Theoretical MO *ab initio* investigation of the reductive C–Cl bond cleavage in benzyl chloride, benzotrichloride† and in the analogous 4-pyridine derivatives

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Reductive electron transfer on the title compounds has been studied theoretically with MO *ab initio* methods, using the 6-31G* basis set and second-order Møller–Plesset perturbation theory, in order to verify the eventual stability of their radical anion and to analyze the C–Cl bond breaking process both in the neutral molecules and in the anions. The effect of the basis set has been tested at single point energies with the 6-311G basis set. The geometries of the neutral molecules and radicals formed after bond dissociation are fully relaxed. The energy profiles of the radical anions as a function of the C–Cl bond distance have been found to be dissociative. The energy of activation and the structure of the activated complex have been studied in the forbidden crossing of the energy profiles of the neutral molecule and radical anion. The results show that the activation energy of the process is affected both by the number of chlorine atoms on the methyl group and by the different aromatic ring, yet the energy of reaction is significantly affected only by the number of chlorine atoms. When compared with reduction potentials determined experimentally in a previous work, these activation energies show an excellent linear relationship. The results are discussed in the frame of the Marcus–Hush model of electron transfer and it appears that chloromethyl derivatives of pyridine and benzene do not strictly follow the same reaction mechanism at the end of applying this model.**

Introduction

The reductive cleavage of the C–Cl bond in homogeneous media and with electrochemical devices has attracted a great deal of attention recently.[1–3] The carbon radicals formed can dimerize,[4–7] abstract protons after further reduction to carbanions[4–7] and react with other chemical species to generate compounds with a new carbon–carbon bond.[8,9] Electron transfer on a neutral molecule RX that undergoes bond breaking can proceed by means of a concerted process or in successive steps through the $RX^{\cdot -}$ radical. The 'theoretical existence' of the radical anion of a molecule does not necessarily attest to a stepwise mechanism, since the driving force of the reaction is likely to give one mechanism an energy advantage over the other.[10] The reduction of benzyl halides occurs through a concerted electron transfer–bond breaking mechanism unless a nitro substituent is present in the ring.[10] Less is known about the reduction of arylmethyl halides polyhalogenated at the methyl group, but results of an electrochemical study[11] on trichloromethylbenzene and on the corresponding derivatives of pyridine suggest that these derivatives are also reduced by means of the concerted mechanism.

In modeling the reactions where carbon radicals generated from organic halides are involved, knowledge of the mechanism of radical formation (*i.e.* the thermodynamics and kinetics of the concerted electron transfer–bond breaking process) is crucial, in respect both of the electrochemical process and of the reactions in the homogeneous phase. It is in fact known that carbon radicals generated electrochemically[1,7,11] from benzyl halides are easily further reduced to carbanions and can abstract protons from molecules present in the reaction medium. When the reduction is carried out in the homogeneous phase, for example, with iron(II) ions, dimerization of the radicals formed is the most common chemical reaction.[6] The diffusion of the radicals formed outside the formation cage is in competition with the second electron transfer followed by proton abstraction.

The Marcus–Hush[12] model for outer-sphere electron transfer also applies to concerted processes, although the latter have more the character of inner-sphere processes owing to the bond reorganization of the acceptor. According to this model, the activation free-energy $\Delta G^\ddagger$ is related through a quadratic relationship to the standard free-energy of the forward electron transfer ΔG_o through eqn. (1), where w_R and w_P represent the

$$\Delta G^\ddagger = w_R + \Delta G_o^\ddagger\left(1 + \frac{\Delta G_o - w_R + w_P}{4\Delta G_o^\ddagger}\right)^2 \qquad (1)$$

work necessary to bring reactants and products, respectively, within reacting distance and $\Delta G_o^\ddagger$ is the intrinsic free-energy barrier. The approximation adopted[10] for the inner-sphere process on structurally similar molecules envisages $\Delta G_o^\ddagger$ being a quarter of the bond dissociation energy of the bond undergoing cleavage, other contributions from intramolecular rearrangements and solvent effects being assumed to be nearly constant. The model has been applied[10] successfully to the study of the electrochemical reductive cleavage of arylmethyl (mono) halides. The mechanism of the process, at the molecular level, implies an electron uptake on an unoccupied π^* orbital of the aromatic moiety[13,14] and concerted intramolecular transfer to the C–X bond.

