

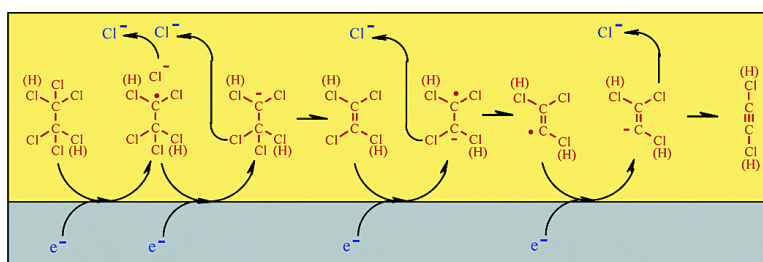
Article

Successive Removal of Chloride Ions from Organic Polychloride Pollutants. Mechanisms of Reductive Electrochemical Elimination in Aliphatic Gem-Polychlorides, α,β -Polychloroalkenes, and α,β -Polychloroalkanes in Mildly Protic Medium

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Abstract: The factors that control the successive reductive expulsion of chloride ions from aliphatic gem-polychlorides are investigated, taking as examples the electrochemical reduction of polychloromethanes and polychloroacetonitriles in *N,N*-dimethylformamide. At each elimination stage, the reaction involves, as a rate-determining step, the transfer of one electron concerted with the cleavage of the carbon–chloride bond. The second step is an immediate electron transfer to the ensuing radical, taking place at a potential more positive than the potential at which the first electron transfer occurs. The carbanion thus formed is sufficiently basic to be protonated by any trace weak acid present in the reaction medium. The three successive elimination steps require increasingly negative potentials. Application of the “sticky” dissociative electron transfer model allows one to quantitatively unravel the factors that control the energetics of the successive reductive expulsion of chloride ions. The large potential gaps between each stage stem primarily from large differences in the dissociative standard potentials. They are also strongly affected by two cumulative intrinsic activation barrier factors, namely, the bond dissociation energy of the substrate that decreases with the number of chlorine atoms and the interaction between chloride ion and the radical that increases in the same direction. In the case of α,β -polychloroethanes ($\text{Cl}_3\text{C}-\text{CCl}_3$, $\text{Cl}_2\text{HC}-\text{CCl}_3$, $\text{Cl}_2\text{HC}-\text{CHCl}_2$, $\text{ClHC}-\text{CHCl}_2$) too, the first step is a dissociative electron transfer with sizable ion–radical interactions in the product cluster. Likewise, a second electron transfer immediately leads to the carbanion, which however prefers to expel a second chloride ion, leading to the corresponding olefin, than to be protonated to the hydrogenolysis product. The ion–radical interaction in the product cluster plays a major role in the control of the reduction potential. The reduction of the α,β -polychloroethenes ($\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{ClHC}=\text{CCl}_2$, $\text{ClHC}=\text{CHCl}$) follows a similar $2e^- - 2\text{Cl}^-$ reaction sequence, leading then to the corresponding alkynes. However, unlike the polychloroethane case, the expulsion of the first chloride ion follows a stepwise electron transfer/bond cleavage mechanism. The reduction potential is thus essentially governed by the thermodynamics of the anion radical formation.

Introduction

Common chlorinated solvents, such as polychloroethenes, polychloroethanes, and polychloromethanes, form one of the main groups of environmental pollutants present in the soils and underground waters of many industrial sites. This contamination is particularly dangerous in view of their toxicity or even carcinogenic character.¹ Degradation mechanisms and nature of the ensuing products in various environmental configurations have been actively investigated.² It was shown that although these pollutants undergo biotransformations, these are slow and may lead to secondary stable pollutants. These difficulties have aroused interest for several abiotic approaches. Among them

reduction by metals, typically iron,³ palladium deposited on iron or porous glass material,⁴ and mixed iron oxides such as pyrite and magnetite,⁵ have been mostly developed, without leading however to fully satisfying results because of deactivation of the reducing material. Direct electrochemical reduction is another approach, which has been developed in ex situ conditions, involving, for example, carbon⁶ or nickel electrodes.⁷ Although rationalization of product distribution has been

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attempted in some cases, a sound comprehension of the reaction mechanisms, on which predictive rules could be based, is lacking.

Another interesting issue concerns the implication of low-valent cobalamin and other cobalt corrinoids in the enzymatic reduction of a large variety of organic halides in many anaerobic bacteria.^{8,9} Here too, the reduction mechanisms are not fully understood despite the availability of a wide body of data concerning the redox chemistry of cobalt corrinoids¹⁰ and the possible implication of organo-cobalt intermediates.¹¹ The implication of cobalt corrinoids as cofactors in several isolated reductive dehalogenation enzymes has been demonstrated.^{12,13}

This brief overview of previous work clearly points to the necessity of a more systematic analysis of reaction mechanisms and structure reactivity relationships, leading to predictive rules. Since we are dealing with a succession of reactions that couple electron transfer and bond breaking, the concepts, rooted in a large body of data, that have been demonstrated to apply in this field^{14–25} could form the base of this analysis. It is also worth noting that several recent attempts to unravel reaction

mechanisms by means of quantum chemical calculations concern the same polychloride pollutants.²⁶

Among these many studies, electrochemistry has proved to be an efficient approach to the analysis of electron-transfer bond breaking problems. We thus inaugurated this series of investigations by an electrochemical study of three families of compounds, gem-polychlorides, α,β -polychloroalkenes, and α,β -polychloroalkanes.

Since we wish to emphasize the coupling between electron transfer and C–Cl bond breaking in these compounds, minimizing other associated reactions such as proton transfers, we selected an aprotic solvent, namely *N,N'*-dimethylformamide (DMF) as the reaction medium.

Cyclic voltammetry, possibly complemented by the convolution method,²⁷ was our main tool for investigating the reaction kinetics and mechanisms. It was also our main tool for product identification. In the present case, this approach is more accurate than preparative-scale electrolysis followed by product extraction and identification. The reason is that, with many of the molecules investigated here, several close-spaced waves are observed, with some of them being close to the discharge of the supporting electrolyte. As a consequence, because of uncertainties in the control of the electrode potential over its whole surface, electrolysis is anticipated to produce hard-to-

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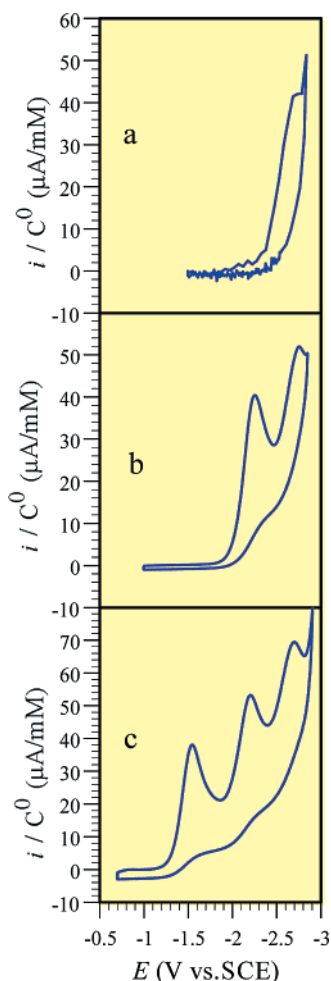


Figure 1. Cyclic voltammetry of CH_2Cl_2 (a), CHCl_3 (b), and CCl_4 (c) on the same GC electrode, in DMF + 0.1 M *n*-Bu₄ClO₄. Scan rate: 0.2 V/s. Temperature: 25 °C. On the vertical axis, the current is normalized versus the concentration.

