Electron Transfer in the Reactions of Organic Trichloromethyl Derivatives with Iron(II) Chloride

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Reduction of trichloromethyl derivatives $RCCl_3$ [**1**, R = Ph; **2**, R = PhC(O); **3**, R = EtOC(O)] with iron(II) chloride in acetonitrile, has been studied in order to examine the mechanism of the electron transfer (ET) process and the reactions of the radicals formed. Substrates **1–3** afforded different product compositions and the cause was identified as differences in the reactivity of radicals which is substantially of two types: reductive coupling and proton abstraction after further reduction to a carbanion coordinated to the metal ion. Compound **1** gave only coupling products, compound **2** only hydrogenated products and compound **3** a mixture of coupling and hydrogenated products depending on experimental conditions. Proton abstraction by the carbanion was found to occur from water molecules, which should be present in the coordination shell of the metal ion, and not from the solvent. The different behaviour of compounds **1–3** is attributed to the presence of substituents which are able to stabilize the radical and carbanionic intermediates. Rate constants at different temperatures were measured and the activation parameters calculated. The three substrates differ only slightly in reaction rates, in the order **1** > **2** > **3**. Activation enthalpies are very close to each other and this agrees with the almost equal values of C–Cl bond dissociation energies of compounds **1–3**, empirically determined. Large, negative entropies of activation were found, suggesting that an ordered activation complex should be formed in order that electron transfer from the metal ion to the organic halide can take place.

Halogenated hydrocarbons are reductively dehalogenated by cytochrome P450 under anaerobic conditions.[1] The toxic effects of many of these compounds or of their derivatives, which are commonly employed in industry and commerce and administered for medicinal purposes, have been associated with this reaction: some of them are suspected of having human carcinogenic activity.[2]

The reductive cycle,[3] constructed on the basis of experimental evidence, involves an initial step in which the halocarbon binds to a hydrophobic site of the enzyme near, but not attached, to the haem unit and a reductive electron transfer (ET) takes place; a halogen ion is eliminated and a radical is generated.[4] The radical formed is believed to be responsible, together with the final products, for the toxicity of halogenated hydrocarbons.[5] In biological tissues, the toxicity of haloalkyl radicals may be due to their reactivity towards the constituent molecules of these materials.

Evidence for the formation of radicals in these processes comes from the detection of the proposed reaction products[6] and from their direct EPR observation[7] in the case of a number of haloalkanes. Electron transfer to alkyl halides is dissociative:[8–11] the radical anion probably has some stability in the case of polyhalogenated alkanes. The transition state for electron transfer requires an energy contribution originating mainly from Franck–Condon restrictions[12] and, owing to the requirement that the C–halogen bond be virtually broken in the transition state, a positive and large enthalpy of activation is expected for these reactions. The electron transfer step should thus be rate-determining and fast subsequent reactions should involve the radicals both within and outside the 'cage' in which they were generated.

Dissociative decomposition of haloalkanes in presence of Fe^{II} salts has also been reported and compounds originating from the intermediate radicals characterized.[13–18] These reactions were found to occur with a measurable rate at room temperature for carbon tetrachloride[13,18] and benzotrichloride[14–17] by employing $FeCl_2$ in different solvents and the products are usually those expected from dimerization of the radicals formed. In the case of carbon tetrachloride the formation of chloroform was also observed,[13] yet products containing hydrogen were not observed[14] in the corresponding reaction on benzotrichloride. With the $FeCl_2$·LiCl system benzotrichloride yields[16,17] dichlorostilbene (mainly in the *cis* form) and carbon tetrachloride[13,18] forms mainly tetrachloroethylene; in the latter case, the reaction seems to proceed through dichlorocarbene.

We deemed it of interest to gain further information, through simple reaction models, on the more complex processes occurring in biological systems and our attention was focussed on two aspects: (*i*) the relative rates of the dissociative process involving halo compounds with different structural features, and (*ii*) the reactions involving the radicals formed in the ET step from the halo compounds and the mechanism of these processes. The substrates chosen were **1–3**, containing the CCl_3

$PhCCl_3$	$PhC(O)CCl_3$	$EtOC(O)CCl_3$
1	**2**	**3**

group. These molecules react with $FeCl_2$ at a rate which permits measurements in a temperature range around room temperature and reaction products can be observed after reasonable time intervals. The solvent employed was acetonitrile (MeCN), which is a moderately good solvent both for the organic substrates and iron(II) chloride (in the hydrated and anhydrous forms).