The increase in the number of halogen atoms on the methyl group, *i.e.* in benzotrichloride with respect to benzyl chloride, makes the C–X bond weaker;[15] it is therefore to be expected that the effect on $\Delta G_o^\ddagger$ will be transferred to $\Delta G^\ddagger$, which should decrease as a result. The dependence of $\Delta G^\ddagger$ on ΔG_o implies that the latter should also decrease, and the relative stability of the radicals $ArCCl_2^\cdot$ and $ArCH_2^\cdot$, with respect to the original molecules, should therefore be in favour of the former. When the aryl moiety is changed, *e.g.* from benzene to the electron-poor pyridine ring, the energy of the first vacant π^* orbital, where the free-electron is accommodated, can also be expected to change (*i.e.* to drop below that of benzene[16]), with a consequent effect on $\Delta G^\ddagger$. The question is whether the changes in $\Delta G_o^\ddagger$ and ΔG_o occur to the same extent in pyridine and benzene derivatives (and, generally speaking, in arylmethyl

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† The IUPAC name for benzotrichloride is α,α,α-trichlorotoluene.

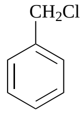
Table 1 Total molecular energy, zero-point vibrational energy (ZPE), vibrational correction to the enthalpy $\Delta H(298)$, entropy $S(298)$ for the molecules **1**–**8** obtained from MO *ab initio* calculations with the 6-31G* basis set (see text)[a]

	Total molecular energy (au)	ZPE/kcal mol^{-1}	$S(298)$/cal mol^{-1} K^{-1}	$\Delta H(298)$/kcal mol^{-1}
1	−729.654 916	80.71	83.85	85.39
2	−1647.697 422	67.59	95.22	73.54
3	−745.677 774	73.01	84.11	77.63
4	−1663.719 362	59.85	95.17	65.74
5	−269.990 180	75.39	74.48	79.44
	−270.134 983[b]			
6	−1188.049 267	63.90	90.72	69.36
	−1188.238 037[b]			
7	−286.011 782	67.73	75.56	71.72
8	−1204.070 342	56.27	90.15	61.63
Cl	−459.553 533			
	−459.586 248[b]			
Cl$^-$	−459.652 104			
	−459.700 264[c]			

[a] Unscaled frequencies were used. [b] At PMP2/6-311G**//6-31G* (fc) level of theory. [c] At MP2/6-311G**//6-31G* (fc) level of theory.

derivatives with different aromatic rings) and whether they can be considered structurally similar with the purpose of applying the Marcus–Hush relationship.

In order to verify the behaviour, under reductive electron transfer, of halogenated arylmethyl derivatives with a different number of halogen atoms on the methyl group and with different aromatic rings, we chose the monochloro and trichloro derivatives of benzene and of 4-pyridine (compounds **1**–**4**). The investigation was carried out at the theoretical level with an MO *ab initio* approach, the aim being to examine the dissociation behaviour of the C–Cl bond in the neutral molecules and in their radical anions. The energy of the transition state and the activated complex for the electron transfer will be investigated in the region of the forbidden crossing of the dissociation profiles of the neutral molecule and of the corresponding radical anion with a procedure previously[14] tested for benzyl chloride. The energies of activation and of reaction will be compared with experimentally determined parameters for the reductive behaviour of these molecules when known.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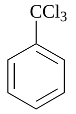
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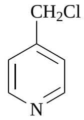
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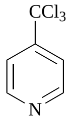
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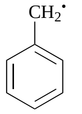
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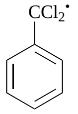
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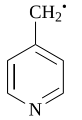
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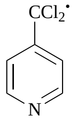
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Theoretical methodology

The MO *ab initio* approach was applied to molecules **1**–**8** by employing the procedures of the GAUSSIAN92[17] and GAUSSIAN94[18] series of programs, run on an IBM AIX/6000 workstation and on a Silicon Graphics 4CPU MIPS R 10000 elaborator. Total molecular energies of compounds **1**–**4** and of the corresponding radicals **5**–**8** were obtained with the 6-31G*[19] basis set and full molecular relaxation. For molecules **1**, **2**, **5** and **6**, the energies were calculated with the 6-311G** basis set[20] as well without further geometry relaxation (single points) (6-311G**//6-31G*). Calculated energies at the MP2 (second-order Møller–Plesset) level of perturbation,[21] MP2/6-31G*//6-31G* and MP2/6-311G**//6-31G*, frozen core (fc), were employed for **1**–**4**, and projected (PMP2),[22] in order to remove spin contamination, for **5**–**8**. For the radicals, the wavefunctions were at the spin unrestricted Hartree–Fock level (UHF). For the radicals of phenyl derivatives the calculated eigenvalue of the spin squared operator $\langle S^2 \rangle$, after spin projection, was 0.75–0.76, while for pyridyl derivatives values higher than 1 were obtained, indicating contamination from electronic levels of spin multiplicity higher than a doublet.

Harmonic frequency calculations were carried out to characterize the global minimum of molecules **1**–**8** and to determine the zero-point vibrational energies, ZPEs, molecular entropy S°_{298} and thermal vibrational corrections to the enthalpy $\Delta H(298)$. The potential energy profiles for the neutral molecules **1**–**4** and for their radical anions were obtained at fixed values of the C–Cl coordinate while relaxing all the remaining geometrical parameters at the MP2/6-31G*//6-31G* level (RHF and UHF with spin projection for molecules and ions, respectively). For compound **1** energy profiles were also calculated at the MP2/6-311G**//6-31G* level, in order to check the influence of the basis set on the dissociation energy profiles.

