Reductive electron transfer on trichloromethyl derivatives of benzene and pyridine studied by electrochemical methods

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The electrochemical reduction of α,α,α-trichlorotoluene (benzotrichloride) and of the corresponding isomeric pyridine derivatives has been investigated by cyclic voltammetry and microcoulometry. Three irreversible diffusion controlled reduction waves have been observed in the voltammetry of the trichloromethyl derivatives and are found to correspond to the progressive two-electron reduction of derivatives where a chlorine atom is substituted by a hydrogen atom. The peak potentials E_p show that reduction of the pyridine derivatives is easier than that of the benzene derivatives with the same number of chlorine atoms, the more positive shift occurring for the 4-substituted compounds. The experimental findings would indicate a concerted electron transfer-bond breaking (C−Cl) mechanism for all the compounds examined, as well as for the chloromethyl and dichloromethyl derivatives formed after Cl/H substitution. Electron uptake appears to be the rate-determining step of the reductive cleavage of these molecules. The effects of the different aromatic rings and of the degree of halogen substitution of the methyl group on the reduction potentials are discussed.

Introduction

It is now accepted[1] that aliphatic nucleophilic substitution can proceed through a radical mechanism, and the literature contains numerous reports dealing with this subject.[2] The electron transfer step from an outer-sphere donor $D^{\bullet -}$ to an acceptor molecule RX should involve a radical anion $RX^{\bullet -}$ as an intermediate in the case of a stepwise mechanism or, in the case of a concerted mechanism, an activated complex structurally similar to the radical anion. In an electrochemically mediated process the electron comes from one electrode, yet the two limiting reaction routes are of the same type.[3,4] Alkyl halides undergo[1b] dissociative electron transfer in homogeneous and heterogeneous media. The dissociative electron capture of methyl chloride has been supported by both experimental[5] and theoretical[6] evidence, yet electron attachment to polyhalogenated methanes gives rise to the formation of radical anions in the gas phase as well as in solid matrices.[7]

The situation appears more complex when reductive electron transfer occurs on arylmethyl halides. Experimental results[3] show that a stepwise reaction, with the intermediacy of the radical anion, takes place for ring-substituted nitrobenzyl chlorides and bromides, yet for the molecules with poor electron-withdrawing substituents, including benzyl chloride and benzyl bromides themselves, a concerted electron transfer–bond breaking mechanism occurs. Recently, we reported[8] the results of *ab initio* MO calculations showing the dissociative nature of the radical anion of benzyl chloride. A molecular complex between the benzyl radical and the chloride anion was nevertheless demonstrated[8] on the dissociation path. Ion–molecule complexes of this kind were revealed[9] through photofragmentation techniques in other molecular systems with chlorine bonded to an unsaturated system. These complexes nevertheless behave as labile species and are not likely to survive in solution at room temperature. In benzyl halides the C−Hal bond does not lie in the nodal plane of the π* orbital where the electron is captured[10] and symmetry arguments would suggest that the fragmentation of the radical anion of these molecules is straightforward. The stepwise mechanism found for a number of these molecules thus requires a deeper insight into the factors governing the stepwise and concerted routes.

Thermodynamically,[3] in terms of driving forces, the potentials $E°(RX/R^{\bullet} + X^{-})$ and $E°(RX/RX^{\bullet -})$ determine the preferential mechanism and, by increasing negative values for the formation of the radical anion, favour the concerted route; kinetics[3] dictate that the dissociative electron transfer requires a higher intrinsic barrier than that of the outer-sphere formation of $RX^{\bullet -}$. On the other hand, a temporary radical anion is characterized by one electron occupying an accessible π* orbital of the aromatic ring before being transferred to the departing halide anion. The ground-state fragments correlate with the initial anion in benzyl chloride; nevertheless, substituents on the ring are able to influence the energy of the low-lying π* orbital and the C−X bond dissociation energy to a different extent, thus allowing the transition from one mechanism to the other. This occurs for example in benzyl chloride[3] when a nitro substituent is introduced into the ring: the decrease in the energy of the low-lying π* orbital overcomes the dissociation energy of the C−X bond.