Experimental

Compounds.—Acetonitrile (Aldrich, HPLC Grade) was distilled on P_2O_5 and stored over molecular sieves (Merck 0.5 nm) under an argon atmosphere. $FeCl_2$·$4H_2O$ (Aldrich) and anhydrous $FeCl_2$ (K & K Laboratories) were protected from oxygen and moisture under an argon atmosphere.[19] Benzotrichloride (Aldrich) **1**, α,α,α-trichloroacetophenone[20] **2**, ethyl trichloroacetate (Aldrich) **3**, trichloromethylmesitylene[21] **7**, 1,1,1-trichloroethane (Aldrich) **8** and 1,1,1-trichloro-2-phenyl-

Table 1 Results of the reactions carried out on substrate **1** (S) with iron(II) chloride in MeCN solution

No.	[S]/mol dm^{-3}	Iron salt	Molar ratio [S]:[Fe^{II}]	Reaction conditions	Product (yield %)
1	0.033	$FeCl_2$·$4H_2O$	1:1	40 °C, 3 h	$PhCCl_2CCl_2Ph$ (50)
2	0.033	$FeCl_2$·$4H_2O$	1:1	82 °C, 2.5 h	$PhCCl_2CCl_2Ph$ (74), PhCOOH (8)
3[a,b]	0.034	$FeCl_2$·$4H_2O$	1:1	25 °C, 30 h	$PhCHCl_2$ (5.0) $PhCCl_2CCl_2Ph$ (3.1) PhCOOH (11.6) PhC(O)SPh (5.9) PhSSPh (28.6)

[a] The reaction was carried out in presence of PhSH and the molar ratio [PhSH]:[S] was approximately 2. [b] No $PhCCl_3$ was present in the reaction products and the amount of unchanged PhSH was 46%.

Table 2 Results of the reactions carried out on substrate **2** (S) with iron(II) chloride in MeCN solution

No.	[S]/mol dm^{-3}	Iron salt	Molar ratio [S]:[Fe^{II}]	Reaction conditions	Product (yield %)
1	0.085	$FeCl_2$·$4H_2O$	1:2	25 °C, 48 h	$PhC(O)CHCl_2$ (52.4)
2	0.085	$FeCl_2$·$4H_2O$	2:1	82 °C, 23 h	$PhC(O)CHCl_2$ (32.2)
3	0.085	$FeCl_2$	1:2	25 °C, 24 h	$PhC(O)CHCl_2$ (55.8)

ethane[22] **9** were degassed by distillation in a vacuum line before reaction with the Fe^{II} salt.

The organic reaction products were identified and quantitatively determined by GLC analysis and mass and ^1H NMR spectroscopy. The total amount of the identified reaction products was always higher than 90% based on the molar quantity of the substrate employed. Tetrachloro-1,2-diphenylethane had the physical properties previously reported;[14] 1,1,2,2-tetrachloro-1,2-dimesitylethane had m.p. 137–139 °C (decomp.) (from CH_3CN); $\delta_H(CDCl_3)$ 2.20 (6 H, s, *p*-Me), 2.32 (12 H, s, *o*-Me), 6.80 (4 H, s, ring-H) (Found: C, 59.3; H, 5.6; $C_{20}H_{22}Cl_4$ requires C, 59.4; H, 5.5%). The latter compounds are the coupling products from **1** and **7**, respectively, and were isolated[14] from reaction of **1** and **7** with Fe^{II} salt in preparative runs. An independent synthesis of diethyl tetrachlorosuccinate[23] **5** and diethyl dichloromaleate[24] (*cis*-**6**) was also performed.

Kinetic Measurements.—A Varian–Cary 13 spectrophotometer with instrumental zero adjustment at 530 nm and thermostatic control of the cell compartment (±0.5 °C) was employed. The absorbance measurements for determining rate constants were automatically performed every 0.5 s.