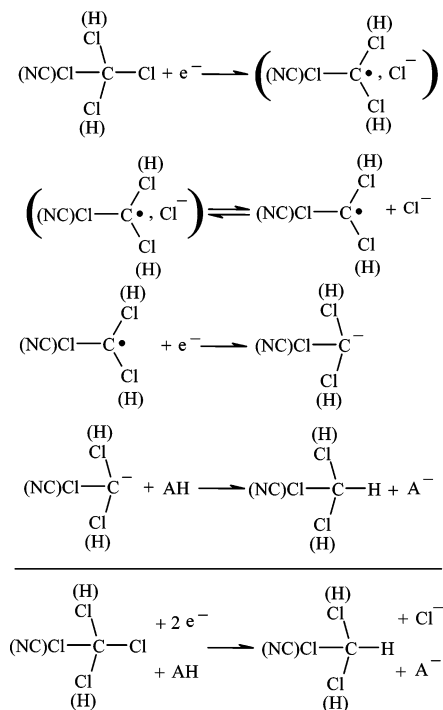
decipher mixtures where the substrate-to-product filiations would be impossible to trace back in most cases.

Results and Discussion

Gem-Polychlorides (Polychloromethanes and Polychloroacetonitriles). The *polychloromethanes*, CCl_4 , CHCl_3 , CH_2Cl_2 , compose the first family we investigated (CH_3Cl does not show a reduction wave before the discharge of the supporting electrolyte). Typical cyclic voltammograms of the three compounds, obtained in DMF on a glassy carbon electrode, are shown in Figure 1. In all three cases, a small amount of acetic acid (ca. equimolar to the substrate) was added to the solution to avoid secondary father–son reactions between the bases generated upon reduction and the starting reactants.^{24a} Addition of the acid makes the peak height pass from a less-than-two-electron stoichiometry to a two-electron stoichiometry.

The simplest case is that of CH_2Cl_2 , which exhibits a single irreversible wave. Comparing the peak current with that of a one-electron reversible couple such as anthracene, under the assumption that the ratio of the diffusion coefficients is the inverse of the ratio of the equivalent sphere radii according to the Stokes–Einstein law, the following relationships may be used to estimate the overall number of electrons, n , exchanged

Scheme 1



in this irreversible reduction.²⁸

$$i_p^{1e,rev} = 0.446 \times FSC^0 \sqrt{D_{\text{anthracene}}} \sqrt{\frac{Fv}{RT}}$$

$$i_p^{ne,irr} = n \times 0.496 \times FSC^0 \sqrt{D_{\text{substrate}}} \sqrt{\frac{\alpha Fv}{RT}}$$

(i_p : peak current. S : electrode surface area. C^0 : bulk concentration. D : diffusion coefficient. v : scan rate). The transfer coefficient, α , is obtained for example from the peak width, $E_{p/2} - E_p$:

$$\alpha = 1.856 \frac{RT}{F} (E_{p/2} - E_p) \quad (1)$$

We thus found that the total number of electrons exchanged is equal to 2 after addition of the acid. The radical chloromethyl formed upon a first electron transfer is indeed readily reduced at the electrode surface, more readily than the starting molecule, leading to the reaction sequence shown in Scheme 1.

The cyclic voltammetric reduction of chloroform is shown in Figure 1b. It exhibits two successive irreversible two-electron waves. The second of these is the same as the single wave observed with CH_2Cl_2 , thus showing that the reduction product of CHCl_3 is indeed CH_2Cl_2 . As expected along the same lines, the cyclic voltammetric reduction of carbon tetrachloride exhibits three successive irreversible two-electron waves (Figure 1c), the two last of which correspond to the reduction of CHCl_3 and CH_2Cl_2 , respectively. The slight increase of the peak current of the first wave from CCl_4 to CHCl_3 and CH_2Cl_2 is due to an increase of the diffusion coefficient paralleling the decrease in size of the substrate molecule. The overall reaction sequence is thus as summarized in Scheme 1 for all three compounds. In each case, the first electron transfer reaction is the rate-

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determining step, the second electron transfer reaction being easier than the first, in line with the observation that there is neither splitting of the two-electron wave, nor change in the apparent number of electrons exchanged, upon raising the scan rate. The fact that the symmetry factor (transfer coefficient), α , ranges between 0.30 and 0.37 strongly suggests that electron transfer and cleavage of the first C–Cl bond are concerted.

In the original version of the dissociative electron transfer theory, the activation free energy, ΔG^\ddagger , is related to the reaction standard free energy, ΔG° , according to eq 2:^{25a}

$$\Delta G^\ddagger = \frac{D_R + \lambda_0}{4} \left(1 + \frac{\Delta G^\circ}{D_R + \lambda_0} \right)^2 \quad (2)$$

where D_R is the bond dissociation energy of the reactant RX, and λ_0 , the solvent reorganization energy. The theory implies that the products form a purely repulsive state. In fact, as seen earlier in the case of CCl_4 ,^{24a,b} there may be a sizable interaction between the caged fragments resulting from dissociative electron transfer that survives polar solvents such as DMF. The interaction was shown to be essentially of the charge (Cl^-)-induced dipole ($^{\bullet}\text{CCl}_3$) type, but the cluster may as well be viewed as a σ -anion radical involving a long three-electron bond. It is expected that the interaction, even weakened, should persist with the two other members of the family. We may then apply a modification of the dissociative electron-transfer model,^{14a,25a} which allows for the existence of an interaction in the clustered products.^{14a,24a} In its simplest version, this “sticky dissociative electron transfer” model leads to the following activation–driving force relationship:

$$\Delta G^\ddagger = \frac{(\sqrt{D_R} - \sqrt{D_P})^2 + \lambda_0}{4} \left[1 + \frac{\Delta G^\circ - D_P}{(\sqrt{D_R} - \sqrt{D_P})^2 + \lambda_0} \right]^2 \quad (3)$$

where D_P is the interaction energy in the radical–ion pair, under the approximation that the solvent reorganization energy, λ_0 , is independent of the extent of bond breaking. In the more refined version we used here, provision is made for a variation of λ_0 with the progress of bond breaking as in the following expressions of the free energy of the reactant and product systems, G_R and G_P , respectively,

$$G_R = D_R Y^2 + \lambda_0(Y) X^2$$

$$G_P = \Delta G^\circ - D_P + D_R \left(1 - \sqrt{\frac{D_P}{D_R}} - Y \right)^2 + \lambda_0(Y) (1 - X)^2$$

as a function of two reaction coordinates X and Y . X is a nominal charge borne by the molecule, varying from 0 to 1, serving as index for solvent reorganization. Y stands for bond breaking, being expressed, in the framework of a Morse curve approximation, by:

$$Y = 1 - \exp[-\beta(y - y_{\text{RX}})]$$

with

$$\beta = \nu(2\pi^2\mu/D_R)^{1/2}$$

(ν : bond length. y_{RX} : equilibrium value of y in the reactant

system. ν : frequency of the cleaving bond. μ : reduced mass. D_R : bond dissociation energy of the starting molecule).

$$\Delta G^\circ = E - E_{\text{RX/R}^{\bullet} + \text{X}^-} \quad (4)$$

is the standard free energy of the reaction leading to complete dissociation (E : electrode potential. $E_{\text{RX/R}^{\bullet} + \text{X}^-}^\circ$: standard potential of the $\text{RX/R}^{\bullet} + \text{X}^-$ couple).