Results and discussion

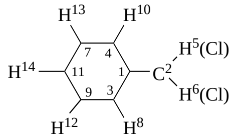
The molecular geometry and total molecular energies obtained from MO *ab initio* calculations for compounds **1**–**4** have already been reported by us.[23,24] The total molecular energies for **1**–**4** and for the corresponding radicals **5**–**8** at the same level of theory, are reported in Table 1. The most relevant geometrical features of the radicals are collected in Table 2. For the benzyl radical, **5**, the geometrical features are in agreement with results reported previously.[25] The calculated geometries of the radicals **5**–**8** show that they are completely planar in their global minimum. The geometrical structure of the CH$_2$ and CCl$_2$ groups do not differ significantly in the derivatives of benzene and pyridine.

The procedure[14] adopted for studying the dissociation pattern of the C–Cl bond of benzyl chloride was applied in this work to molecules **2**–**4**, and the energy profiles were constructed for fixed values of the C–Cl distance, d(C–Cl), at the MP2/6-31G*//6-31G* level (frozen core) and the energy for the dissociated species was arbitrarily set at 6.0 Å. The relative plots are shown in Figs. 1–4. These plots are interpolated with an excellent level of approximation by a Morse equation[26] [eqn. (2)],

Table 2 Most significant geometrical features of radicals **5**–**8** at UHF/6-31G*//6-31G* level

	5	**6**	**7**	**8**
Bond distances/Å				
C^2–H^5(Cl)	1.074	1.723	1.073	1.720
C^2–H^6(Cl)	1.074	1.723	1.073	1.720
C^1–C^2	1.405	1.416	1.403	1.416
C^1–C^4	1.428	1.427	1.425	1.422
C^1–C^3	1.428	1.427	1.425	1.422
C^3–C^9	1.390	1.391	1.387	1.391
C^4–C^7	1.390	1.391	1.387	1.391
C^7–C^{11}	1.405	1.402	1.355	1.388
C^9–C^{11}	1.405	1.402	1.355	1.338
C^9–H^{12}	1.076	1.075	1.070	1.075
C^{11}–H^{14}	1.075	1.075	—	—
Bond angles/°				
(Cl)H^5–C^2–H^6(Cl)	117.58	114.07	117.87	114.61
C^1–C^2–H^5(Cl)	121.21	122.96	121.07	122.70
C^1–C^2–H^6(Cl)	121.21	122.96	121.07	122.70
C^3–C^1–C^2	121.30	121.12	121.87	121.95
C^4–C^1–C^2	121.30	121.12	121.87	121.95
C^1–C^3–C^9	121.04	120.66	119.86	119.30
C^1–C^4–C^7	121.04	120.66	119.86	119.30
C^3–C^9–C^{11}	120.43	120.78	122.96	124.04
C^4–C^7–C^{11}	120.43	120.78	122.96	124.04
C^1–C^4–C^{10}	118.98	119.86	119.90	121.10
C^1–C^3–C^8	118.98	119.86	119.90	121.10
C^3–C^9–C^{12}	119.74	119.23	120.79	119.88
C^4–C^7–C^{13}	119.74	119.23	120.79	119.88
C^7–C^{11}–C^{14}	120.17	120.31	—	—
Torsional angles[a]/°				
C^5–C^1–C^2–H^5(Cl)	0.0	0.0	0.0	0.0
C^3–C^1–C^2–H^6(Cl)	0.0	0.0	0.0	0.0

[a] The rings are completely planar.



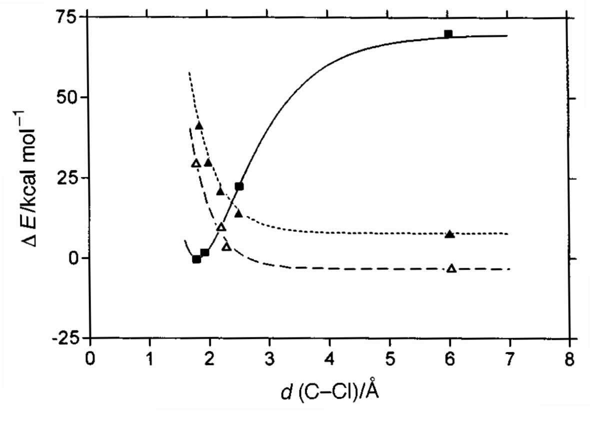


Fig. 1 Energy profile for the C–Cl bond dissociation of compound **1** (—) and of its radical anion (.....) obtained with the 6-31G* basis set, energy profile for the radical anion obtained with the 6-311G** basis set (---) (see text). The curves are fits to Morse (neutral molecule) and exponential (radical anions) functions.

$$\Delta E = D\{1 - \exp[-a(R - R_o)]\}^2 \qquad (2)$$

where R_o is the equilibrium bond distance and D is the bond dissociation energy.