In order to determine the partial reaction order referring to each reagent, large $[RCCl_3]/[Fe^{II}]$ ratios were employed, in the range 14–30. Concentrations of Fe^{II} were in the range 4×10^{-4}–3.5×10^{-3} mol dm^{-3}. Solutions of $FeCl_3$ were prepared from the anhydrous iron salt weighed in calibrated flasks before addition of the solvent with appropriate amounts of water or of other reagents. Calibration plots were constructed in order to obtain the concentration of the Fe^{III} species from absorptions measured at 361 nm under the reaction conditions adopted. Solutions of Fe^{II} were prepared by weighing the iron salt directly in the spectrophotometer cell.

For kinetic measurements the original cell was modified for the addition of the reagents to the iron(II) solution under an argon atmosphere. The substrates were injected into the UV cell through a rubber septum cap when the absorbance of the Fe^{II} solution reached constant values ($t = 0$). In order to set up a reliable method for the measurement of Fe^{III} concentration in MeCN solution, an appropriate value of $\varepsilon_{361}(FeCl_4^-)$ had to be selected. To this end, extinction coefficients for solutions of different concentrations of anhydrous and hydrated $FeCl_3$ and of mixtures $FeCl_3$–$FeCl_2$·$4H_2O$ in MeCN solution, in the presence of LiCl, Et_4NCl and of the substrates **1**–**3** were measured. For Fe^{III} concentrations in the range 10^{-2}–10^{-4} mol dm^{-3} the Lambert–Beer law is followed in the spectral region 300–400 nm, and this agrees with the presence of a single chemical species absorbing in this region, *i.e.*, the tetrachloroferrate ion. The presence of substrates **1**–**3** does not significantly affect the value of the extinction coefficient $\varepsilon_{361}(FeCl_4^-)$. For kinetic measurements we thus adopted the value given in eqn. (1) obtained as an average value of those determined in presence of Cl^- ions. This value is close to that obtained by Meek and Drago[25] and by Asscher and Vofsi.[13]

$$\varepsilon_{361}(FeCl_4^-) = 7300 \pm 300\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}} \qquad (1)$$

Statistical elaborations of experimental data were performed on an IBM mod. 30286 personal computer. ^1H NMR spectra were run on a Bruker WP 80 spectrometer.

Results

The results of the reactions carried out on substrates **1**–**3** under an argon atmosphere are collected in Tables 1–3 (see the Experimental section).

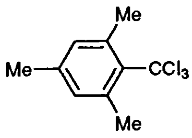
Compound **1**.—In agreement with previous findings[14,16,17] only the coupling product, tetrachloro-1,2-diphenylethane, is obtained in the reaction with $FeCl_2$·$4H_2O$, together with small amounts of benzoic acid from the hydrolysis of the compound. The results are collected in Table 1. When the reaction is carried out at 82 °C and monitored by GLC analysis the results show that hydrolysis becomes significant when 70% of the coupling reaction has occurred. Products of chlorine–hydrogen substitution were not observed, nor were unsaturated compounds from dechlorination of tetrachloro-1,2-diphenylethane detected in the reaction conditions employed.

Compound **2**.—Results for the reactions carried out on this substrate are reported in Table 2. Only the product of chlorine–hydrogen substitution was detected. A significant decrease in the overall reaction rate is observed on going from the anhydrous to the hydrated iron salt (compare reactions 1 and 3).

Table 3 Results of the reactions carried out on substrate **3** (S) with iron(II) chloride in MeCN solution

