radical anions on the ground-state anionic potential surface does not necessarily imply that they will be formed during the reaction. It is known that

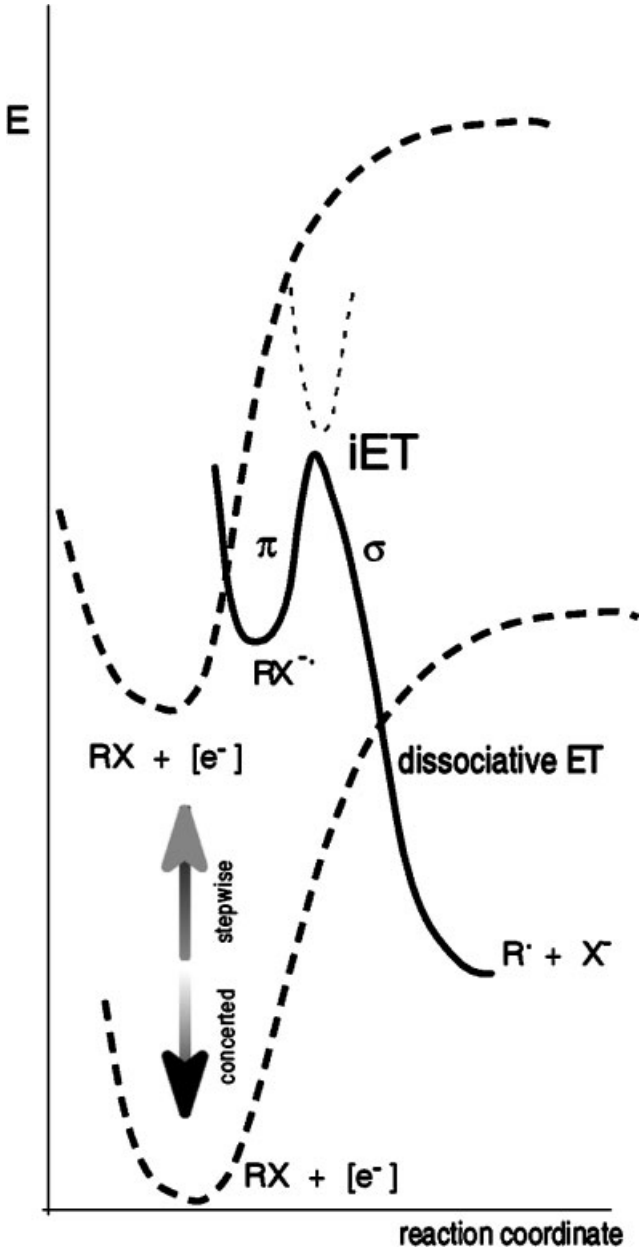


Figure 1. Schematic profiles for ET to an haloaromatic or haloaliphatic compound with π acceptor. The reaction can switch between concerted dissociative and stepwise pathways by modification of the driving force. The energy of RX + [e] depends on the electrode conditions (heterogeneous ET) or the potential of the donor (homogeneous ET) (see ref. 2)

the minimum energy reaction path followed depends on, among other factors, the driving force of the reaction (electrode potential, oxidation potential of the donor, etc.) (Fig. 1).[14] For instance, the thermal ET initiation from $^{-}CMe_2NO_2$ ion to *p*-$O_2NC_6H_4CH_2Cl$[12] and to *p*-$O_2NC_6H_4CMe_2Cl$[15] is interpreted to be possible through a dissociative pathway. On the other hand, the radical anions of these compounds are intermediates under electrochemical initiation.[12,15]

Taking into account these considerations, and in order to determine theoretically the mechanism in play in the case of the phenyl derivatives **7** and **8** in which the π and σ systems may interact through the flexible bridges —$C(CH_3)_2$— and —$CH_2C(CH_3)_2$—, respectively, we present a detailed study of the anionic potential surfaces of **6**, **7** and **8**. This system is particularly interesting as the LUMO of **7**, localized on the phenyl ring, is of lower energy than the σ^* C—Cl LUMO of neopentyl chloride (**6**), and **7** is nine times more reactive than **6**. However, even though **7** and **8** have LUMOs of similar energy, the latter has a reactivity lower than that of **7** and similar to that of **6**.