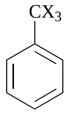
In the case of α,α,α-trichlorotoluene (benzotrichloride) the reduction potential is positive to that of benzyl chloride; the change in $E°(RX/RX^{\bullet -})$ can be estimated as being of the order of 0.6–0.8 V according to reduction potentials reported in the literature,[11] and the C−Cl bond dissociation energy decreases by *ca.* 220 meV (*ca.* 5 kcal mol^{-1}; 1 cal = 4.184 J).[12] These values would suggest that, with respect to benzyl chloride, a stepwise mechanism cannot be excluded *a priori* for benzotrichloride. Owing to the strong electron-withdrawing character of the ring nitrogen in the trichloromethyl derivatives of pyridine, there is an enhanced probability of the occurrence of a stepwise mechanism, especially if the effect of the heteroatom is to decrease the energy of the low-lying π* orbital to a greater extent than the bond dissociation energy of the C−Cl bond. Of course this reasoning refers to reactions in the vapour phase and ignores the effect of solvents, which can still represent a driving force conducive to the concerted mechanism even in the presence of factors which favour the stability of a temporary radical anion.

Some of us have recently reported[13,14] that a number of ring substituted benzotrichlorides and the isomeric trichloromethylpyridines, $ArCCl_3$, react in anaerobic conditions and acetonitrile solution with Fe^{II} ions. For the majority of the compounds examined the reaction products were dimeric

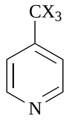
$ArCCl_2CCl_2Ar$ molecules, and experimental evidence suggests that the process takes place through a rate-determining reductive electron-transfer producing the chloride anion and the $ArCCl_2^{\bullet}$ radicals which dimerize rapidly. In the case of 2- and 4-trichloromethylpyridines, the reaction compound was almost exclusively the $ArCHCl_2$ derivative, which is assumed to result from further reduction to the carbanion of the $ArCCl_2^{\bullet}$ radical co-ordinated to the metal ion.

The electrochemical reduction of benzotrichloride has been investigated in the past few years[15] and, more recently, by Gisselbrecht and Lund.[16] The results of these investigations show that the electrochemical behaviour of benzotrichloride depends very much on experimental conditions. When the mercury electrode is employed, a surface effect occurs and, as a function of experimental conditions, either the dimeric product derived from the coupling of the $C_6H_5CCl_2^{\bullet}$ radical or the stepwise Cl/H substitution compounds are obtained.

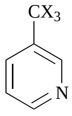
Accordingly, the aim of the present investigation is to examine the behaviour, under reductive electron transfer, of trichloromethyl derivatives of benzene and of pyridine (compounds **1a**–**4a**) by electrochemical methods in order to gain insight into the mechanism involved in the reduction of these molecules and, eventually, to learn more about the structural features of their radical anions. The experimental approach will be based on cyclic voltammetry and the conclusions will be supported with a number of descriptors obtained from MO calculations.



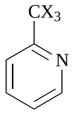
1a,b,c



2a,b,c



3a,b,c



4a,b,c

a = CCl_3; **b** = $CHCl_2$, **c** = CH_2Cl

Experimental

Compounds

The trichloromethyl derivatives **1a**–**4a** and reference compounds **1b**, **1c** were either commercial products or were synthesized according to known procedures.[14] Compounds **1a**–**4a**, **1b**, **1c** and the solutions of reaction products obtained after the electrochemical measurements were analysed by GLC and HPLC techniques (the latter being employed to detect the presence of dimeric products $ArCCl_2CCl_2Ar$ which are thermally unstable[14]). GLC was carried out with a Hewlett-Packard 5890 instrument fitted with an HP5 phenylsilicone column (phase 5%) and HPLC with a Hewlett-Packard 1090 unit fitted with a RP-18 (25 cm) column. The solutions employed in GLC were 2×10^{-4} mol dm^{-3} in anhydrous diethyl ether with helium as carrier gas. The eluent for HPLC was $MeCN–H_2O$, the amount of the two components being optimized for each reaction mixture. A Hewlett-Packard 5898A spectrometer was employed for GLC–MS measurements.

Electrochemical measurements

The electrochemical behaviour of compounds **1a**–**4a**, **1b**, **1c** was examined in dichloromethane (DCM) (Fluka, $H_2O < 0.005\%$) and MeCN (Fluka, $H_2O < 0.01\%$). The solution concentrations were 1×10^{-4} –5×10^{-4} mol dm^{-3}. Tetrabutylammonium perchlorate (TBAP) at constant ionic strength ($I = 0.1$ mol dm^{-3}) was employed as base electrolyte.