The values of a for the molecules examined are reported in Table 3. The bond dissociation energy used in eqn. (2) is known experimentally only for compound **1**. We estimated the values for compounds **1**–**4** from calculated total molecular energies and these are reported in Table 3. The effect on D values of basis set implementation was tested for benzyl chloride and benzotrichloride, since the total molecular energies for these molecules and for the corresponding radicals (**5** and **6**) were obtained in the 6-311G** basis set as well. Addition of polarization functions produces changes of a few kcal mol^{-1} in the D value of the molecule with a higher number of chlorine atoms, without changing the fundamental trend of the dissociation behaviour in these two molecules. Comparing the D values of the four molecules at the same level of theory, one finds that the

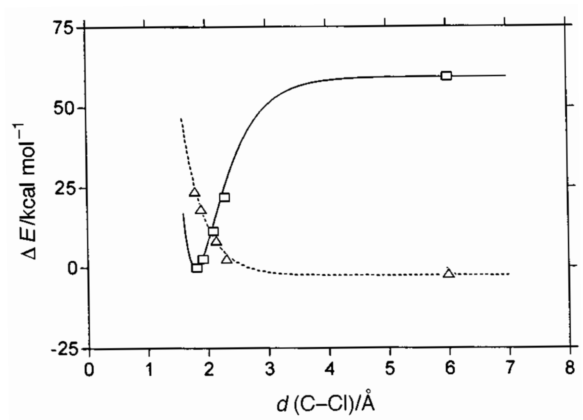


Fig. 2 Energy profile for the C–Cl bond dissociation of compound **2** (—) and of its radical anion (.....) obtained with the 6-31G* basis set. The curves are fits to Morse (neutral molecule) and exponential (radical anions) functions.

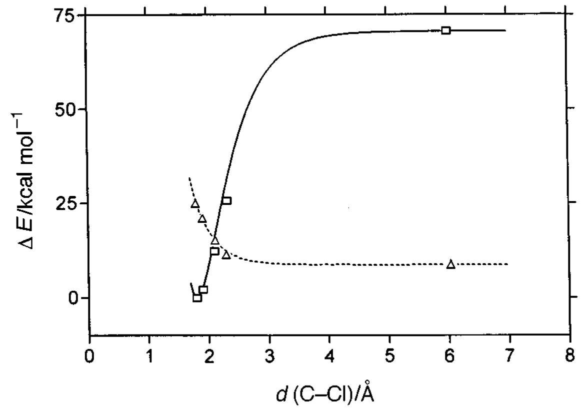


Fig. 3 Energy profile for the C–Cl bond dissociation of compound **3** (—) and of its radical anion (.....) obtained with the 6-31G* basis set. The curves are fits to Morse (neutral molecule) and exponential (radical anions) functions.

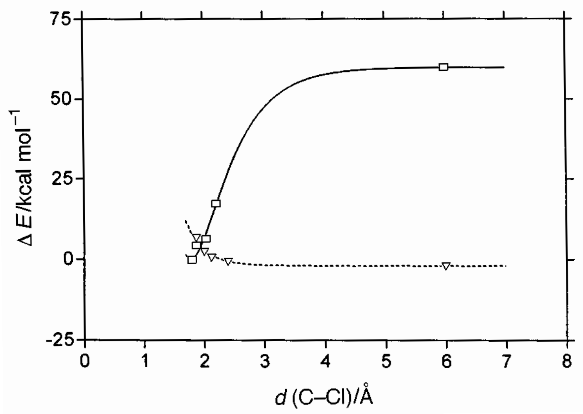


Fig. 4 Energy profile for the C–Cl bond dissociation of compound **4** (—) and of its radical anion (.....) obtained with the 6-31G* basis set. The curves are fits to Morse (neutral molecule) and exponential (radical anions) functions.

Table 3 Bond dissociation energies D of compounds **1**–**4** from *ab initio* total molecular energies[a] and coefficients a for the Morse equation (2)

Compound	D/kcal mol^{-1}	a
1	69.8, 68.3[b], 72.2 ± 1.5[c], 68.9[d]	1.905
2	59.4, 63.2[b]	2.15
3	70.6	1.90
4	59.9	1.96

[a] With the 6-31G* basis set where not otherwise specified. [b] With the total molecular energies at MP2/6-311G**//6-31G* level. [c] Experimental value: D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.*, 1982, **33**, 493. [d] Experimental value reported in ref. 13.

C–Cl bond dissociation energy does not significantly change on passing from benzene to pyridine derivatives with the same chloromethyl group, while the bond strength is firmly dependent on the number of chlorine atoms.