Since the density of electric charge on the molecule varies during the reaction, λ_0 is considered as a function of Y , varying from a “reactant value” λ_0^{R} to a “product value” λ_0^{P} , that is, assuming a linear variation:

$$\lambda_0(Y) = (1 - Y)\lambda_0^{\text{R}} + Y\lambda_0^{\text{P}} = \lambda_0^{\text{R}} + (\lambda_0^{\text{P}} - \lambda_0^{\text{R}})Y$$

Thus, at the transition state (quantities are marked with \ddagger),

$$\Delta G^\ddagger = D_R Y^{\ddagger 2} + [\lambda_0^{\text{R}} + (\lambda_0^{\text{P}} - \lambda_0^{\text{R}}) Y^{\ddagger}] X^{\ddagger 2} \quad (5)$$

$$Y^{\ddagger} = \left(1 - \sqrt{\frac{D_P}{D_R}} \right) X^{\ddagger} - \frac{\lambda_0^{\text{P}} - \lambda_0^{\text{R}}}{2D_R} X^{\ddagger} (1 - X^{\ddagger}) \quad (6)$$

$$\Delta G^\circ = D_P + D_R \left(1 - \sqrt{\frac{D_P}{D_R}} \right) \left[2Y^{\ddagger} - \left(1 - \sqrt{\frac{D_P}{D_R}} \right) \right] + [\lambda_0^{\text{R}} + (\lambda_0^{\text{P}} - \lambda_0^{\text{R}}) Y^{\ddagger}] (2X^{\ddagger} - 1) \quad (7)$$

Application of these equations to the experimental data aims at both testing the validity of the model and determining the interaction energy D_P . It involves the following steps:

(i) derivation of the value of ΔG^\ddagger at the peak potential, ΔG_p^\ddagger , according to:²⁹

$$\Delta G_p^\ddagger = \frac{RT}{F} \left[\ln \left(Z^{\text{el}} \sqrt{\frac{RT}{\alpha F \nu D}} \right) - 0.78 \right] \quad (8)$$

where ν is the scan rate and D is the diffusion coefficient (taken as equal to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in average). α is the transfer coefficient, which is extracted from peak width through eq 1. The pre-exponential factor is taken as equal to the electrochemical collision frequency, $Z^{\text{el}} = (\sqrt{RT/2\pi M})$ (M , molar mass). The resulting figures are listed in Table 1.

(ii) Estimation of $E_{\text{RX/R}^{\bullet} + \text{X}^-}^\circ$, the standard potential of the $\text{RX/R}^{\bullet} + \text{X}^-$ couple, comes from:

$$E_{\text{RX/R}^{\bullet} + \text{X}^-} = -D_R + T\Delta S^\circ + E_{\text{X}^{\bullet}/\text{X}^-}^\circ$$

where ΔS° is the bond dissociation entropy. Concerning this factor, it is important to note that the standard values calculated in gas phase have to be corrected for the change in the standard state when passing from the gas to the liquid phase (1 atm and 1 mol/L respectively) which amounts to decreasing each of the values obtained by $R/F \ln(22.4)$, that is, 0.268 meV/(mol K). ΔS° was estimated by quantum chemical calculations, leading to the values listed in Table 1. The standard potential for chloride oxidation is taken equal to 1.81 V vs SCE.^{24a} Once $E_{\text{RX/R}^{\bullet} + \text{X}^-}^\circ$ is known, the value of ΔG° at the peak, ΔG_p° , may be obtained from eq 4.

(iii) estimation of D_R to be used indirectly in the above derivation of $E_{\text{RX/R}^{\bullet} + \text{X}^-}^\circ$ and directly in the three governing equations requires a particularly critical evaluation of pertinent

(29) Savéant, J.-M. *J. Phys. Chem. B* **2002**, *106*, 9387.

Table 1. Parameters for the Application of the “Sticky Dissociative Electron Transfer” Model to Gem-Polychlorides

compd	Z_R^a (cm/s)	$T\Delta S^\ddagger$ ^b (eV)	$E_{RX/R+X}^\circ$ ^c (V vs SCE) (eV)	a_R^d (Å)	λ_0^R ^e (eV)	λ_0^\ddagger ^f (eV)	D_R^g (eV)	D_P^h (eV)
CCl ₄	5065	0.35	-0.825	3.37	0.890	1.078	2.985 ± 0.03	0.161 ± 0.016
CHCl ₃	5750	0.34	-1.090	3.14	0.955	1.13	3.24 ± 0.03	0.097 ± 0.013
CH ₂ Cl ₂	6814	0.335	-1.325	2.94	1.02	1.182	3.47 ± 0.05	0.076 ± 0.018
NCCCl ₃	5228	0.345	-0.325	3.42	0.878	1.098	2.48 ± 0.03	0.053 ± 0.011
NCCHCl ₂	5992	0.33	-0.550	3.17	0.946	1.145	2.69 ± 0.03	0.037 ± 0.010
NCCH ₂ Cl	7230	0.315	-0.755	2.93	1.024	1.192	2.88 ± 0.03	0.037 ± 0.010

^a Heterogeneous collision factor. ^b Standard entropic term at the temperature of the experiment. ^c Dissociative standard potential. ^d Hard sphere radius of the reactant. ^e Reactant solvent reorganization energy. ^f Averaged solvent reorganization energy at the transition state (variations do not exceed 4% in the covered range of driving forces). ^g Substrate bond dissociation energy. ^h Ion–radical interaction energy.

literature data, since a small error on D_R results in a large error on D_P .³⁰

$$\Delta D_P \approx \frac{3 - \sqrt{D_P/D_R}}{1 + \sqrt{D_R/D_P}} \Delta D_R$$

The ensuing values of D_R are listed in Table 1.

(iv) The solvent reorganization energies are derived from the approximate relationship:^{25d}

$$\lambda_0(\text{eV}) = \frac{3}{a(\text{Å})}$$

the radii being obtained from density data for the substrate and from crystallographic data for Cl⁻ ($a_P = 1.81$ Å). Thus in all cases, throughout this paper,

$$\lambda_0^P = 1.66 \text{ eV}$$

(v) Since all parameters are known, with the exception of D_P , $\Delta G_p^\ddagger/\Delta G_p^\circ$ curves may then be generated from eqs 5–7, for test values of D_P and compared to the experimental data until a good agreement is reached.

Application of this procedure to the three polychloromethanes leads to the results shown in Figure 2 and to the values of D_P listed in Table 1. There is a good agreement between the theoretical predictions and the experimental data points, thus validating the “sticky” dissociative electron transfer model and the values found for the interaction energy between the caged fragments.