No.	[S]/mol dm^{-3}	Iron salt	Molar ratio [S] : [Fe^{II}]	Reaction conditions	Product (yield %)^a
1	0.058	$FeCl_2$	1 : 2	25 °C, 48 h	EtO_2CCHCl_2 (43), $EtO_2CCCl_2CCl_2CO_2Et$ (12)
2	0.086	$FeCl_2$	1 : 2	82 °C, 40 h	EtO_2CCHCl_2 (18), $EtO_2CCCl_2CCl_2CO_2Et$ (45) $EtO_2CCCl{=}CClCO_2Et$ (22 *cis*, 2.5 *trans*)
3	0.110	$FeCl_2{\cdot}4H_2O$	1 : 2	25 °C, 6 H	EtO_2CCHCl_2 (12), $EtO_2CCCl_2CCl_2CO_2Et$ (11)
4	0.100	$FeCl_2{\cdot}4H_2O$	1 : 2	82 °C, 24 h	EtO_2CCHCl_2 (40), $EtO_2CCCl_2CCl_2CO_2Et$ (28) $EtO_2CCCl{=}CClCO_2Et$ (11 *cis*)
5	0.082	$FeCl_2$ (+ D_2O, 0.533M)	1 : 2	25 °C, 48 h	$EtO_2CC(H,D)Cl_2$ (17) $EtO_2CCCl_2CCl_2CO_2Et$ (35) $EtO_2CCCl{=}CClCO_2Et$ (2.9 *cis*, 2.3 *trans*)
6	0.121	$FeCl_2$	1 : 2	25 °C, 48 h (in CD_3CN)	EtO_2CCHCl_2 (38.5), $EtO_2CCCl_2CCl_2CO_2Et$ (9.4), $EtO_2CCCl{=}CClCO_2Et$ (1 *cis*)
7	0.093	$FeCl_2{\cdot}4H_2O$	1 : 2	25 °C, 48 h (in CD_3CN)	EtO_2CCHCl_2 (28), $EtO_2CCCl_2CCl_2CO_2Et$ (19) $EtO_2CCCl{=}CClCO_2Et$ (6 *cis*)
8	0.082	$FeCl_2{\cdot}4H_2O$	1 : 2	25 °C, 48 h (+ 5% H_2O)	EtO_2CCHCl_2 (3), $EtO_2CCCl_2CCl_2CO_2Et$ (9)

^{a} Yields were determined by GLC analysis, with an experimental error of about 2%; the percentage of unchanged **3** is not indicated.



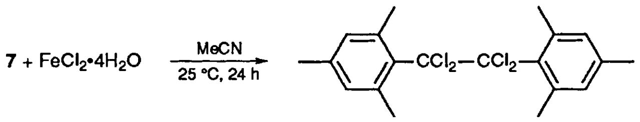
7

$MeCl_3$

8

$PhCH_2CCl_3$

9



Scheme 1

Compound **3**.—The reactivity of this substrate toward Fe^{II} is more complex than those of substrates **1** and **2**. The schemes of the reactions carried out are reported in Table 3. Compound **3** yields three different reaction products: that of chlorine–hydrogen substitution, the coupling product and the unsaturated *cis*/*trans* derivatives **6** formally derived from dechlorination of the coupling product. The relative amount of these reaction products depends on reaction conditions. On increasing the amount of water present in the reaction medium, the amount of $RCHCl_2$ decreases (compare reactions 1 and 6 with 8 and 7).

Reactions of Fe^{II} *with other substrates*.—In order to have additional results concerning the reactions of the radicals formed in the dissociative ET step, substrate **7** was considered. The steric effect of the methyl groups in *ortho* position to the reaction centre, was judged to influence the coupling reaction and, probably, to favour the route for chlorine–hydrogen substitution at the same time. The results of reactions carried out on substrate **7** are summarized in Scheme 1. Quantitative determination by GLC of the coupling product, which is the main reaction product (isolated yield > 70%), was not feasible owing to the thermal instability[21] of the compound. From the ^1H NMR analysis of the reaction mixture, the hydrogenated product $RCHCl_2$ was not detected.

Compounds **8** and **9** were tested at 60 °C with $FeCl_2{\cdot}4H_2O$ in MeCN, but no reactions were observed.

Rate constants relative to the reactions of substrates **1**–**3** with $FeCl_2{\cdot}4H_2O$ were measured in order to obtain activation parameters. A spectrophotometric method (see the Experimental section) was employed, and the absorption band at 361 nm belonging to $FeCl_4^-$ species,[19,25,26] was monitored.