COMPUTATIONAL PROCEDURES

The system was studied with the AM1 semiempirical method, as implemented in AMPAC,[16] the B3LYP functional and the MP2 procedure, as implemented in the Gaussian 98 package of programs.[17]

The equilibrium geometries were obtained with complete optimization without applying symmetry constraints. Stationary points were characterized by calculating their Hessian matrix with the usual criteria.[18]

The AM1–UHF formalism was applied to find π and σ anionic intermediates following the procedure described previously.[11] The conformational potential surfaces of compounds **7** and **8** and their anionic states were obtained with this formalism, scanning the two or the three main torsion angles of the bridge. The main anionic conformers thus located were then refined within the AM1/CI approach which was also used in the study of their respective potential surfaces.

The CI calculations for the ground and first excited states were performed with the AM1/RHF Hamiltonian within the subspace of all possible excitations of five electrons into five molecular orbitals, from SOMO − 2 up to SOMO + 2 (100 configurations, CI = 5). This level of CI has been successfully used in studies of the reactivity of open-shell systems, including ET reactions in radical cations[19] and reactions with biradicals[20] or radical anions[11] as intermediates.

Potential energy surface explorations within the B3LYP[21] DFT[22] functional were performed for all the compounds under study with full geometry optimization, without symmetry constraints. The spin and charge localization was obtained from the Mulliken analysis. Reasonably good agreement was obtained by using either the standard basis set 3–21G*, 6–31G** and the ECP LANL2DZ (LANL2DZ is defined as the Dunning and Huzinaga full double zeta D95 for the first-row elements, using the Los Alamos effective potential from Na to Bi[23]). The thermodynamics of the reaction were evaluated with different bases, the highest level being 6–311++G(2*d*,*p*). The zero-point energy corrections were performed with frequency calculations at the B3LYP/6–31G** level (the spin contamination obtained

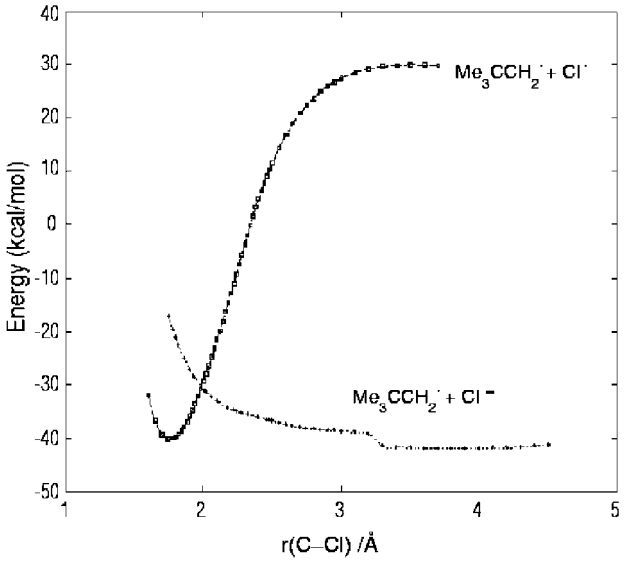


Figure 2. AM1 profiles for the neutral and anionic curves of neopentyl chloride (**6**)

with this functional for radicals and RAs was almost negligible with all bases. With PMP2, certain spin contamination appears at the π region of the profile, with $<S^2>$ expectation values up to 0.78 after projection). The anionic surfaces of **7** and **8** were also explored at the PMP2/LANL2DZ level.

The effect of the solvent was incorporated by means of the Tomasi's polarized continuum model (PCM), choosing acetonitrile as model polar solvent.[24] The energy corrections were obtained for the gas-phase structures.

RESULTS AND DISCUSSION

Both the AM1 and B3LYP procedures calculate the ET to neopentyl chloride as a dissociative reaction. No minimum could be located on the anionic potential surface by either procedure (Fig. 2), except for a loose complex between the dissociated fragments. Our results are in agreement with previous calculations on aliphatic systems such as methyl and trifluoromethyl halides.[25]

A different profile is predicted for the phenyl- and benzyl-substituted derivatives **7** and **8**. According to AM1/UHF or CI, π RAs will be formed by ET to **7** and **8** which have the unpaired electron localized mainly on the phenyl ring. The AM1/UHF and CI energy required for the *intra*-ET from the π to the C—Cl σ^* surface is presented in Table 1.