Voltammetry. The voltammetric measurements were performed using a PAR 273 Potentiostat/Galvanostat system. A glassy carbon (GC) electrode was used as working electrode, a Pt sheet as counter electrode and aqueous Ag/AgCl, KCl as reference electrode. The diameter of the glassy carbon electrode was 2 mm and its surface was accurately polished and ultrasonically rinsed before each run. The reference electrode was contained in a glass tube, separated from the solution by a glass frit of medium porosity which was located a few mm from the working electrode. The voltammetric curves were recorded at a scan rate ranging from 0.05 to 20 V s^{-1}.

All the potential values reported were determined with an accuracy of ±5 mV and referred to aqueous saturated calomel electrode (SCE).

The voltammetric curves of compounds **1a**–**4a** show three irreversible diffusion controlled waves. The electron stoichiometry of each wave is 2 both in DCM and in MeCN, whatever the scan rate. This electron number was determined by comparing the i_p values with those of the first one-electron reversible wave of anthracene in the same medium and under the same experimental conditions.[3] The transfer coefficient (α) values were derived from slopes of the E_p–log v (v = scan rate) plots, according to $\alpha = (F/2RT)\mathrm{d}E_p/\mathrm{d}\log v$ and from the peak widths using the equation $\alpha = (1.85RT/F)/(E_{p/2} - E_p)$. Since the voltammetric behaviour is quite similar in both solvents, the voltammetric data, recorded in this work, correspond to those determined in MeCN.

Microcoulometry. To identify the reduction products and to determine the number of electrons involved in the overall reductive process, coulometric measurements were performed with the same instruments employed for voltammetry. The depolariser concentration was 10^{-3} mol dm^{-3} in MeCN. TBAP (0.05 mol dm^{-3}) was used as base electrolyte. The electrolytic cell consisted of two compartments separated by a sintered glass disk; a glassy carbon electrode, with a surface of *ca.* 1 cm^2, was used as working electrode, a Pt sheet as the counter and aqueous Hg/Hg_2Cl_2, $NaCl_s$ as reference electrode. An electrolysis potential was selected close to the E_p value. The number of electrons involved in the reduction, 2 in all the cases examined, was determined by integration of the current–time curves. α,α-Dichlorotoluene (benzylidene chloride) **1b** (80%) and benzyl chloride **1c** (20%) are formed at the potential of the first wave. Benzyl chloride (65%) and toluene (35%) were the products of electrolysis at the second wave. From benzyl chloride only the formation of toluene was observed. All the electrolysis products were identified by mass spectrometry measurements. The coulometric solutions were diluted with water (1:2 ratio) and extracted with diethyl ether; the separated organic layer was dried with $MgSO_4$, concentrated and examined using the GLC–mass spectrometer.

MO calculations

These were performed at the semi-empirical level with the AM1 method[17] and at the *ab initio* level with the 6-31G* basis set and full geometry relaxation (6-31G*//6-31G*) with the GAUSSIAN 92 package.[18] Restricted Hartree–Fock (RHF) for closed shell molecules and unrestricted Hartree–Fock (UHF) for radicals were employed. Calculations were run on CRAY T3D MCA 128–8 and Silicon Graphics MIPS R 10 000 supercomputers.

Results and discussion

The cyclic voltammetric behaviour of benzotrichloride, **1**, at different concentrations and scanning speeds shows three diffusion controlled irreversible waves, each involving two electrons. The central wave is rather broad and nearly a shoulder of the third wave. In Fig. 1, two typical examples are reported and the experimental results of the molecules examined are set out in Table 1. The second and third waves are practically coincident with the two waves shown by benzylidene chloride **1b**. In the case of the latter molecule, of the two waves observed, that at the more negative potential is coincident with the single wave observed for benzyl chloride **1c**. In the range of scanning speeds employed the waves are irreversible for compounds **1b** and **1c** as well. The voltammetric behaviour of **1a**–**c** suggests that the two-

Table 1 Results of the cyclic voltammetric experiments carried out on compounds **1a**–**4a**, **1b** and **1c** (at scan rate $v = 0.2$ V s^{-1})