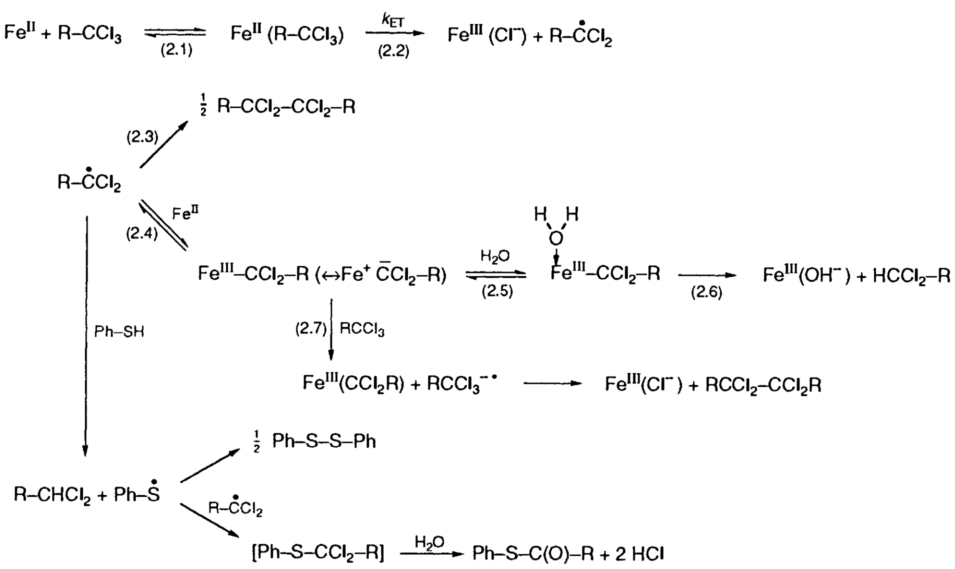
The initial rate method[27] was employed and absorbance measurements referred to the first 10% of the reaction. For substrate **1** the reaction with Fe^{II} ions has previously been reported[14] to be first order with respect to Fe^{II} and $RCCl_3$. For substrates **2** and **3**, the reaction was found to be first order relative to both reagents.

Activation parameters, collected in Table 5 (see later), were derived from measurements in the temperature interval 10–55 °C and calculated with standard formulas.[27,28]

Since rate constants were obtained in dilute and homogeneous solutions by processing only the results of the first 10% of the reaction, the yields of the reaction products, referred to longer reaction times, do not fit the calculated rate constants.

Discussion

The reduction of alkyl halides, by radical anions or metal



Scheme 2

reagents, is widely accepted as an ET process in which radical formation occurs.[12] According to the Marcus theory,[29] an outer-sphere dissociative ET mechanism [12,30] appears to be the best choice where radical anions are concerned, whereas an inner-sphere mechanism, involving a halogen atom transfer, seems more appropriate in the case of metal reagents. The reactions involving these radicals are usually fast processes. The results of the reactions performed on substrates **1**–**3** show that the main differences in product composition are in the amounts of hydrogenated and dimeric products: only the coupling product, $RCCl_2$–CCl_2R for **1**, only the hydrogenated product, $RCHCl_2$ for **2** and a mixture of the two for **3**, the relative amounts depending on reaction conditions.

Compounds giving only coupling products, such as **1**, differ structurally from those yielding hydrogenated compounds, **2** and **3**, in the fact that **2** and **3** possess groups which can stabilize both a radical and a carbanion generated at the halogenated reaction centre and can also behave as ligands towards the metal ion through the oxygen atoms of the carbonyl and alkoxy groups.[31] The results listed in Table 3, relative to reactions carried out with D_2O and CD_3CN clearly show that the hydrogen in $RCHCl_2$ is derived from water molecules and not from the solvent. The isotopic H/D effect observed in the reaction of **5** when compared with the reaction 1, confirms this conclusion. The increase in the water content in the reaction medium (Table 3, reactions 6, 7 and 1, 8) makes the coupling process more competitive than chlorine–hydrogen substitution.

In Scheme 2 we report the sequence of reaction steps which seem to explain our experimental results. To each step depicted the following comments are appropriate.

(2.1) Fe^{II} indicates a ferrous ion and the surrounding ligands (Cl^-, MeCN solvent and, possibly, H_2O). $RCCl_3$ enters the inner coordination shell of the metal ion, seemingly through a Cl atom of the CCl_3 group.