As can be seen from Table 1, the *intra*-ET accompanied by dissociation is favored for $\mathbf{7}^{-\cdot}$ with respect to $\mathbf{8}^{-\cdot}$ by approximately 4 kcal mol^{-1} (1 kcal = 4.184 kJ). The higher activation required for $\mathbf{8}^{-\cdot}$ can be rationalized on the basis of the longer bridge that mediates the process, 5.5 Å for $\mathbf{8}^{-\cdot}$ vs 4.2 Å for $\mathbf{7}^{-\cdot}$.

The degree of adiabaticy of the *intra*-ET was evaluated

Table 1. Summary of AM1-CI results for the anionic species $\mathbf{7}^{-\cdot}$ and $\mathbf{8}^{-\cdot}$

RA	$\mathbf{7}^{-\cdot}$	$\mathbf{7_1}^{-\cdot}$[a]	$\mathbf{8}^{-\cdot}$
ΔH_f(RA)[b]	−14.3	−12.8	−20.4
ΔH_f(RA*)[c]	2.7	1.2	−0.2
$E^{\ddagger}_{\pi\sigma}$[d]	6.9	13.1	11.3
$2H_{\pi\sigma}$[e]	10.1	1	9.1
ε(SOMO)[f]	0.31	0.45	0.35

[a] Conformer of $\mathbf{7}^{-\cdot}$ shown in Fig. 3.
[b,c] Heats of formation (in kcal mol^{-1}) of the ground-state π RA and of the excited state at the geometry of the transition state, respectively.
[d] Activation energy for the π–σ interconversion.
[e] Degree of adiabaticity in terms of the electron transfer matrix element $H_{\pi\sigma}$ in kcal mol^{-1} (see text); note that for values greater than 1.5 kcal mol^{-1}, the process is expected to be typically adiabatic, with a probability equal to 1 of happening.
[f] SOMOs energies in eV.

as the energy difference between the CI ground state surface (root 1) and the first excited surface (root 2) at the transition-state geometry.[26] Based on this difference, the reaction for the most stable conformers of both compounds is estimated as highly adiabatic. It is relevant to point out the importance of the relative geometric disposition of both groups in relation to the bridge. For example, in a less stable conformer of $\mathbf{7}^{-\cdot}$ shown in Fig. 3 and labelled $\mathbf{7_1}^{-\cdot}$, for which the σ^* C—Cl is orthogonal to the phenyl π system, the *intra*-ET is non-adiabatic and hence it will have a lower probability of occurring unless a conformational change takes place (the barriers of interconversion between the main conformers were, in general, lower than the barrier for the *intra*-ET).

In Fig. 4, the B3LYP/6–31G** LUMOs calculated for **6** and the most stable conformers of **7** and **8** are presented. As can be seen, this MO is σ for **6** and π–σ for **7** and **8** with a lower σ participation in **8**.

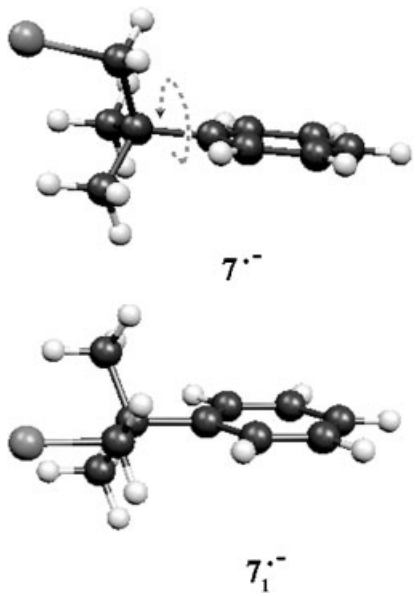


Figure 3. A lower stabilized conformer of $\mathbf{7}^{-\cdot}$, with the halogen lying on the phenyl plane