	1st wave			2nd wave			3rd wave		
Compound	E_p/V	$E_{p/2}$/V	i_p/μA	E_p/V	$E_{p/2}$/V	i_p/μA	E_p/V	$E_{p/2}$/V	i_p/μA
1a	-1.76_0	-1.65_0	6.2	-2.16_0	-2.05_0	6.8	-2.34_0	-2.24_0	5.0
1b				-2.15_5	-1.99_0	16.9	-2.34_5	-2.20_0	12.3
1c							-2.33_5	-2.16_0	4.6
2a	-1.46_5	-1.33_5	8.6	-1.76_0	-1.63_0	6.3	-2.03_0	-1.88_0	5.7
3a	-1.60_0	-1.42_0	8.4	-1.92_0	-1.81_0	8.4	-2.11_0	-2.02_0	7.3
4a	-1.72_0	-1.55_0	5.8	-2.00_0	-1.89_5	4.8	-2.18_5	-2.04_0	4.1

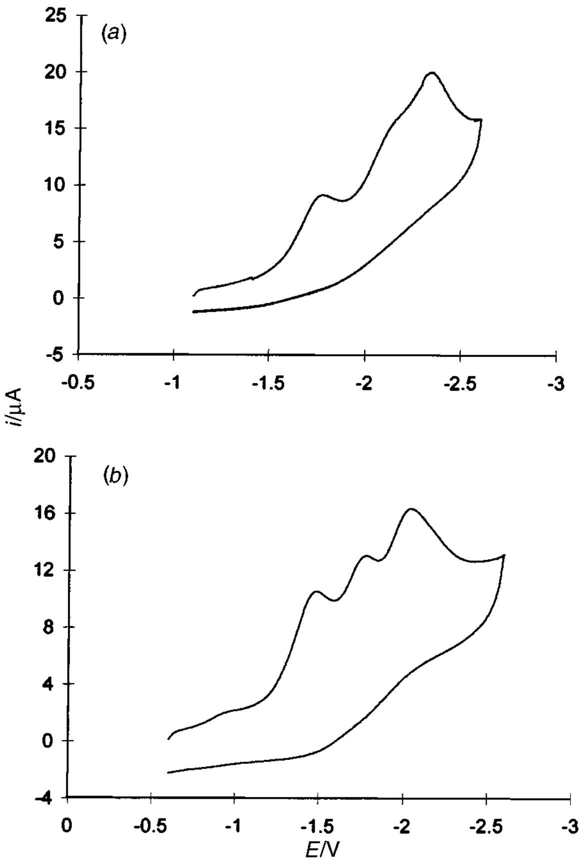


Fig. 1 Cyclic voltammetry of (*a*) benzotrichloride and (*b*) 4-trichloromethyl pyridine (scan rate $v = 0.2$ V s^{-1}) in ACN

electron reduction of these compounds leads to the stepwise formation of derivatives where a chlorine atom is substituted by a hydrogen atom, in accordance with the reactions included in Scheme 1. This is confirmed by the coulometric study of the

$$ArCCl_3 \xrightarrow{e^-} ArCCl_2^{\bullet} + Cl^- \qquad (1)$$

$$ArCCl_2^{\bullet} \xrightarrow{e^-} ArCCl_2^- \xrightarrow{BH} ArCHCl_2 \qquad (2)$$

$$ArCHCl_2 \xrightarrow{e^-} ArCHCl^{\bullet} + Cl^- \qquad (3)$$

$$ArCHCl^{\bullet} \xrightarrow{e^-} ArCH_2Cl^{\bullet} \xrightarrow{BH} ArCH_2Cl \qquad (4)$$

$$ArCH_2Cl \xrightarrow{e^-} ArCH_2^{\bullet} + Cl^- \qquad (5)$$

$$ArCH_2^{\bullet} \xrightarrow{e^-} ArCH_2^- \xrightarrow{BH} ArCH_3 \qquad (6)$$

BH can be either H_2O or CH_3CN

Scheme 1

reduction processes at potentials more negative with respect to the voltammetric waves.