Reductive cleavage of the *polychloroacetonitriles* was examined in a similar manner. A small amount of acetic acid (ca. equimolar to the substrate) was likewise added to the solution to avoid secondary father–son reactions between the bases generated upon reduction and the starting reactants.^{15e} Similarly also, the monochloro derivative is reduced to acetonitrile upon an overall 2e process, the dichloro derivative is reduced to the monochloro, and the trichloro derivative is reduced to the

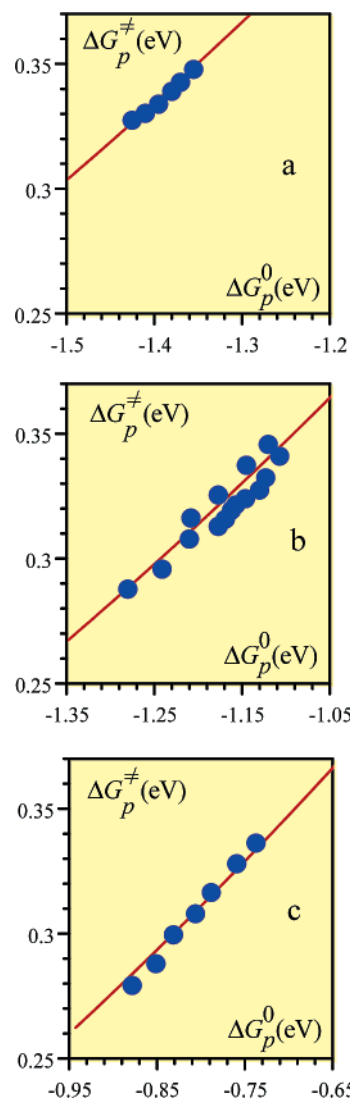


Figure 2. Activation–driving force plots derived from the variation of the peak potential with the scan rate using eqs 8 and 4 (blue dots) and simulated by means of eqs 5–7 and the parameter values listed in Table 1 for CH₂Cl₂ (a), CHCl₃ (b), and CCl₄ (c).

(30) (a) Obtained from the differentiation of eq 2. (b) The bond dissociation energies were derived from selected experimental enthalpies of formation reported in the following references: CCl₄,^{30c,f,i,j} CHCl₃,^{30c,g,h,j} CH₂Cl₂.^{30c–e,j} (c) Kolesov, V. P. *Rus. Chem. Rev.* **1978**, *47*, 599. (d) Paddison, S.; Tschuikow, E. *Int. J. Chem. Kinet.* **1987**, *19*, 15. (e) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343. (d) *CODATA Key Values for Thermodynamics*; Cox, J. D., Wagman, D. D., Medvedev V. A., Eds.; Hemisphere Publishing Corp.: New York, 1989. (f) Gutman, D.; Hudgens, J. W.; Johnson, R. D., III; Timonen, R. S.; Seetula, J. A. *J. Phys. Chem.* **1991**, *95*, 4400. (g) Rayez, M. T.; Rayez, J.-C.; Sawerysyn, J.-P. *J. Phys. Chem.* **1994**, *98*, 11342. (h) Seetula, J. A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3069. (i) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data*; The American Chemical Society and The American Institute of Physics, 1998; Monograph 9, 4th ed., Part 1. (j) *CRC Handbook of Chemistry and Physics*, 82th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2002.

dichloro as follows from the number and location of the cyclic voltammetric waves (Figure 3). As with the polychloromethanes, the slight increase of the peak current of the first wave from NCCCl₃ to NCCHCl₂ and NCCH₂Cl is due to an increase of the diffusion coefficient as the size of the substrate molecule decreases.

The reaction sequences for each of the three chloroacetonitrile derivatives are summarized in Scheme 1. The same analysis of

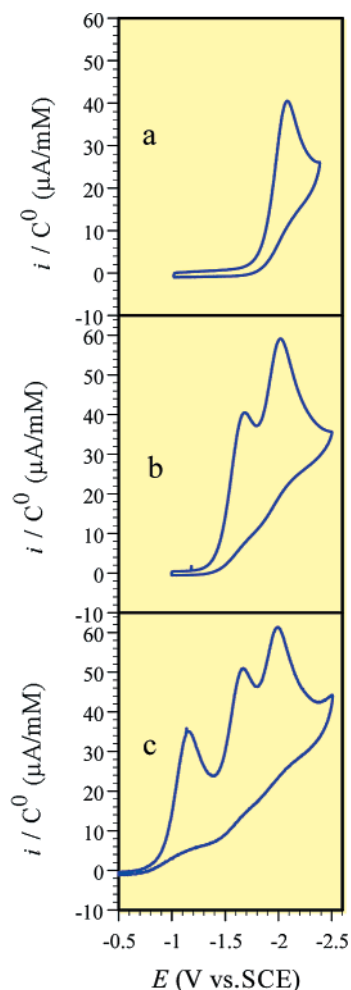


Figure 3. Cyclic voltammetry of NCCH₂Cl (a), NCCHCl₂ (b), and NCCCl₃ (c) on the same GC electrode, in DMF + 0.1 M *n*-Bu₄ClO₄. Scan rate: 0.2 V/s. Temperature: 25 °C. On the vertical axis, the current is normalized versus the concentration.

the variations of the peak potential with the scan rate as for the polychloromethanes was carried out for the polychloroacetonitriles, using the parameter values listed in Table 1. It led to the activation–driving force plots shown in Figure 4a', b', c' and to the values of the interaction energy in the clustered products reported in Table 1.

A somewhat different analysis may be conducted from the convolutive transformation of the cyclic voltammetric responses obtained for several values of the scan rate.^{27,29} The time-dependent current, $i(t)$, is transformed by convolution with the time function $1/\sqrt{\pi t}$, which characterizes linear diffusion:

$$I = \frac{1}{\sqrt{\pi}} \int_0^t \frac{i(\eta)}{\sqrt{t-\eta}} d\eta$$

The original peak-shaped curve is thus transformed into an S-shaped curve leveling off at a value noted I_l . For irreversible processes, the heterogeneous potential-dependent rate constant $k(E)$ is then simply obtained from^{27c} (see Supporting Information)

$$\ln[k(E)] = \ln(\sqrt{D}) - \ln\left(\frac{I_l - I}{i}\right)$$

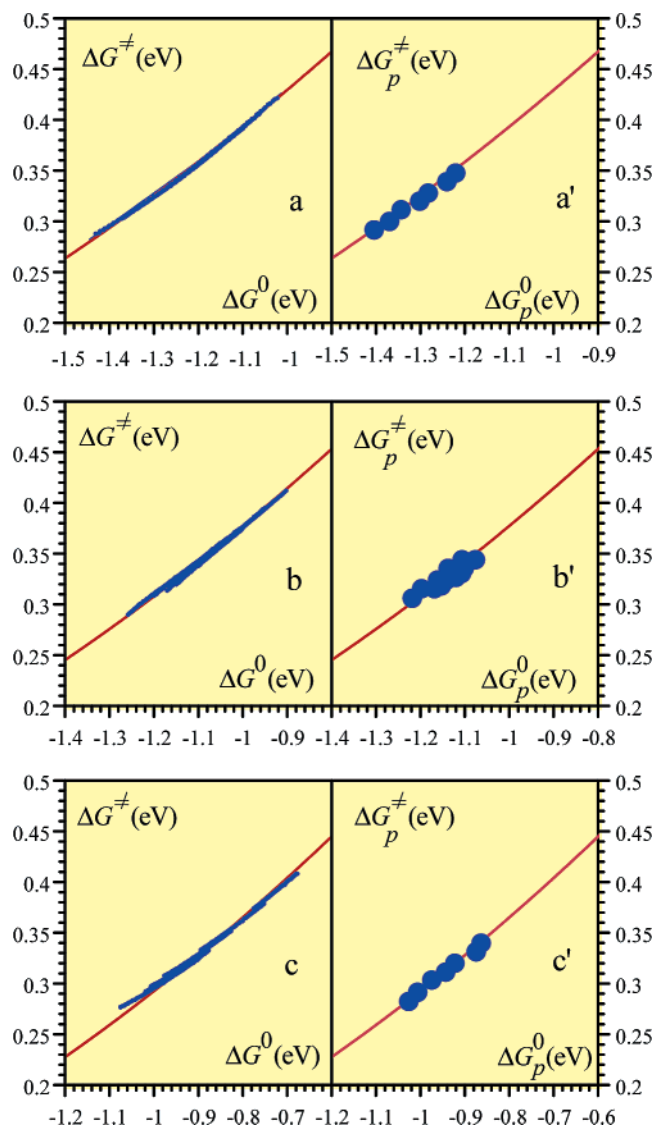


Figure 4. Activation–driving force plots derived from the variation of the peak potential with the scan rate using eqs 8 and 4 (blue dots) and simulated by means of eqs 5–7 and the parameter values listed in Table 1 for NCCH₂Cl (a), NCCHCl₂ (b), and NCCCl₃ (c).

with:

$$I_l = FSC^0\sqrt{D}$$

(S : electrode surface area. C^0 : bulk concentration. D : diffusion coefficient).