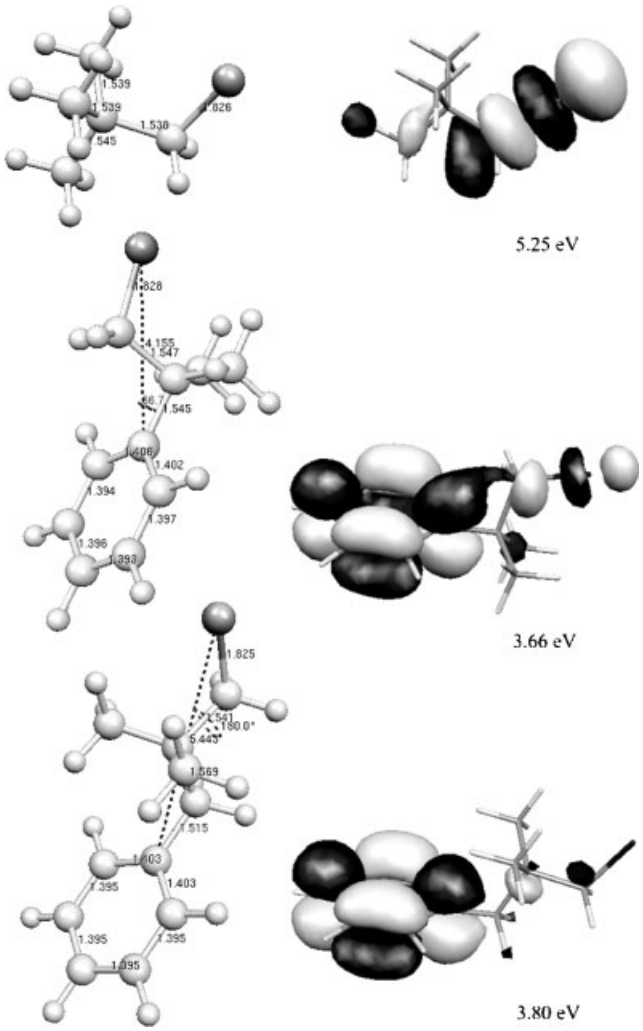


Figure 4. Right: geometries of the most stable conformers of **6**, **7** and **8**, refined at the B3LYP/6–31G** level. Left: HF canonical LUMOs with the corresponding energies

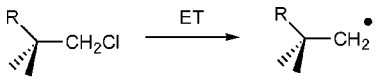
The anionic potential profiles shown by B3LYP for **7** and **8** reveal a different behavior from that proposed by AM1. The gas-phase anionic surface for **8** is shown in Fig. 5(a) (solid line). The π–σ conversion (followed by inspection of the charge and spin distribution) that accompanies the dissociation occurs gradually, without a π minimum, affording a radical–chloride anion loose complex. A similar profile is obtained at the PMP2/LANL2DZ level [Fig. 5(b), solid line profile], except for the appearance of a very shallow minimum, corresponding to a π RA, which drops to the loose complex with a very low barrier. In the case of **7** the π–σ overlap is higher than for **8** and either B3LYP or MP2 found the π–σ evolution without barriers [a π structure was found with MP2, being a shallow shoulder, with no characterizable barrier for its conversion to the loose complex; it was not possible to find a π anionic intermdiate by using both UHF and CASSCF(9,8) procedures, in addition to B3LYP].

In order to model the reactions in solution, MeCN was included in the calculations to determine its effect on the relative stability of the π and σ zero-order anionic surfaces. In the presence of a polar solvent the π and σ species are expected to be stabilized to a different extent depending on their charge localization. Two possibilities can be considered: (a) the π system suffers the higher stabilization with the probable appearance of a π intermediate or (b) the stabilization is stronger for the σ species, at elongated C—Cl distance. In this case the probability of finding a relatively long-lived π intermediate will be even smaller. The latter is indeed the case [see the dashed line profiles in Fig. 5(a) and (b)]. As shown in Fig. 5(c), the solvation at the σ complex is greater than at the π zone, and it is even stronger for the fragmentation products.

In all cases, the loose complexes disappear or became unimportant in solution. In the case of $\mathbf{8}^{-\cdot}$, the dissociation of the π structure found at the MP2 level is exothermic by more than 58 kcal mol^{-1} (against 28.7 kcal mol^{-1} in the gas phase) after overcoming a very small barrier (<1 kcal mol^{-1}). In contrast to AM1 profiles, where relatively stable π RAs were found, the first principles results point to a dissociative ET for **6–8** since the anionic surfaces have no π minima or only slightly stabilized π structures.