The calculated energy of the Cl and Cl$^-$ species allows one to estimate the electron affinity of chlorine E_{ea}(Cl): this quantity turns out to be strongly dependent on the basis set, since a value of 61.85 kcal mol^{-1} is obtained at the MP2/6-31G* level which becomes 71.55 kcal mol^{-1} at the MP2/6-311G** level of theory. Basis set implementation enhances the calculated values of E_{ea}(Cl), which nevertheless remains lower than the experimental value[26] (83.2 kcal mol^{-1}). This conclusion would suggest that differences between the energy of neutral molecules and that of their radical anions at different C–Cl bond distances are underestimated.

The temporary radical anion of the molecules examined, ArCY$_2$X$^{\bullet -}$ (where Y = H or Cl, and X = Cl), should be generated by the uptake of one electron on the lowest vacant π^* orbital of compounds **1**–**4**. The molecule rearranges in order to attain the structure of the activated complex for the electron transfer and fulfill Franck–Condon restrictions.[3] The main change in molecular structure should involve elongation of the C–Cl bond which undergoes cleavage in the process. The pattern of the molecular energy values of the radical anions of **1**–**4** for different C–Cl bond distances was constructed from energies at the PMP2/6-31G*//6-31G* level. The calculated energy profile for the radical anions examined is dissociative, as appears in Figs. 1–4 (dotted lines). The profiles were interpolated with exponential functions. At bond distances in the range 3–4 Å the energy profile has the tendency to form a broad minimum and deviates from the exponential decay. Energy minima in this region could not be characterized as critical points of the energy hypersurface (according to the Hessian matrix). Even if convergence was not obtained in the calculations, a tendency to form radical–anion molecular complexes, where the chloride anion is weakly bonded to the hydrogens of the radical or to the π-electron cloud of the aromatic ring, is apparent in the different attempts to characterize energy minima. As regards benzyl chloride, **1**, one of these molecular complexes was characterized[14] at the theoretical level, while experimental evidence of such a type of complex, based on photofragmentation techniques, has been reported in the literature.[27]

Before entering into the details of the energy profiles in relation to the electron transfer mechanism, there are two points worth making, concerning the theoretical results. The first regards the level of the theoretical approach in relation to the choice of the basis set. In fact, on examining the dissociation pattern obtained with the 6-311G** basis set one observes (Fig. 1) that the energy profile (energy values refer to the neutral molecule and are taken as zero at the same level of theory) has lower values than that obtained with the 6-31G* basis set. This implies that the crossing of the energy profiles of the neutral molecule and of the radical anion occurs at lower energy values and shorter bond distances when calculations are carried out with the implemented basis set. Since the higher level computations are considerably more time-consuming, we carried out calculations for all the molecules using the 6-31G* basis set, assuming that quantities abstracted from the plots of the larger basis set, which most probably provides more reliable results, are shifted by a constant amount and that the trend in results obtained with the two basis sets are therefore similar.

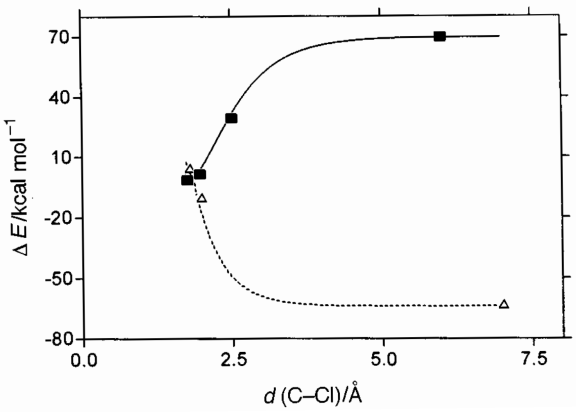


Fig. 5 Energy profile for the C–Cl bond dissociation of compound **1** and of its radical anion calculated for an acetonitrile solution. The curves are fits to Morse (neutral molecule) and exponential (radical anions) functions.

The second point to note is that measurement of the reductive behaviour of these molecules is carried out in solution.[10,11] Accordingly, we attempted to examine the solvent effect on the dissociation profiles of the neutral molecule and of the radical anion of compound **1**. The solvent effect was calculated through the self consistent reaction field (SCRF) approach using the isodensity surface polarized continuum model (IPCM) implemented on the GAUSSIAN94 package.[18] An acetonitrile solution (ε = 37.5 dm^3 mol^{-1} cm^{-1}) was simulated and the results are shown schematically in Fig. 5 (6-31G* basis set). The effect on the dissociation profile of the neutral molecule is slight and the bond dissociation energy is scarcely affected (69.8 kcal mol^{-1} for the free molecule against 69.6 kcal mol^{-1} on acetonitrile). The solvent effect on the energy profile of the anion is considerable and increases with the dissociation of the molecule: in the case of the dissociated PhCH$_2^\bullet$ + Cl$^-$ species the solvent has the effect of lowering the total energy content by 72.3 kcal mol^{-1}. The solvent effect lowers the activation energy of the electron transfer but the relevant effect is on the driving force of the process, which is greatly enhanced.