Thus in the first step of data processing, eq 8 is replaced by

$$\Delta G^\ddagger = \frac{RT}{F} \ln\left[\frac{Z^{el}}{k(E)}\right] = \frac{RT}{F} \left\{ \ln(Z^{el}) - \ln(\sqrt{D}) + \ln\left[\frac{I_l - I}{i}\right] \right\}$$

and, in step (ii), the driving force is defined by eq 4. The results, still using the parameter values from Table 1, are displayed as activation–driving force plots in Figure 4a, b, c leading to the same values of the interaction energy in the clustered products as those derived from peak potential data (Table 1). There is again a good agreement between theoretical predictions and experiment both for the peak potential data and the potential-dependent rate constant deriving from convolution. The “sticky” dissociative electron transfer model is thus validated as well as

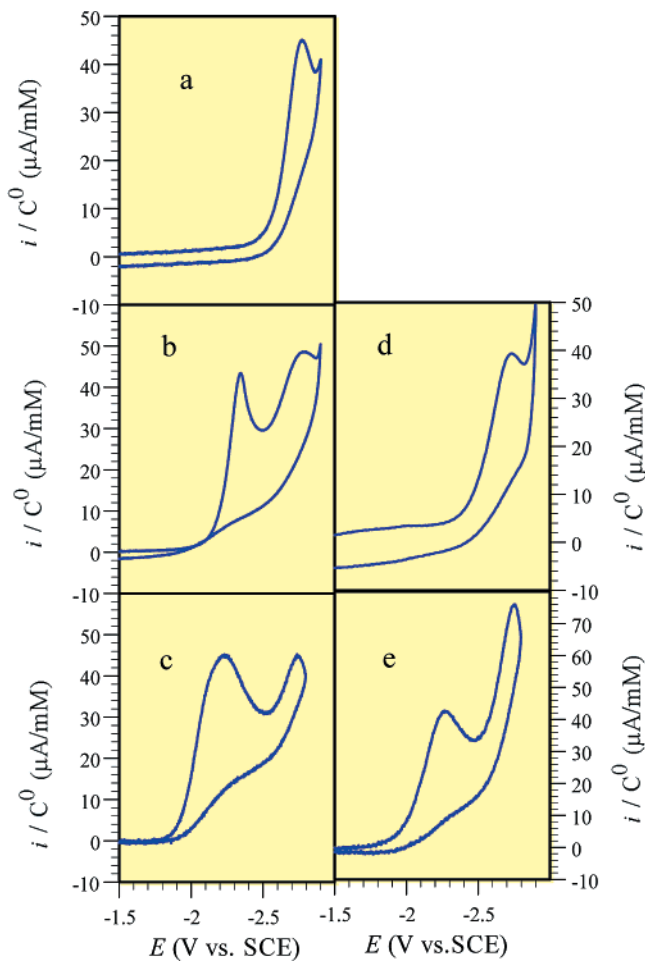


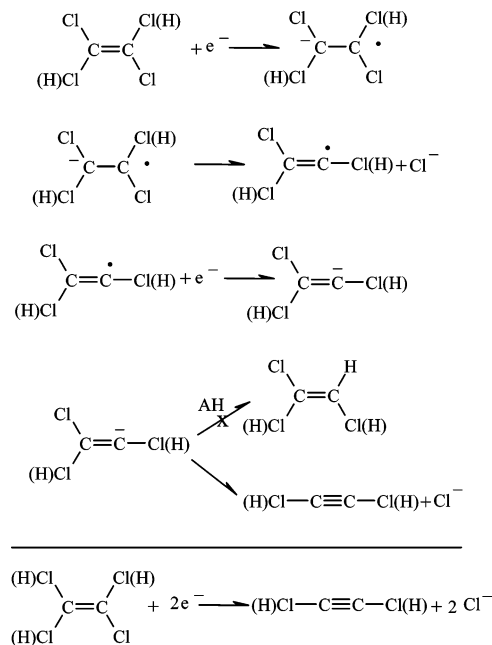
Figure 5. Cyclic voltammetry of ClHC=CHCl (a), ClHC=CCl₂ (b), Cl₂C=CCl₂ (c), ClC≡CH (d), and ClC≡CCl (e) on the same GC electrode, in DMF + 0.1 M *n*-Bu₄ClO₄ + EtOH (50 equiv). Scan rate: 0.1 V/s. Temperature: 25 °C. On the vertical axis, the current is normalized versus concentration.

the ensuing values found for the interaction energy between the caged fragments.

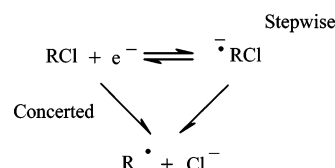
α,β -Polychloroalkenes (Cl₂C=CCl₂, ClHC=CCl₂, ClHC=CHCl). Tetrachloroethylene gives rise to two closely spaced two-electron irreversible waves followed, at a substantially more negative potential, by another two-electron irreversible wave (Figure 5c). Based on peak location, it clearly appears that the second and third waves do not correspond to the reduction of trichloroethylene (Figure 5b) but rather to the reduction of dichloroacetylene (Figure 5e). Passing now to the reduction of trichloroethylene (Figure 5b), the identification of the second wave is more ambiguous. The analogy with tetrachloroethylene suggests a similar reaction leading to chloroacetylene (Figure 5d) rather than 1,2-dichloroethene (figures 5a). We may thus conclude that the reduction of both trichloroethylene and tetrachloroethylene involve elimination of two chloride ions with concomitant formation of a new carbon–carbon bond (Scheme 2).³¹ Finally, *cis* and *trans* 1,2-dichloroethenes exhibit the same cyclic voltammetry behavior. They give rise to an irreversible rather broad two-electron wave located close to the supporting electrolyte discharge current rise (Figure 5a).

Whether the first electron transfer–bond breaking process goes through the intermediacy of the π^* anion radical as shown in Scheme 2 or not, a vinyl radical is formed, which is easier

Scheme 2



Scheme 3



to reduce than the starting molecule. The fate of the vinyl carbanion might be to be protonated thus leading to hydrogenolysis of the carbon–chlorine bond or to expel a chloride ion to yield the corresponding alkynes. This is indeed what happens with both trichloroethylene and tetrachloroethylene at least in the mildly acidic medium where we have carried out the reaction. The product formed and the reaction sequence leading to it are not known in the case of dichloroethylene. We may infer from the results obtained with trichloroethylene and tetrachloroethylene that it is similar thus leading to acetylene rather than to vinyl chloride, the reduction of which cannot anyway be observed in the available potential “window”.

The next question to be addressed, for unraveling the factors that control the successive reductive expulsion of chloride ions, is whether the first electron transfer–bond breaking process goes through the intermediacy of the π^* anion radical (Scheme 3).