Based on Savéant's proposal,[2,27] the activation energy for these outer-sphere ET (inner sphere for the acceptor that cleaves) can be estimated from the crossing point between the potential surface of the neutral chloride and its anionic surface. The activation energy for dissociation, thus estimated, is presented in Table 2 and Fig. 6, where the neutral and anionic profiles are shown in terms of their relative energy with respect to the energy of the radical plus the halide ion infinitely separated, which is taken as zero by definition.

As can be seen, the relative energy for the crossing that accompanies the dissociation is similar for **6** and **8**. The anionic surfaces of both compounds have similar relative energies. This behavior can be ascribed to the similar stability of the radicals formed by dissociation in both cases [Eqn. (3)].

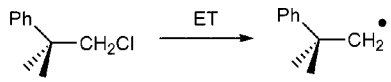


6 R=CH_3
8 R=CH_2Ph

14 R=CH_3
15 R=CH_2Ph

(3)

On the other hand, the anionic surface of **7** is of lower energy at all C—Cl distances, a fact that can be attributed to the higher stability of the radical being formed due to a stronger effect of the phenyl substituent through the shorter bridge [Table 2, Eqn. (4)].



7 **16** (4)

Based on the theoretical calculations presented,

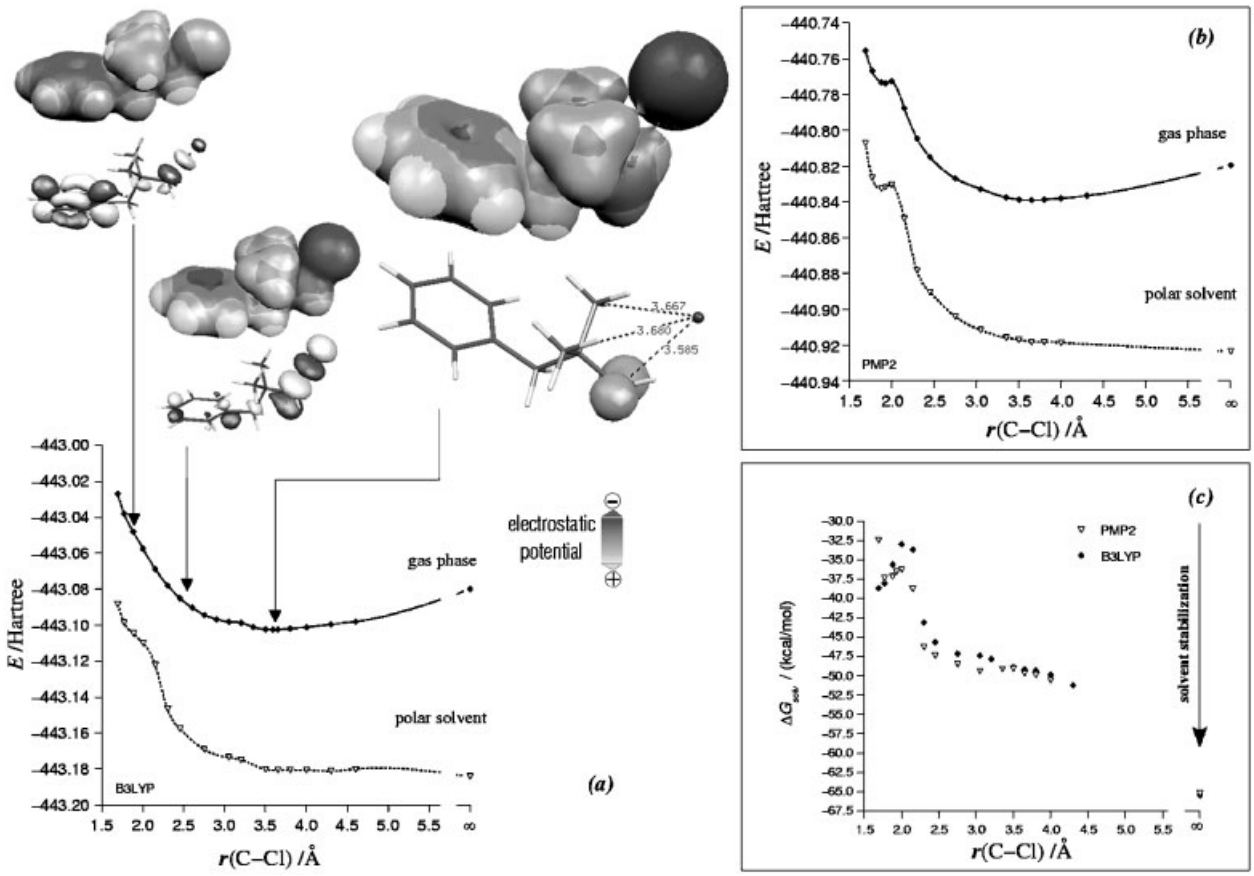


Figure 5. (a) Anionic profiles obtained for **8** at the UB3LYP/LANL2DZ level in the gas phase (solid line) and in MeCN as solvent (dashed line). The π–σ interconversion can be followed either in the electrostatic potential or in the SOMO diagrams (upper left corner). The complex afforded at a C—Cl distance of ~3.6 Å is clearly of electrostatic type between the radical (unpaired spin density in yellow isosurface) and the halide ion. (b) The corresponding profiles obtained at the PMP2/LANL2DZ level. (c) Variation of the solvent stabilization along the bond-breaking coordinate

different mechanistic paths can be envisaged to interpret the experimental results of the reactions proposed to occur by the $S_{RN}1$ process.[4] In competition experiments of pairs of these compounds in the presence of Ph_2P^- ion, the propagation chain shown in Scheme 1 can be considered on the basis of the AM1 results.