Table 2 Electron transfer coefficient[a] α for compounds **1a**–**4a**, **1b** and **1c** at different scan rates

Scan rate/V s^{-1}	1a	1b	1c	2a	3a	4a
0.05	0.38	0.37	0.26	0.34	0.40	0.33
0.20	0.32	0.29	0.22	0.31	0.31	0.23
0.40	0.28	0.27	0.19	0.24	0.25	0.24
1.00	0.28	0.26	0.17	0.20	0.18	0.22
10.00	0.21	0.19	—	0.18	0.16	0.19

[a] Defined in the Experimental section.

The voltammetric behaviour of the trichloromethyl pyridines **2a**–**4a** is similar to that of benzotrichloride, and the coulometric determination combined with mass spectrometry indicates that the reaction sequence reported in Scheme 1 applies to these molecules as well. Products different from those deriving from H/Cl substitution were never observed in the coulometric experiments. The E_p values show that the ease with which the trichloromethyl pyridines reduce decreases in the order **2a** > **3a** > **4a**.

The reaction products and the two-electron transfer in each reduction wave indicates that H/Cl substitution occurs through the formation of the radical and further reduction to carbanion. The reduction potential of the $ArCl_2^{\bullet}/ArCl_2^-$ couple is expected to be positive to that of the $ArCCl_3$ molecule, by analogy with the behaviour of benzyl radicals with respect to benzyl chloride.[19,20] A semi-empirical estimate (AM1) of the reduction potential of the α,α-dichlorobenzyl radical (−1.14 V) based on empirical correlations[12] with the adiabatic electron affinity shows that this value is positive to that of benzotrichloride.

Evidence regarding the single steps constituting the mechanism of the whole process is not immediately forthcoming from the experimental results. Nevertheless, the values of the electron transfer (ET) coefficient α,[3] shown in Table 2, <0.5 for all the molecules examined, and the linear correlation linking E_p to the potential scan rate with a slope ranging between 100 and 170 mV indicates that a reductive cleavage of the C–Cl bond occurs under the kinetic control of a heterogeneous ET.

The experimental details obtained in this work for benzyl chloride coincide closely with the results reported previously,[3] and the similar experimental behaviour of all the molecules examined would lead one to suppose that their reduction is best accounted for by the concerted mechanism.

In benzotrichloride, and even more so in the trichloromethyl pyridines, the dissociative π^*–σ^* orbital where the electron is transferred should be lower in energy than in benzyl chloride. Furthermore, calculations at the semi-empirical AM1 level showed[12] that the energy profile of the radical anion of benzotrichloride as a function of the C–Cl bond distance has a minimum.

The energy of the first unoccupied orbital (LUMO) of the $ArCH_2Cl$, $ArCHCl_2$ and $ArCCl_3$ molecules was calculated at the *ab initio* HF/6-31G*//6-31G* level and plotted, Fig. 2, against the experimental values of E_p. The LUMO of these molecules is of π^* type and extends over the atoms of the ring and of the chlorinated methyl group. The entries in Fig. 2(*a*) show a satisfactory proportionality and suggest that the incom-

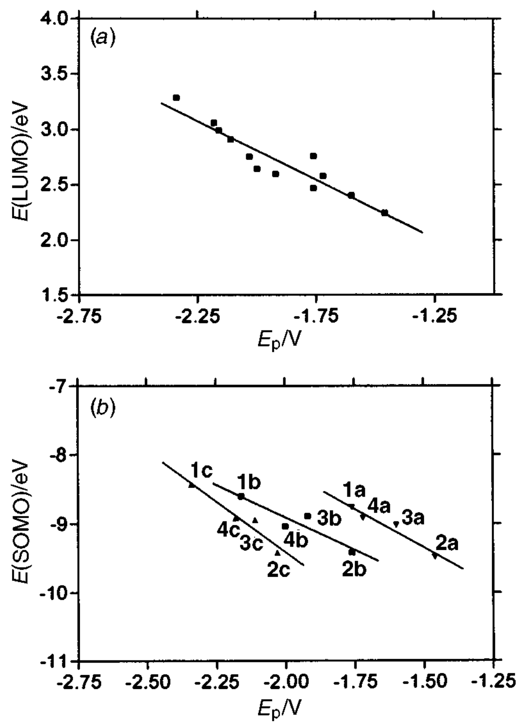


Fig. 2 Diagram of (*a*) the energy of the first unoccupied π orbital (LUMO) of ArCXYCl (X, Y = H or Cl) molecules and (*b*) the energy of the singly occupied orbital (SOMO) of the radicals ArCXY$^•$ against the peak potentials E_p. Calculated energies are at *ab initio* 6-31G*//6-31G* level.