(2.2) The dissociative electron transfer is the rate-determining step: $RCCl_3$ dissociates into Cl^-, which remains coordinated to the ferric ion, while a radical $R\dot{C}Cl_2$ is released. In the case of substrates **2** and **3** the radical is stabilized by the adjacent carbonyl group, while a benzylic-type radical is formed from **1**.

Homocoupling of the radical occurs in step (2.3).

(2.4) The radical may, alternatively, couple with a ferrous ion, forming an organoiron(III) compound which can also be considered as a carbanion coordinated to the ferric ion. The stabilization of the radical by adjacent substituents, and even more the stabilization of the corresponding carbanion, should be important in favouring this path, as in the case of substrate **2** and, to a lesser extent, **3**. An increase in the number of the water molecules in the coordination shell of the metal ion, besides lowering the reducing power of the Fe^{II} salt (a decrease of the overall reaction rate is observed in the order $FeCl_2 > FeCl_2{\cdot}4H_2O > FeCl_2{\cdot}4H_2O$ + added water), makes the homocoupling more competitive, as observed for substrate **3** (see data of Table 3). Steric effects can be invoked as well, particularly in the case of the mesitylene derivative **7**, in favouring the hydrogenated over the coupling product, yet the former was not experimentally observed.

(2.5) A water molecule (if not already present) enters the inner coordination shell of the Fe^{III} ion.

(2.6) A proton from water is intramolecularly transferred to an incipient carbanion departing from Fe^{III}, and the hydrogenated product $RCHCl_2$ is released. An analogous path has been previously proposed[32] for chlorine–hydrogen substitution in organic halides in the presence of Cr^{II} species. In the reactions studied here, support comes from the observation that the carbanion cannot easily be displaced from the metal centre by less basic ligands and from the experimental observation that an increase in the water concentration in the medium instead of favouring the protonation process leading to $RCHCl_2$, seems to inhibit it. It is also interesting to note that from **2** we obtained only the hydrogenated product, even though we used carefully anhydrous conditions (anhydrous $FeCl_2$ in anhydrous MeCN). Evidently, under these conditions, the organoferric intermediate, (carbanion coordinated to the Fe^{III} species) could survive until water was added in the final work-up of the reaction. As mentioned above, radicals stabilized by an adjacent carbonyl group, like those from **2** and **3**, are mesomeric, so their coupling with the Fe^{II} species (step 2.4) can occur through the oxygen, instead of carbon atom, with the formation of an enolate anion coordinated to Fe^{III}. The subsequent intramolecular protonation would lead, however, to the same final result.

The hydrogenated product $RCHCl_2$ could be more directly formed from the radical $R\dot{C}Cl_2$ by hydrogen-atom abstraction from a water molecule. This possibility can be dismissed on the following basis: (*i*) the H–OH bond strength is 119 kcal mol^{-1} compared with values lower than 100 kcal mol^{-1} for H–CCl_2R molecules[33] ($\dot{O}H$ radical stronger hydrogen abstractor than $R\dot{C}Cl_2$); (*ii*) it has been reported[14] that benzotrichloride **1** is not reduced to $PhCHCl_2$ by $FeCl_2{\cdot}4H_2O$ even dissolved in ethyl alcohol: only homocoupling of the radical is observed and not hydrogen abstraction from the hydroxylic solvent; (*iii*) the

Table 4 Reaction of compound **5** in the presence of iron salts under different physical conditions

No.	[**5**]/mol dm^{-3}	Reagent employed		Reaction conditions	Products (yield %)
		[$FeCl_3$]/ mol dm^{-3}	[$FeCl_2$·$4H_2O$]/ mol dm^{-3}		
1	0.017	—	—	82 °C, 25 h	No reaction
2	0.017	0.02	—	82 °C, 25 h	No reaction
3	0.017	0.002	0.002	82 °C, 48 h	*cis*-**6** (5.4)
4	0.017	0.002	0.033	82 °C, 48 h	*cis*-**6** (77), *trans*-**6** (9)
				82 °C, 108 h	*cis*-**6** (81), *trans*-**6** (9)
5	0.017	—	0.016	82 °C, 3 h	*cis*-**6** (24), *trans*-**6** (3.2)
				7 h	(29) (3.5)
				25 h	(32) (3.6)
				48 h	(33.7) (3.6)
				360 h	(43) (4.2)