From Figs. 1–4, the activation energy $\Delta E^\ddagger$ for the concerted electron transfer–bond breaking process can be estimated from the crossing of the energy profiles of the neutral molecule and of the radical anion. A free electron not contributing to the total energy of the neutral molecule is assumed to be present. The C–Cl bond length of the activated complex, $\Delta r^\ddagger$, is also obtained from the crossing of the energy profiles. The energies and geometries of the transition state and the energy of reaction E_o are summarized in Table 4. For benzyl chloride, the activation energy $\Delta E^\ddagger$ decreases at the MP2/6-311G**/UHF/6−31G* level, yet is still higher than the electrochemical estimate[10] of 7.84 kcal mol^{-1} (free-energy of activation measured in solution).

The $\Delta r^\ddagger$ values change with the molecular structure and, at a qualitative level, their decrease mirrors the lowering of E_o values, in agreement with the Hammond postulate.[28] Similarly, E_o and $\Delta E^\ddagger$ values have a qualitative parallel behaviour, in agreement with the Evans–Polanyi principle.[29]

In order to derive information regarding the reductive electron transfer on the molecules examined, the results of *ab initio* calculations can be analyzed in the light of the Marcus–Hush activation-driving force relationship [eqn. (1)] written[12,30] in the form of eqn. (3), where the work terms are assumed to be constant for the molecules examined. In eqn. (3), $\Delta E^\ddagger$, $\Delta E_0{}^\ddagger$ and

Table 4 Reaction energies E_o, activation energies $\Delta E^‡$ and geometry $\Delta r^‡$ of the activated complex of the electron transfer reaction

		$\Delta E^‡$/kcal mol^{-1}			$\Delta r^‡$/Å		
Compound	E_o[a]	*b*	*c*	*d*	*b*	*e*	*f*
1	7.93, −3.24[g]	20.6, 14.8[g]	21.64	11.39	0.39, 0.33[g]	0.48	0.30
2	−2.48	10.2	13.64	5.33	0.20	0.35	0.19
3	8.71	14.2	22.27	11.91	0.30	0.52	0.33_5
4	−1.94	4.7	14.02	5.59	0.12	0.36	0.20

[a] Relative to the energy of the global minimum of the neutral molecule ($E_{R^\cdot} + E_{Cl^-} - E_{RX}$). [b] From the crossing of the energy profiles reported in Figs. 1–4. [c] From eqn. (3), where E_o stands for ΔE. [d] From eqn. (3), by employing $\Delta E = D - E_{ea}$(Cl) where D is the calculated bond dissociation energy. [e] From eqns. (4) and (5) by employing $\Delta E = E_o$. [f] From eqns. (4) and (5) with $\Delta E = D - E_{ea}$(Cl). [g] At the MP2/6-311G**//6-31G* level.

$$\Delta E^‡ = 4\,\Delta E_o^‡\left(1 + \frac{\Delta E}{4\,\Delta E_o^‡}\right)^2 \qquad (3)$$

ΔE are the activation barrier, intrinsic barrier and driving force ($-\Delta E$), in that order. The ΔE values can be assimilated to the E_o values reported in Table 4.

It was noted above that at the PMP2/6-31G*//UHF/6-31G* level the electron affinity of chlorine is underestimated as are the total molecular energies of radical anions. Accordingly, the values of $\Delta E^‡$ and $\Delta r^‡$ are also calculated empirically through eqns. (3)–(5). Two different approaches for ΔE (E_o) were employed: one refers to the E_o values from *ab initio* calculations and the other to the relation $\Delta E = D - E_{ea}$(Cl), where the electron affinity of chlorine is 83.2 kcal mol^{-1}. The two sets of $\Delta E^‡$ values are reported in Table 4. The set derived from the second approach, which accounts for correct values of E_{ea}(Cl), shows effectively lower values. However, the effect of the different heterocyclic ring is no longer reproduced since the $\Delta E(E_o)$ values account only marginally for this variable. Empirical estimates[30] of the geometry of the activated complex, $\Delta r^‡$, were derived from eqns. (4) and (5) where ν_o is the stretching

$$\Delta r^‡ = (1/\beta)[\ln 2 - \ln(1 - \Delta E/D)] \qquad (4)$$

$$\beta = \nu_o(2\pi^2\mu/D)^{\frac{1}{2}} \qquad (5)$$

frequency of the C–Cl bond (742 cm^{-1} for *p*-cyanobenzyl chloride[31]) and μ is the reduced mass of C and Cl atoms.