In agreement with these results and the calculated LUMOs, the ET of Eqn. (8) will be favored for the better electron acceptors **7** and **8**. The relative reactivity will then depend on the lifetime of $\mathbf{7}^{-\cdot}$ and $\mathbf{8}^{-\cdot}$: the longer the bridge, the slower is the *intra*-ET or, in other words, $\mathbf{8}^{-\cdot}$ lives long enough to transfer its extra electron to **6** [step (6) faster than step (7)] and thus it is less reactive than **7**. In this context, two factors are relevant to interpret the dynamic of the dissociation: the reduction potential of the substrate, more positive for **7** and **8** than for **6**, and the bond dissociation energy, which depends on the phenyl/C—Cl distance through the bridge.

On the other hand, on the basis of DFT results, Scheme 2 can be proposed.

According to this interpretation, the outer-sphere ET to the three compounds [Eqn. (8′)] will follow a concerted dissociative pathway. This reaction has a lower activation energy and affords the most stable radical for **7**. On these bases, not only the higher relative reactivity of **7** vs **8** is explained, but also the similar relative reactivity of **8** and **6** which have similar relative energy profiles (Figure 6, Table 2). Here the relevant factor for the cleavage is the bond dissociation energy of the RAs. In agreement with

Table 2. Summary of B3LYP results[a]

Compound	$E^{\ddagger b}$	$E_r(RX)^c$	D^d
6	17.2	−5.67 (−14.8)	77.52
7	<1	2.01 (−14.2)	71.05
8	17	−5.18 (−14.6)	77.16

[a] All energies in kcal mol^{-1}.
[b] Diabatic estimation of the barrier for the gas phase process $RX + e \rightarrow R^{\cdot} + X^-$, see Fig. 6.
[c] $(-\Delta E)$ of the $RX + e \rightarrow R^{\cdot} + X^-$ process, i.e. the relative energy of the neutral substrates with respect to the dissociation products at the B3LYP/6–311++G(2*d*,*p*)//B3LYP/6–31G** level; from inspection of Fig. 6, the B3LYP/3–21G* results without zero-point corrections are in parentheses.
[d] C—Cl bond dissociation energies [B3LYP/6–311++G(2*d*,*p*)//B3LYP/6–31G**].