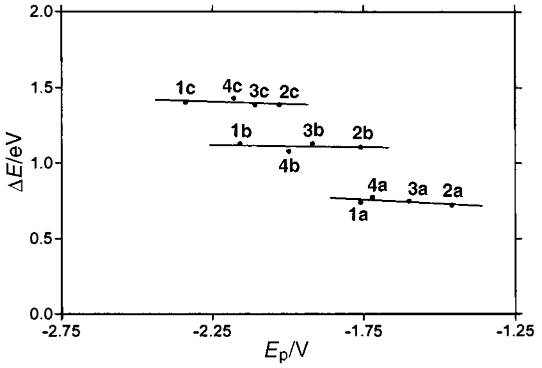


Fig. 3 Diagram of the C–Cl bond breaking energies calculated *ab initio* against the peak potentials E_p for compounds **1–4**

ing electron is accommodated on a vacant orbital with characteristics similar to those of the π* orbital. The SOMO energy for the radicals ArCX$_2^•$, obtained at the UHF/6-31G*//6-31G* level, plotted against the E_p values, shows different, approximately linear, plots [Fig. 2(*b*)] for the molecules differing in the number of their chlorine atoms. The electronic structure of the aromatic ring acts almost in the same way in the molecules with the CH_2Cl, $CHCl_2$ and CCl_3 groups. This finding recalls the conclusion, based on experimental results,[20] that the redox potentials of benzyl halides and of the pertinent radicals are correlated. The energy jump from one correlation to the other of Fig. 2(*b*) depends on the different C–Cl bond substitution of the α-carbon.

The energy difference between the total molecular energy of the neutral molecules ArCX$_2$Y (with X = H, Cl) and that of the ArCX$_2^•$ radicals, Δ*E*, should be a measure of the trend of C–Cl bond dissociation energies in the molecules examined. These values, when plotted against the E_p values, again show different, almost linear, plots for the molecules with different chloromethyl groups, as can be observed in Fig. 3. This result confirms that the different aromatic rings have a parallel effect on the cleavage of the C–Cl bond in the three series of molecules. Furthermore, the reduction potential is affected both by the nature of the aromatic ring and by the C–Cl bond dissociation energy: the effect of the former parameter is greater than that of the latter. This can be seen in Fig. 3 by comparing the lines joining compounds with the same chloromethyl groups with those (not drawn) joining compounds with the same aromatic ring (for example that joining **2a**, **2b** and **2c**).

Table 3 Differences in E_p values (scan rate 0.1 V s^{-1}) for compounds **1–4** referred to benzyl chloride and bond dissociation energies estimated with eqn. (2)

		D/kcal mol^{-1}		
Compound	$-\Delta E_p$/V	*a*	*b*	*c*
1a	0.58_0	58.1		55.7
1b	0.15_0	68.0		65.2
1c	0	(71.5)^d		74.1
2a	0.84_0	52.1	57.6	54.7
2b	0.56_0	58.6	64.1	65.1
2c	0.30_0	64.6	70.1	72.9
3a	0.75_0	54.2	55.9	55.1
3b	0.42_0	61.8	63.5	64.9
3c	0.20_0	66.9	68.6	72.9
4a	0.63_0	56.9	59.3	57.0
4b	0.35_0	63.4	65.8	66.6
4c	0.17_0	67.5	69.9	75.4

^{a} Calculated with eqn. (1). ^{b} Corrected for an approximate estimate of the effect of the aromatic ring, see text. ^{c} Estimates from AM1 calculations of heats of formation of Cl and of ArCXYCl (X, Y = H or Cl) and ArCXY$^•$ molecules. ^{d} Ref. 21.