Table 5 Rate constants and activation parameters for the reaction between $RCCl_3$, compounds **1**–**3**, and $FeCl_2$·$4H_2O$ in MeCN solution[a]

Compound	k/10^{-3} dm^3 mol^{-1} s^{-1} [b]	ΔH^*/kcal mol^{-1}	ΔS^*/cal mol^{-1} K^{-1}
1	5.63 ± 0.03 (307)	14.5 ± 0.5	−21.6 ± 2
2	1.45 ± 0.08 (309)	14.4 ± 0.4	−24.9 ± 1
3	0.52 ± 0.01 (307)	12.5 ± 0.8	−32.9 ± 2.5

[a] 1 cal = 4.184 J. [b] Referred to the temperature reported in parentheses (K).

radical from trichloromethylmesitylene **7** should suffer from steric constraints during dimer formation owing to the presence of two *ortho* substituents on the phenyl ring, while hydrogen abstraction should avoid the steric tension: yet no $RCHCl_2$ seems to originate from this radical.

(2.7) Formation of the coupling product through the organoiron(III) and electron transfer to an $RCCl_3$ molecule should be considered as an alternative yet less probable route, since the proton transfer from a water molecule to a carbanion is expected to occur, according to theoretical predictions,[34] with a very low activation energy. A different way for the intermediate $R\dot{C}Cl_2$ radical to partake in homocoupling, even in the case of benzotrichloride **1**, is if the reaction is run with the Fe^{II} salt in the presence of a molecule having an R–H bond with a dissociation energy lower than that of the O–H bond of water and alcohols, *i.e.*, thiophenol (S–H bond dissociation energy 83 kcal mol^{-1}).[35] This step is reported in Scheme 2. Entry 3 of Table 1 represents a preliminary result in the study of this reaction and the results add support, in our opinion, to the proposed mechanism.

From ethyl trichloroacetate **3**, formation of unsaturated compounds, diethyl dichloromaleate (*cis*-**6**) and diethyl dichlorofumarate (*trans*-**6**), formally derived from dechlorination of the dimeric product **5**, was also observed (Table 3). Experiments were carried out to throw light on the formation of these compounds.

As summarized in Table 4, diethyl tetrachlorosuccinate **5**, kept at 82 °C in MeCN for 85 h in presence of $FeCl_3$, is recovered unaltered, while its dechlorination occurs in the presence of iron(II), leading to a mixture of unsaturated compounds **6**, where the *cis* isomer prevails, as found from substrate **3** under the same reaction conditions (Table 3). The *cis*/*trans* ratio (entry 5 of Table 4) during the dechlorination process seems almost constant (near to 10), to within the experimental error of the GLC determination. Furthermore, the *cis*-**6** was recovered unaltered after being refluxed for 64 h in MeCN at 82 °C in the presence both of $FeCl_3$ and $FeCl_2$·$4H_2O$ salts; thus *cis*–*trans* isomerization does not occur under the reaction conditions adopted. The formation of unsaturated products **6**, either from compound **3** or **5** with iron(II), occurred at an appreciable rate only at higher temperature. These data indicate that the unsaturated derivatives **6** from the reaction of compound **3** with iron(II) arise from dechlorination of the saturated coupling product **5**, and not from a carbene-like mechanism as evidenced[13] for the formation of tetrachloroethylene from the reaction of CCl_4 induced by iron(II). Theoretical MO calculations at the semiempirical AM1/MNDO level[36] showed a higher stability for the *trans* isomer and dechlorination of the saturated derivative should thus occur under kinetic control.

Kinetic Results.—The rate constants reported in Table 5 refer to the ET step of the reactions studied and are related to the real unimolecular k_{ET} through eqn. (2), where K is a pre-equilibrium

$$k_{obs} = K k_{ET} \qquad (2)$$

constant.[37] The constant K describes the statistical probability of finding the reactant pair in an internuclear configuration appropriate for reaction. For the reactions studied, beside ligation of the chlorine atom to the metal ion[14] for halogen abstraction, this constant also embodies equilibria involving the other groups present in **2** and **3** which can bind to iron. These compounds are likely to have values of K higher than 1, yet the geometry of the coordinated compound should not coincide with that required for the electron transfer process where the halogen atom reaches the iron ion with the appropriate geometry for halogen abstraction.