In the case of dichloroethylene, the transfer coefficient at 0.1 V/s (Figure 5a) is equal to 0.4, indicating that the reaction is under the kinetic control of either a dissociative electron transfer reaction in case of a concerted mechanism or an outersphere electron transfer reaction in case of a stepwise mechanism. In the first case, we may apply the dissociative electron transfer theory in which provision has been made for a non-negligible interaction between the radical and chloride ion in the product cluster as we have done in the case of gem-polychlorides. The parameters required for the application of the “sticky dissociative electron transfer” model to the present case are listed in Table 2. The value thus found for the energy of interaction between Cl[−] and the radical $\cdot\text{CH}=\text{CHCl}$ in a solvent as polar as DMF, $D_p = 0.325$ eV, is exceedingly large (for example, in the same solvent, the energy of interaction between Cl[−] and the consider-

Table 2. Parameters for the Application of the “Sticky Dissociative Electron Transfer” Model and of the Stepwise Model to the Three α,β -Polychloroalkenes

compd	Z_{el}^b	$T\Delta S^\circ$	E_{RX/RX^\cdot}°	ΔG_p°	v^c	α	ΔG_p^\ddagger	a_R	λ_0^R	λ_0^\ddagger	D_R	D_P	E_{RX/RX^\cdot}°	λ
ClHC=CHCl	6381	0.33	-1.960	-0.817	0.1	0.40	0.338	3.13	0.96	1.12	4.10	0.325	-2.33	2.16
ClHC=CCl ₂	5470	0.34	-1.728	-0.711	1.0	0.43	0.313	3.29	0.91	1.08	3.88	0.345	-2.21	1.68
Cl ₂ C=CCl ₂	4878	0.39	-1.602	-0.598	1.0	0.43	0.310	3.44	0.87	1.05	3.80	0.370	-1.98	1.65

^a Energies in eV, potentials, in V vs SCE, and distances, in Å. ^b In cm/s. ^c In V/s.

ably more electrophilic radical $\cdot\text{CCl}_3$ is only 0.161 eV leading to the conclusion that the concerted mechanism is quite unlikely.

Would the experimental data be in better agreement with a stepwise mechanism in which the initial electron transfer is rate determining? We may use in this case the Marcus–Hush theory of outersphere electron transfer³² according to which

$$\Delta G_p^\ddagger = \frac{\lambda}{4} \left(1 + \frac{E_p - E_{RX/RX^\cdot}^\circ}{\lambda} \right)^2$$

where λ is the global reorganization energy (solvent + intramolecular reorganization). ΔG_p^\ddagger is the same as before, but the standard potential is different. It characterizes the passage from the starting molecule to the π^* anion radical and not to the separated fragments. The above quadratic relationship implies that

$$\alpha_p = \frac{1}{2} \left(1 + \frac{E_p - E_{RX/RX^\cdot}^\circ}{\lambda} \right)$$

and thus:

$$\lambda = \frac{\Delta G_p^\ddagger}{\alpha_p^2}$$

From the parameters in Table 2, it follows that $\lambda = 2.16$ eV and $E_{RX/RX^\cdot}^\circ = -2.33$ V versus SCE. These two values are quite likely. In the overall reorganization energy, the solvent contribution should be close to the value, 0.958 eV, used earlier for λ_0^R . The remainder, 1.2 eV, seems perfectly reasonable for an internal reorganization involving an increase of the C–Cl bond length and possibly a loss of planarity.

We are thus led to conclude that the first stage of the electrochemical reduction of dichloroethylene involves the intermediacy of the π^* anion radical rather than a concerted electron transfer/bond breaking process.

A similar analysis was carried out for trichloroethylene at 1 V/s, a scan rate at which the cyclic voltammetric response is unambiguously controlled by an electron transfer reaction, either the dissociative electron transfer or the initial outersphere electron transfer step in case of a stepwise mechanism. The values of the various parameters used and found for the two mechanisms are listed in Table 2. From the value found for D_P (0.345 eV), it clearly appears that the concerted mechanism is not followed, while the values of E_{RX/RX^\cdot}° and λ found for the stepwise mechanism are perfectly reasonable. We may therefore

conclude that the π^* anion radical is unambiguously an intermediate in the initial process of the reductive expulsion of one chloride ion from trichloroethylene. This is confirmed by the observation that, at 0.1 V/s, the apparent transfer coefficient derived from the peak width is close to 0.6, a clear indication that the reaction is under the mixed control of an electron transfer step and a follow up reaction and, thus, that a stepwise mechanism is followed.

Going now to tetrachloroethylene, we see in Figure 5c that the wave corresponding to the reductive cleavage formation of dichloroacetylene is merged with the reduction wave of dichloroacetylene. We may nevertheless apply the same procedure as in the two preceding cases for distinguishing between the two mechanisms. The values of the various parameters used and found for the two mechanisms are listed in Table 2. From the value found for D_P (0.370 eV), it clearly appears that the concerted mechanism is not followed, while the values of E_{RX/RX^\cdot}° and λ found for the stepwise mechanism are perfectly reasonable. We may therefore conclude that the π^* anion radical is unambiguously an intermediate in the initial process of the reductive expulsion of one chloride ion from tetrachloroethylene as it is for di- and trichloroethylene.

α,β -Polychloroalkanes (Cl₃C–CCl₃, Cl₂HC–CCl₃, Cl₂HC–CHCl₂, ClH₂C–CHCl₂). Typical cyclic voltammograms obtained with the four compounds investigated are displayed in Figure 6. Ethanol was added to the solution in the same amount as for the corresponding –2Cl chloroethylenes for a better characterization of these compounds in case they would be the products of the reduction of polychloroalkanes.

ClH₂C–CHCl₂ exhibits a single irreversible two-electron wave (Figure 6a). It shows no trace of a shoulder in the supporting electrolyte discharge current that could correspond to the reduction of 1,2-dichloroethane as seen on the voltammogram of an authentic sample. Cl₂HC–CHCl₂ shows two successive irreversible two-electron waves (Figure 6b). It clearly appears that the second wave is not the wave of ClH₂C–CHCl₂ (Figure 6a) but rather that of ClHC=CHCl (Figure 5a). Cl₂HC–CCl₃ shows three successive irreversible two-electron waves (Figure 6c), which do not correspond to the formation of ClH₂C–CHCl₂ (Figure 6a) but rather to the formation of the corresponding chloroalkene, namely, ClHC=CCl₂ (Figure 5b). Finally, Cl₃C–CCl₃ shows four successive two-electron waves (Figure 6d), with the two waves in the middle being almost completely merged.³³ In this case too, the corresponding chloroalkene, namely, Cl₂C=CCl₂ (Figure 5c) is formed rather than the hydrogenolysis product, Cl₂HC–CCl₃ (Figure 6c).

The chloride ion expulsion reaction scheme is thus the same in all cases (Scheme 4). The values of the transfer coefficient

(31) An alternative cleaving pathway for the second C–Cl bond would be an homolytic cleavage of the neutral radical followed by the reduction of the chlorine radical. However, the direct reduction of the neutral radical is very favorable, whereas the homolytic cleavage is largely endergonic (ca. 1.3 eV), as revealed by quantum chemical calculations.

(32) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979. (c) Hush, N. S. *J. Chem. Phys.* **1958**, *28*, 962. (d) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (e) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(33) The two merging waves in Figure 6d seems a little more separated, with the first wave higher, than in the voltammogram of tetrachloroethylene (Figure 5c). This is in fact expected since, in the first case, this double wave appears on top of the descending branch of the first reduction wave of Cl₃C–CCl₃. Thus the first of the two merging waves is lifted up more than the second.