The empirical values of $\Delta r^‡$ follow the trend of those obtained from the crossing of energy profiles: at the quantitative level they agree better when obtained from ΔE values that account for the correct electron affinity of chlorine.

The reduction potentials of compounds **1**–**4** were derived from an experimental study[11] of the reductive electron transfer of α-chloroderivatives of toluene and picolines carried out with cyclic voltammetry. The concerted electron transfer–bond breaking (C–Cl) mechanism was proposed as the most probable one[11] for these molecules. The reported[11] reduction potentials E_p (in volts) (acetonitrile solution, referred to aqueous saturated calomel electrode, SCE, scan rate 0.1 V s^{-1}) are: **1**, −2.33; **2**, −1.76; **3**, −2.03; **4**, −1.46. At first sight, these E_p values show that they 'see' the presence of a different number of chlorine atoms (CH_2Cl and CCl_3 groups) and the different aromatic ring. The plot of the $\Delta E^‡$ values obtained from the crossing of energy profiles (column *c* of Table 4) as a function of the experimental E_p values is shown in Fig. 6 and reveals excellent linearity (correlation coefficient 0.9978). An analogous linear plot is obtained even at a lower level of theory (MP2/3-21G*/3-21G*, $r = 0.9943$) showing that the correlation is not a peculiarity of the particular basis set employed.

An immediate conclusion is suggested by this plot: theoretical results relative to the activation step for the electron transfer–bond breaking process, even though referring to isolated molecules, mirror the behaviour of the reduction of these molecules in solution. Unfortunately SCF convergence problems did not allow us to obtain reliable results for the radical anions in solution in the interval of the crossing energy profiles and to compare the activation energies in different solvents.

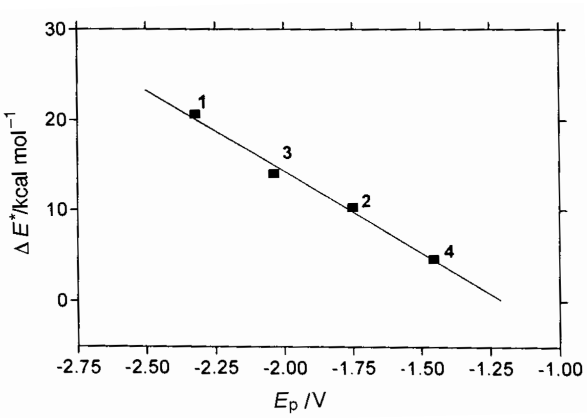


Fig. 6 Diagram of the calculated energies of activation $\Delta E^‡$ for the reductive C–Cl bond cleavage *vs.* the experimental reduction potentials E_p (in volts, SCE electrode) for compounds **1**–**4**

For an electrochemical reaction, eqn. (1) can be reduced[10] to eqn. (6), where E° is the standard potential and φ_r the electrical

$$\Delta G^‡ = \Delta G_o^‡\left(1 + \frac{E_p - E^\circ - \varphi_r}{4\Delta G_o^‡}\right)^2 \qquad (6)$$

potential at the reaction site. Assuming that eqns. (1) and (6) represent a satisfactory model for the set of molecules examined here, the linear behaviour of activation barriers as a function of driving forces indicates that the compounds under study fall in the 'equilibrium region'[3] of the Marcus–Hush correlation, where the quadratic relationship becomes nearly linear.

The following represents an attempt to gain further insight into the physical meaning of this correlation. The thermodynamic terms reported in Table 1 can be employed to estimate the free-energy of the electron transfer reactions, ΔG_o, the values obtained are reported in Table 5. These ΔG_o values are related[10] to the standard potential E°; thus, for the molecules examined, the corresponding E° values were calculated and are reported in Table 5: these values were referred to benzyl chloride, **1**, for which a value of −0.87 V has been reported[10] (*vs.* SCE). A comparison of the ΔG_o values (equivalent to a comparison of E° values) shows that, in terms of free-energy, substitution of the CH_2Cl with the CCl_3 group has the effect of lowering the free-energy of reaction by 8.3 ± 0.2 kcal mol^{-1}, yet the effect of the ring is much smaller, amounting to only 0.7 ± 0.1 kcal mol^{-1} on going from the phenyl to the pyridyl derivatives. Analogous conclusions stem from the ΔE values reported in Table 4. On the other hand, the activation energies are increased by 10.0 ± 0.4 kcal mol^{-1} when the number of chlorine atoms is increased and by 6.0 ± 0.4 kcal mol^{-1} when the aromatic ring is changed.