The observed rate constants, reported in Table 5, differ only slightly for substrates **1**–**3** and in the order **1** > **2** > **3**. The activation parameters show that the enthalpy of activation is similar for the three molecules examined. Since the C–Cl bond in the transition state is virtually broken,[12] these values seem to indicate close values of the C–Cl bond energy in these molecules. An attempt has been made to evaluate C–Cl bond-dissociation energies (E_{bd}) in these molecules from their heats of formation and those of the radicals formed.[38] The E_{bd} values were calculated by means of Benson's empirical scheme,[39] since they are not known experimentally and are reported in Table 6. With due consideration of the approximations involved in these estimates, it can be concluded that almost the same energy is required for homolytical breakage of the C–Cl bond in

Table 6 Bond dissociation energies[a] E_{bd} in kcal mol^{-1} for the C–Cl bond in a number of molecules participating in the ET reactions

Molecule	E_{bd}
1	66
2	66
3	66
8	73
$PhCH_2Cl$	69
$PhCHCl_2$	67

[a] The heats of formation for the compounds and the radicals in the equation:

$$E_{bd}(R{-}Cl) = \Delta H_f^\circ(R) + \Delta H_f^\circ(Cl) - \Delta H_f^\circ(R{-}Cl)$$

were constructed using Benson's additive scheme.[39] For the radicals the group contributions $\Delta H_f^\circ[\dot{C}{-}(C_d)(Cl_2)] = 16$ kcal mol^{-1} and $\Delta H_f^\circ[\dot{C}{-}(C)(Cl_2)] = 24$ kcal mol^{-1} were employed, obtained from a least-squares treatment of radicals of known heats of formation.

compounds **1–3**, whereas higher energy is required for the unreactive substrate **8** and for benzaldichloride and benzyl chloride.

The entropy of activation has large, negative values for the substrates examined and this suggests an ordered activation complex of similar structure for the three molecules. Previously reported[40] reactions of substrate **1** with vanadium(II) showed a negative ΔS^* value which was somewhat smaller than that found with a Cr^{II} reductant; this was judged to be an indication that an outer-sphere reaction occurs with V^{II} and an inner-sphere reaction with Cr^{II}. On the basis of this conclusion, an inner-sphere process is likely to occur for the reductions studied here. The higher ΔS^* value found for compound **3** relative to the other substrates should account for the greater lowering of the degrees of freedom in this molecule compared with **1** and **2** in the molecular reorganization for reaching the structure of the activated complex.

Conclusions

The trichloromethyl derivatives **1–3** undergo a dissociative ET process and the radicals formed undergo coupling reactions and proton abstraction after further reduction to a carbanionic species. The reaction steps should include a pre-equilibrium in which the substrate is weakly bound to the Fe^{II} ion and reorganization of the complex to allow halogen transfer to the metal ion is required, according to the negative entropy of activation found for the three molecules. The enthalpy of activation of substrates **1–3** is similar and should account for the similar values of bond dissociation energies of these molecules, since in molecules having stronger C–Cl bonds no reaction was observed under the conditions here employed. Hydrogenated compounds $RCHCl_2$ are formed from substrates which are able to stabilize the reaction intermediates, and the water present in solution seems to have an important role in both competition with the reagents for inclusion in the coordination shell of the metal, and for proton donation to the carbanion generated from radical reduction. The results relative to trichloromethylmesitylene **7** have shown that sterically crowded reaction centres are also preferentially involved in coupling over hydrogenation reactions. The absence of groups able to bind to the metal centre should not favour the formation of the carbanion intermediate.

The unsaturated dimers, diethyl dichloromaleate (*cis*-**6**) and diethyl dichlorofumarate (*trans*-**6**) occur by dehalogenation by Fe^{II} of the reductive coupling product of substrate **3**, diethyl tetrachlorosuccinate **5**, and not by the carbene mechanism described[13] for CCl_4 with Fe^{II} ions and for RCX_3 (X = halogen) under reducing conditions and in the presence of an iron porphyrin.[41]

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