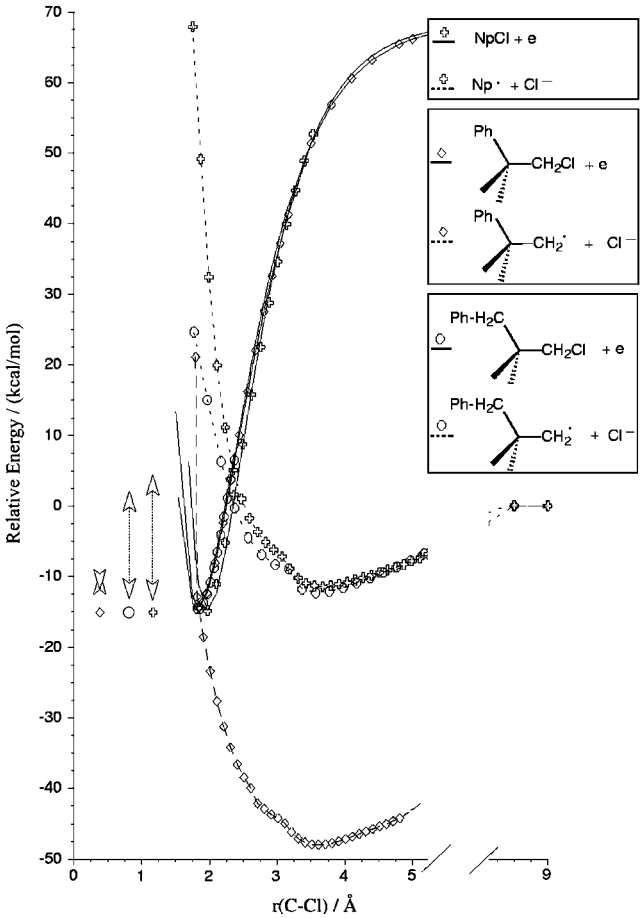
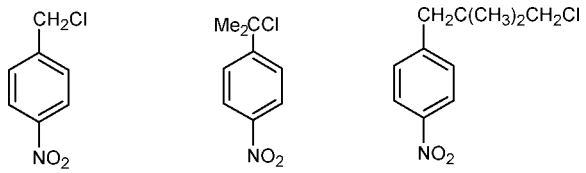


Figure 6. Comparison of the relative energy profiles for **6**–**8** and their anionic surfaces (B3LYP/3–21G*). The relative energies are taken in reference to the dissociation products (see text)

Savéant's model for dissociative ET, according to which the logarithms of the rate constants for cleavage can be related to the bond dissociation energy of the neutrals, our calculated values are of the right order for the three species (similar for **8** and **6** and ~6.5 kcal mol^{-1} smaller for **7**, Table 2).

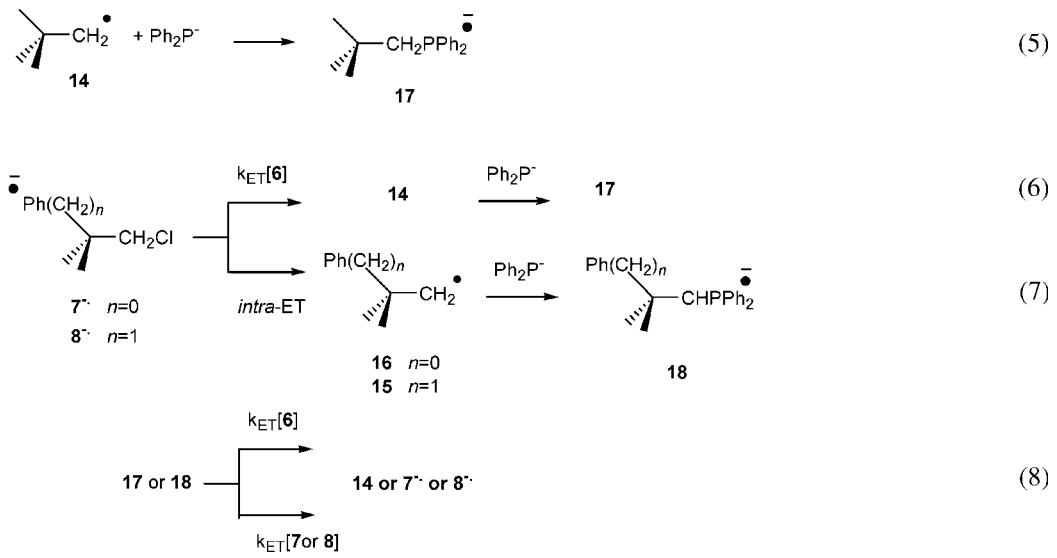
In the light of the first principles results, it can be concluded that AM1 overestimates the stability of the π RAs, as previously observed for the halobenzene family[11,28] (however, in the case of π-stabilized systems this overestimation still gives the right relative order of reactivity; on the other hand, in the halobenzene family, the known exothermic RA cleavage is calculated as endothermic). Further, the ET to $PhCH_2Cl$ is proposed as dissociative on electrochemical basis[2] but a π minimum can be localized by AM1 on its anionic potential surface.