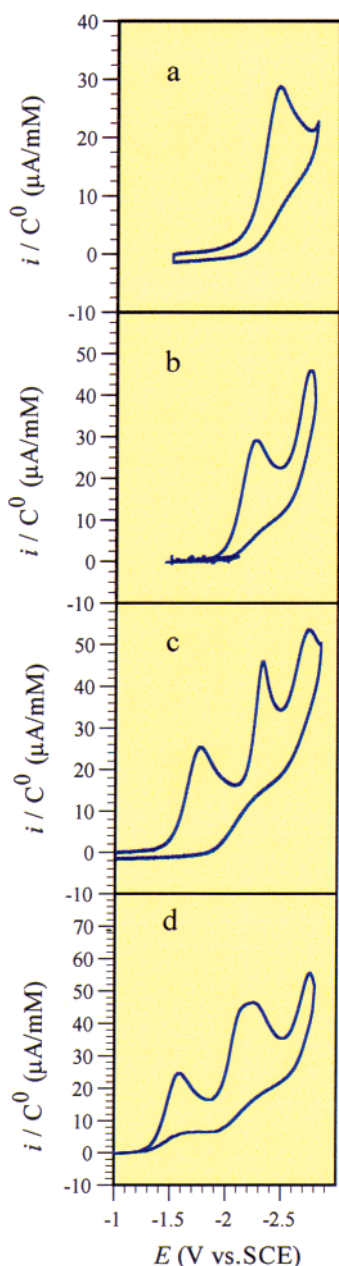
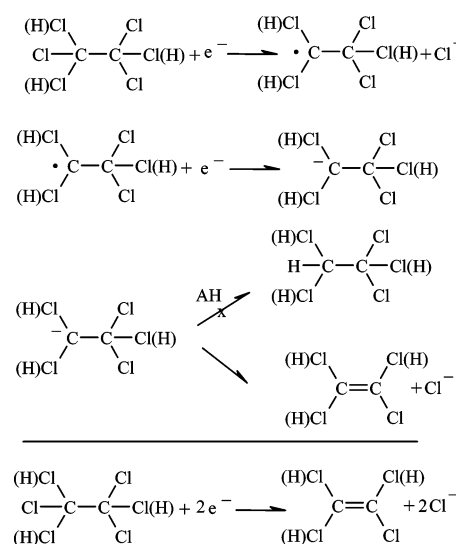


Figure 6. Cyclic voltammetry of $\text{ClH}_2\text{C}-\text{CHCl}_2$ (a), $\text{Cl}_2\text{HC}-\text{CHCl}_2$ (b), $\text{Cl}_2\text{HC}-\text{CCl}_3$ (c), and $\text{Cl}_3\text{C}-\text{CCl}_3$ (d) in DMF + 0.1 M $n\text{-Bu}_4\text{ClO}_4$ + EtOH (50 equiv). Scan rate: 0.1 V/s. Temperature: 25 °C. On the vertical axis, the current is normalized versus concentration.

at the first wave of each compound, ranging between 0.3 and 0.4, suggest that the first electron transfer and the expulsion of the first chloride ion are concerted processes as expected for aliphatic molecules and indeed found earlier for the aliphatic gem-polychlorides. However, one may alternatively consider a stepwise process kinetically controlled by a slow electron transfer. In this case, following the same arguments as previously done for polychloroalkenes, the standard free enthalpies of the outersphere electron transfer reactions may be extracted and are found to lie between -0.80 and -1.38 eV at 0.1 V/s (going from $\text{Cl}_3\text{C}-\text{CCl}_3$ to $\text{ClH}_2\text{C}-\text{CHCl}_2$). This rules out a two steps mechanism since it would be in contradiction with the formation of highly energetic aliphatic anion radicals (with the extra electron in a σ^* orbital). The radical formed is, as in many other cases, easier to reduce than the starting molecule thus yielding

Scheme 4



the corresponding carbanion. The latter, at least in the mildly acid medium in which we operate, prefers cleave off losing a second chloride ion yielding the corresponding olefin than being protonated to form the hydrogenolysis product. This reaction sequence has been amply documented in previous studies of the reduction of α,β -dibromoalkanes.³⁴

Activation-driving force ($\Delta G_p^\ddagger - \Delta G_p^\ominus$) plots, derived from the variations of the peak potential with the scan rate by means of eqs 8 and 4, respectively, are displayed in Figure 7.

Among the parameters required for the application of the “sticky dissociative electron transfer” model to these data, a correct estimation of the bond dissociation energy is particularly important, owing to the transmission of error to the value of the ion-radical interaction energy in the product cluster as discussed earlier in the paper. Since two of the bond dissociation energies in the series are not experimentally known, we used a quantum chemical calculation, at the B3P86/6-311++G** level, to estimate the bond dissociation energy with an empirical correction³⁵ aiming at a satisfactory reproduction of the experimental data in the present series and with polychloromethanes (Table 3). The other parameters required by the application of the model are listed in Table 4. The good agreement between the theoretical predictions and the experimental data (Figure 7) validates the model, leading to the values of the ion-radical interaction energy in the product cluster reported in Table 4. As expected, the interaction energy increases with the number of chlorines borne by the molecule, which causes an increase of the partial positive charge borne by the interacting carbon.³⁶ It is noteworthy that the energy of ion radical interaction in the product cluster plays a quite significant role.

Concluding Remarks

The mechanism of the successive reductive elimination of the chloride ions is the same in both families of compounds of *gem-polychlorides* (Schemes 1 and 2). At each elimination stage, it involves, as rate-determining step, the transfer of one electron concerted with the cleavage of the carbon-chloride bond. The second step is an immediate electron transfer to the ensuing

(34) (a) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464. (b) Lexa, D.; Savéant, J.-M.; Schäfer, H.; Su, K. B.; Vering, B.; Wang, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 6162.

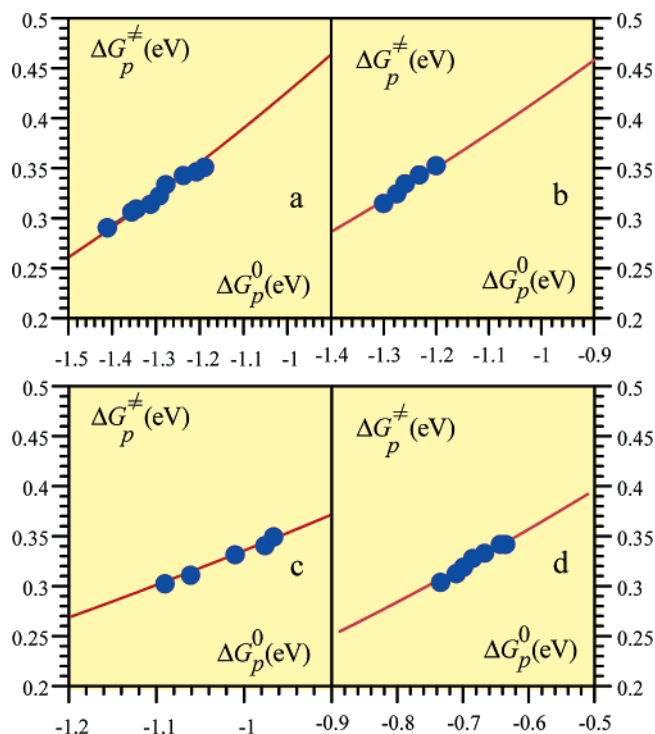


Figure 7. Activation-driving force plots derived from the variation of the peak potential with the scan rate using eqs 8 and 4 (blue dots) and simulated by means of eqs 5–7 and the parameter values listed in Table 4 for ClH₂C–CHCl₂ (a), Cl₂HC–CHCl₂ (b), Cl₂HC–CCl₃ (c), and Cl₃C–CCl₃ (d).