The driving force $-\Delta G_o$ or ($-\Delta E$) measures the relative stability of reagents and products, and $\Delta E^‡$ accounts for the transition state of the electron transfer–bond breaking process:

Table 5 Calculated enthalpies ΔH_D and free-energies ΔG_D of the bond dissociation process, free-energies of reaction $-\Delta G_o$ and standard potentials E° of the electron transfer reaction, for compounds **1**–**4**

Compound	$\Delta H_D{}^a$/kcal mol^{-1}	$\Delta G_D{}^b$/kcal mol^{-1}	$\Delta G_o{}^c$/kcal mol^{-1}	$E_o{}^d$/V
1	60.88	61.31	0.54	−0.87
2	53.87	52.85	9.01	−0.50
3	61.74	61.93	−0.07	−0.89
4	54.59	53.73	8.13	−0.54

[a] $H_{Cl} + H_R - H_{RX}$. [b] $G_{Cl} + G_R - G_{RX}$. [c] $G_{RX} - G_R - G_{Cl}$. [d] Values scaled with respect to that of compound **1** reported in ref. 13.

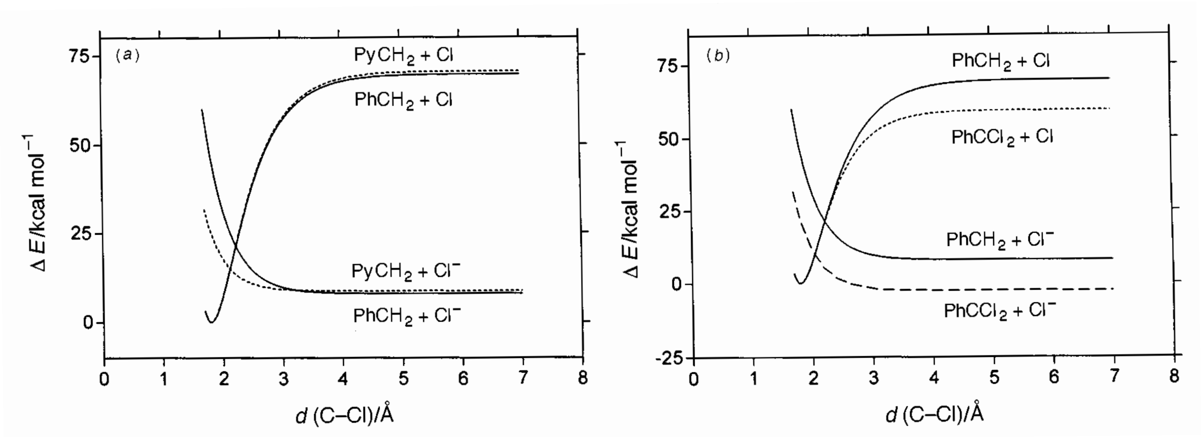


Fig. 7 Schematic comparison of energy profiles of neutral molecule and radical anion for α-chloroarylmethyl derivatives showing: (*a*) the effect of changing the aromatic ring and (*b*) the effect of changing the number of chlorine atoms in the methyl group

$-\Delta G_o$ and $\Delta G^\ddagger$ ($\Delta E^\ddagger$) are correlated with the electrochemical potentials E° and E_p. The relative free-energy content of reactants and products is significantly affected by the number of chlorine atoms on the methyl group and only slightly by the different aromatic ring, while the transition state is also affected by the different aromatic ring. The driving force and activation energy of the whole set of the molecules examined do not therefore appear to obey a single correlation of the Marcus–Hush type.

The electron transferred on the molecules examined should be accommodated in the lowest vacant π* orbital, which is of lower energy in the pyridyl than in the phenyl derivative.[16] The crossing point of the energy profile of neutral molecules and radical anions in the concerted process relative to the molecules examined should be dictated by the energy required to enter the π* orbital and reach the breaking point of the C–Cl bond. The former quantity should be almost constant in phenyl derivatives, yet is expected to dictate a difference when activation energies for electron transfer in derivatives of pyridine and benzene having the same CY_2Cl group are compared. A tentative schematic representation of these situations is depicted in Fig. 7.

In conclusion, the experimental reductive behaviour of a group of molecules should be handled carefully in order to formulate the mechanism of the electron transfer process, especially when the results are employed to derive the fine structure of molecules. At a quantitative level the Marcus–Hush relationship is a good approximation for accommodating the reduction pattern of aromatic derivatives having different substituents and the same aromatic ring. But when the aromatic ring is changed, more attention is required in order to verify whether approximations introduced to derive this correlation are satisfied. The assumption that the work terms of eqn. (1) are constant and that $\Delta G_o{}^\ddagger$ is a quarter of the bond dissociation energy is valid for molecules with molecular structures more similar than is usually believed. By the same reasoning substitution of ΔG_o with ($E_p - E^\circ - \varphi_r$), in the case of electrochemical reactions, seems strictly valid only when all the molecules obey a very similar mechanism of electron transfer-bond breaking. As a general rule, work terms w_R and w_P appearing in eqn. (1), which, in the case of aromatic derivatives, account for the electron income onto the π* orbital as well, should not be considered a constant contribution when dealing with molecules with different structures of the aromatic moiety.

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