The similar electrochemical behaviour of benzyl chloride and benzotrichloride, and of the analogous pyridine derivatives, assumed to be represented by a concerted electron transfer-bond breaking mechanism, suggests that the theory of dissociative electron transfer[3] can be applied to all these molecules with the same degree of confidence. Tentative values of the C–Cl bond dissociation energy were derived[3] from the differences in peak potentials for substituted benzyl chlorides by means of the simple expression, eqn. (1), which contains a

$$\Delta D = -(2/3)\Delta E_p \qquad (1)$$

number of simplifying assumptions, and the energy differences are calculated with respect to benzyl chloride. Estimated bond dissociation energies are in reasonable agreement with values from different literature sources. The approximations assume that the molecules are of similar size, that the quadratic character of the activation-driving force relationship can be ignored and that the peak potentials, at the same scan rate, are close enough to be considered as having been obtained under similar physical conditions. In addition to these assumptions, the application of eqn. (1) is equivalent to assuming that the E_p values for benzyl chlorides are governed exclusively by the strength of the C–Cl bond and that the activation energy for electron transfer is dictated by the cleavage of this bond to form the chloride anion. Given the very similar electrochemical behaviour of benzyl chloride and benzotrichloride, the same conclusion should hold for the latter molecule as well. Applying the approximation represented by eqn. (1), one obtains the values of bond dissociation energies reported in Table 3 and referring to benzyl chloride (D = 71.5 kcal mol^{-1}[21]). One qualitative conclusion which stems from these values is that the C–Cl bond becomes weaker as the number of chlorine atoms increases, and that for the same CXYCl (X, Y = H or Cl) group, the C–Cl bond is weaker in pyridine derivatives than in benzene derivatives.

The effect of the aromatic ring on the theoretical bond dissociation energy Δ*E* is small and suggests that the changes in E_p should account more for the changes in the energy of the orbital accommodating the electron. This assumption would imply that the derivation of bond dissociation energy from eqn.

(1) is not altogether straightforward: these energies for molecules with the same CXYCl group and different rings should probably be closer than appears from the application of eqn. (1).

The assumptions introduced[3] for deriving eqn. (1) apply correctly to substituted benzyl derivatives yet probably could not be strictly valid for pyridine and benzene derivatives. Ring rearrangement for the acceptance of the negative charge, even though likely to require only a moderate amount of energy, is not expected to be strictly the same for the two classes of molecules. The *D* values reported in Table 3 for compounds **1a**, **1b** and **1c** are likely to be a satisfactory estimate of their bond dissociation energies, yet for pyridine derivatives the values are comparable only within the molecules with the same aromatic substrate.

An approximate estimate of the energy lowering involved should be possible from the comparison of the SOMO energies in the $RCXY^{\bullet}$ radicals which should be related to the energy required for entering the lowest vacant orbital of the neutral molecule. If the energy difference of the SOMOs of the molecules with different aromatic rings is assumed to represent the contribution of the internal reorganization energy[1b] (λ_i) to the activation energy of the electron transfer process, then a quantity of the order of $\lambda_i/4$ should be subtracted from the *D* values obtained from eqn. (1). Corrections of the order of 5.5, 1.6 and 2.4 kcal mol^{-1} for 4-, 3- and 2-pyridine derivatives, in that order, should be introduced. The values of *D* corrected in this way are reported in Table 3: in the case of the trichloromethyl derivatives, in particular, a small difference still survives which would appear to reflect the effect of the aromatic ring on the strength of the C−Cl bond. Estimates at the semi-empirical AM1 level, reported in Table 3, show a satisfactory agreement with these corrected *D* values.

A final point regards the different reaction products obtained from homogeneous and heterogeneous reduction of these compounds. The electrochemical reduction shows that only derivatives corresponding to Cl/H substitution are obtained while from the reduction with Fe^{II} ions[13,14] these derivatives are obtained only in the case of compounds **2a** and **4a**, compounds **1a** and **3a** affording the dimeric product $ArCCl_2CCl_2Ar$. We believe that, in the homogeneous case, the rate determining ET step involves only one electron and the radical formed after C−Cl breaking diffuses into the solution and couples to give the dimer. Only when the radical formed is co-ordinated by the metal, and the complex lasts long enough to allow reduction by a second molecule carrying the Fe^{II} ion, is the carbanion formed and then protonated. This would appear to be the case for compounds **2a** and **4a**. In the electrochemical process, the electrode can easily provide a second electron to the radical formed, which has a reduction potential positive to that of the original molecule; the carbanion is then readily formed and protonated.