Table 3. Calculated and Experimental C–Cl Bond Dissociation Energies^a

compound	experimental	calculated ^b	corrected ^c
C ₂ Cl ₆	3.10 ± 0.12	2.80	3.06
C ₂ HCl ₅	2.94 ± >0.04	2.82	3.04
C ₂ H ₂ Cl ₄		3.12	3.28
C ₂ H ₃ Cl ₃		3.21	3.33
CCl ₄	2.985 ± 0.03	2.81	2.95
CHCl ₃	3.24 ± 0.03	3.11	3.22
CH ₂ Cl ₂	3.47 ± 0.05	3.38	3.44

^a In eV. ^b B3P86/6-311++G**. ^c Corrected calculated values.³⁵

radical, taking place at a potential more positive than the potential at which the first electron transfer occurs. The carbanion thus formed is sufficiently basic to be protonated by any trace of weak acid present in the reaction medium.

The three successive elimination steps are separated by a large potential gap. These gaps first stem from large differences in the thermodynamic driving forces reflecting large differences in the dissociative standard potentials (Table 1). There are, in addition, two substantial cumulative kinetic effects that amplify this thermodynamic effect. The bond dissociation, D_R , of the

substrate decreases with the number of chlorine atoms, and the interaction between chloride ion and the radical, D_P , increases in the same direction. As can be seen in the approximate eq 3, these two variations decrease the contribution of intramolecular reorganization to the intrinsic barrier, $(\sqrt{D_R} - \sqrt{D_P})/4$. We note that D_P decreases upon elimination of each chlorine atom, in line with fact that the density of positive charge on the radical carbon diminishes accordingly. It is also noteworthy that replacement of one Cl by a CN, the rest of the structure being unchanged, weakens the interaction between the radical and Cl[−].

Reductive chloride ion expulsion in α,β -polychloroalkanes (Scheme 4) starts in the same manner. But, the carbanion resulting from the reduction of the dissociative electron transfer radical prefers expelling a chloride ion yielding the corresponding olefin rather than being protonated to the hydrogenolysis product. Ion–radical interactions in the product cluster are quite significant, in this case too. They increase with the number of chlorine atoms borne by the molecule together with the electrophilicity of the intermediate radical. It is interesting to note that the magnitude of this interaction plays a central role in the control of the reduction potential required to expel the first chloride ion.

Comparison with the polychloromethanes indicate the following order of cluster interaction energies Cl₃C–CCl₃ > CCl₄ > CHCl₃, Cl₂HC–CCl₃ > CH₂Cl₂, Cl₂HC–CHCl₂, and ClH₂C–CHCl₂, in line with the expected inductive effects.

The reduction of the α,β -polychloroethenes follows a similar $2e^- - 2Cl^-$ reaction sequence, leading then to the corresponding alkynes (Scheme 2). However, unlike in the polychloroethane case, the expulsion of the first chloride ion follows a stepwise electron transfer/bond cleavage mechanism. The reduction potential is then essentially governed by the thermodynamics of the anion radical formation.

Experimental Section

Chemicals. *N,N'*-dimethylformamide (Fluka, >99.5%, store on molecular sieves and under argon atmosphere), the supporting electrolyte NBu₄ClO₄ (Fluka, puriss), carbon tetrachloride (Acros, 99.8%), chloroform (Acros, 99.8%), dichloromethane (Aldrich, 99.8%, anhydrous), trichloroacetonitrile (Aldrich, 98%), dichloroacetonitrile (Aldrich, 98%), chloroacetonitrile (Aldrich, 99%), tetrachloroethylene (Aldrich, 99.9+%), trichloroethylene (Aldrich, 99.5+%), *trans*-1,2-dichloroethylene (Aldrich, 98%), *cis*-1,2-dichloroethylene (Aldrich, 97%), hexachloroethane (Acros, 99%), pentachloroethane (Aldrich, 95%), 1,1,2,2-tetrachloroethane (Aldrich, 98%), and 1,1,2-trichloroethane (Aldrich, 97%) were used as received.

Chloroacetylene and dichloroacetylene were synthesized from *cis*-1,2-dichloroethylene and trichloroethylene, respectively. Potassium hydride (35% in mineral oil, Aldrich) was rinsed twice with pentane (Fluka) and once with dry tetrahydrofuran (Aldrich). Dehydrohalogenation of *cis*-1,2-dichloroethylene and trichloroethylene was

Table 4. Parameters for the Application of the “Sticky Dissociative Electron Transfer” Model to Polychloroalkanes

compd	Z_0^a (cm/s)	$T\Delta S^{ob}$ (eV)	$E_{RX/R+X}^c$ (V vs SCE)	a_R^d (Å)	$\lambda_0^R^e$ (eV)	$\lambda_0^{\ddagger f}$ (eV)	D_R^g (eV)	D_P^h (eV)
Cl ₃ C–CCl ₃	4083	0.388	−0.862	3.5	0.86	1.06	3.06 ± 0.03	0.192 ± 0.017
Cl ₂ HC–CCl ₃	4417	0.385	−0.845	3.63	0.826	1.05	3.04 ± 0.03	0.088 ± 0.012
Cl ₂ HC–CHCl ₂	4879	0.365	−1.105	3.13	0.958	1.15	3.28 ± 0.03	0.078 ± 0.011
ClH ₂ C–CHCl ₂	5429	0.354	−1.166	3.33	0.901	1.10	3.33 ± 0.03	0.075 ± 0.011

^a Heterogeneous collision factor. ^b Standard entropic term at the temperature of the experiment. ^c Dissociative standard potential. ^d Hard sphere radius of the reactant. ^e Reactant solvent reorganization energy. ^f Averaged solvent reorganization energy at the transition state (variations do not exceed 4% in the covered range of driving forces). ^g Substrate bond dissociation energy. ^h Ion–radical interaction energy.

induced by potassium hydride and a catalytic amount of methanol in dry tetrahydrofuran as described in the literature.³⁷ The resulting solutions of the chlorinated acetylenes in tetrahydrofuran were used immediately.

Instrumentation. The working electrode was a 3 mm-diameter glassy carbon electrode disk (Tokai) carefully polished and ultrasonically rinsed in absolute ethanol before use. The counterelectrode was a platinum wire, and the reference electrode, an aqueous SCE electrode. The potentiostat, equipped with a positive feedback compensation and current measurer, used at low or moderate scan rates, was the same as previously described.³⁸ All experiments have been done at 25 °C, the double-wall jacket cell being thermostated by circulation of water.

Convolution Procedures. The cyclic voltammograms were recorded by a digital oscilloscope (Nicolet310) and then transferred to a PC. The background-subtracted curves were then transformed by convolution with the function $1/\sqrt{\pi t}$.

Quantum Chemical Calculations. All the calculations were performed with the Gaussian 98 series of programs.³⁹ DFT (B3P86) method and 6-311++G** basis set were used. Minimum energy structures were

fully optimized. Frequency calculations were made to verify that the structures were minima (no imaginary frequencies) and to evaluate thermodynamical functions.

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Supporting Information Available: Convolution procedure for polychloroacetonitriles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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