Even though more investigation with first principles methods is needed, mainly on systems for which the existence of radical anions has been experimentally determined, the results obtained for the following related system reinforces the hypothesis of a concerted dissociative ET to compounds **7** and **8**. Let us consider *p*-nitrobenzyl chloride (**19**), *p*-nitrocumyl chloride (**20**) and the nitro-substituted derivative of **8** (**21**).

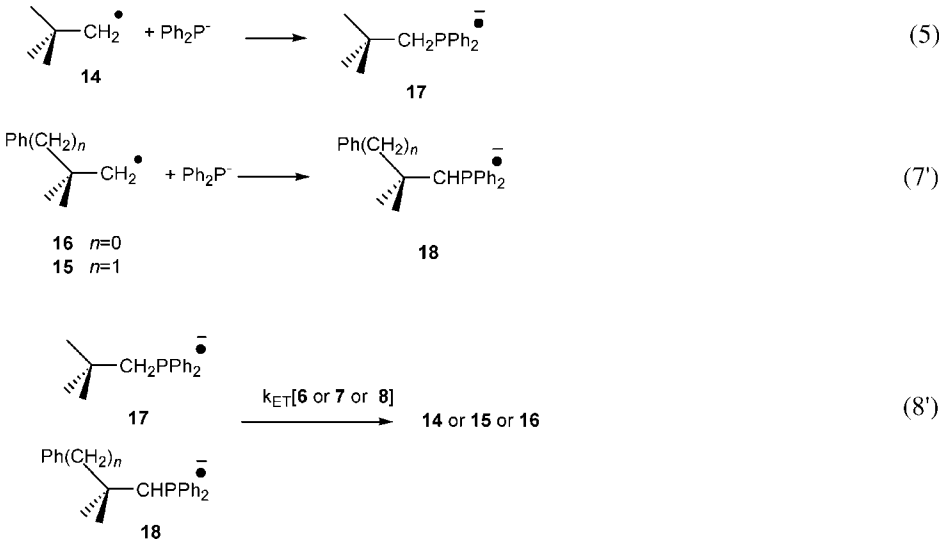


19 **20** **21**

For the anionic surfaces of **19**, **20** and **21**, a π RA true minimum was found with 34.78, 29.90 and 42.17 kcal mol^{-1} relative stability with respect to the



Scheme 1



Scheme 2

corresponding fragmentation products, respectively (B3LYP/LANL2DZ). Even though the nitro group dramatically stabilizes the π anionic surface, the spontaneous ET from $^{-}CMe_2NO_2$ ion to **19** was found to be dissociative and the radical anion of **20** can live only a few nanoseconds under carefully selected conditions.[15,27] For compounds **7** and **8**, whose π systems are much higher in energy owing to the absence of an electron-withdrawing group, it is even less likely to expect relatively long-lived radical anions as intermediates.

CONCLUSIONS

It is concluded that in those compounds in which there is a π–σ overlap, RAs will be formed when the π moiety is highly stabilized as in the case of **19**. In this type of compound, the π anionic potential surface is strongly stabilized with respect to the σ dissociative potential. On the other hand, when the π system is not highly stabilized, as in the case of the phenyl and benzyl derivatives **7** and **8**, the π anionic potential is less stable than the σ potential and thus the outer-sphere ET to them will follow a concerted dissociative path. The relative order of the experimental reactivities for **6–8** is in agreement with these theoretical results. The presence of good electron acceptor groups does not always produce an increase in reactivity, and this depends on the ease of the *intra*-ET, which in turn depends on the rigidity and flexibility of the bridges, the differences in electron affinity between the groups that participate in the *intra*-ET and the stability of the radicals formed by dissociation.

The flexible bridge in **7** and **8** plays an important role in allowing for the π–σ coupling, which results in an adiabatic profile for the most stable conformers.

Although the aromatic system is not highly stabilized, it is responsible of effective intramolecular catalysis in the reactivity of **7**, which is reflected in its lower C—Cl bond dissociation energy ($\sim$6.5 kcal mol^{-1}) or in the lowering of the energy of the σ surface, which correlates with the formation of the halide ion and a more stable radical.

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