Experimental conditions, namely solvent and temperature, can probably affect the destiny of the radical formed in the electrochemical process, and the dimerization route might become feasible: experiments in this direction are in progress.

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References

1 (*a*) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Berlin, 1987; (*b*) J.-M. Saveant, *Adv. Phys. Org. Chem.*, 1990, **26**, 1.

2 N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 734; N. Kornblum, in *The Chemistry of Functional Groups*, ed. S. Patai, Wiley Interscience, New York, 1982, supplement F, p. 361; G. A. Russell, *Adv. Phys. Chem.*, 1987, **23**, 271; G. A. Russell, *Acc. Chem. Res.*, 1981, **22**, 1; R. A. Rossi and R. H. Rossi, *Aromatic Substitution by the* $S_{RN}1$ *Mechanism*, ACS Monographs 178, Washington, DC, 1983.

3 C. P. Andrieux, A. Le Gorande and J.-M. Saveant, *J. Am. Chem. Soc.*, 1992, **114**, 6892.

4 J.-M. Saveant, *J. Am. Chem. Soc.*, 1992, **114**, 10 595.

5 W. E. Wentworth, R. George and H. Keith, *J. Chem. Phys.*, 1969, **51**, 1791.

6 E. Canadell, P. Karafiloglou and L. Salem, *J. Am.Chem. Soc.*, 1980, **102**, 855; T. Clark, *Faraday Discuss. Chem. Soc.*, 1984, **78**, 203; R. Benassi, F. Bernardi, A. Bottoni, M. A. Robb and F. Taddei, *Chem. Phys. Lett.*, 1989, **161**, 79; J. Bertran, I. Gallardo, M. Moreno and J.-M. Saveant, *J. Am. Chem. Soc.*, 1992, **114**, 9576; T. Tada and R. Yoshimura, *J. Am. Chem. Soc.*, 1992, **114**, 1593.

7 R. N. Compton, P. W. Reinhart and C. C. Cooper, *J. Chem. Phys.*, 1978, **68**, 4360; A. Hasegawa and S. Williams, *Chem. Phys. Lett.*, 1977, **46**, 66; A. Hasegawa, M. Shiatani and S. Williams, *Faraday Discuss. Chem. Soc.*, 1977, 157; L. Bonazzola, J. P. Michaut and J. Roncin, *Chem. Phys. Lett.*, 1988, **153**, 52; A. Kuhn and A. Illenberger, *J. Phys. Chem.*, 1989, **93**, 7060; A. Kuhn and E. Illenberger, *J. Chem. Phys.*, 1990, **93**, 357.

8 R. Benassi, C. Bertarini and F. Taddei, *Chem. Phys. Lett.*, 1996, **257**, 633.

9 M. Ichihashi, J. Hirokawa, T. Tsukuda, T. Kondow, C. E. H. Dessent, C. G. Scarton and M. A. Johnson, *J. Phys. Chem.*, 1995, **99**, 1655.

10 R. Dressler, M. Allan and E. Haselbach, *Chimia*, 1985, **39**, 385.

11 *Encyclopedia of electrochemistry of the elements*, Organic Section, ed. A. J. Bard and H. Lund, Marcel Dekker Inc., New York and Basel, 1973, Vol. XIV.

12 F. Taddei, *Gazz. Chim. Ital.*, 1996, **126**, 529.

13 A. Cornia, U. Folli, S. Sbardellati and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1847.

14 U. Folli, F. Goldoni, D. Iarossi, S. Sbardellati and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1017.

15 M. von Stackelberg and W. Z. Shacke, *J. Electrochem. Soc.*, 1949, **53**, 118; S. Wawzonek and R. C. Duty, *J. Electrochem. Soc.*, 1961, **108**, 1135.

16 J.-P. Gisselbrecht and H. Lund, *Acta Chem. Scand., Sect. B*, 1985, **39**, 773.

17 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

18 GAUSSIAN 92, Revision C: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Repogle, R. Gomberts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian Inc., Pittsburg, PA, 1992.

19 D. D. M. Wayner, B. A. Sim and J. J. Dannenberg, *J. Org. Chem.*, 1991, **560**, 4853.

20 F. Maran and E. Vianello, *Tetrahedron Lett.*, 1990, **31**, 5803.

21 K. B. Clark and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1991, **113**, 9363.

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