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ARTICLE

Reductive cleavage of carbon-chlorine bonds at catalytic and non-catalytic electrodes in 1-butyl-3-methylimidazolium tetrafluoroborate

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Dissociative electron transfer (DET) to a series of organic chlorides at glassy carbon (GC), silver and copper electrodes has been studied in 1-butyl-3-methylimidazolium tetrafluoroborate. The overall results of this study show that the ionic liquid behaves like molecular solvents such as acetonitrile and dimethylfomamide. It is found that aromatic chlorides follow a stepwise mechanism, whereas concerted electron transfer/bond cleavage is the preferred reaction mechanism for alkyl and benzyl chlorides. Ag and Cu show catalytic effects only when the DET follows a concerted mechanism, but Ag proves to be a much better electrocatalyst than Cu. A series of substituted benzyl chlorides ($Z-C_6H_4CH_2Cl$, Z = H, 3-OCH$_3$, 3-F, 4-Cl, 3-CF$_3$) shows interesting results providing some insight into the reaction dynamics. The process occurs by a concerted mechanism and albeit a constant standard potential for the whole series, E_p on GC and Cu, which does not show catalytic activity, is significantly affected by the substituents. In contrast, Ag shows good catalytic activity and, as expected, E_p does not change with the substituent. This difference of behavior may be rationalized by considering ion-dipole interactions between $R^•$ and Cl^- as opposed to adsorption of the fragments on the electrode surface.

## 1. Introduction

Reductive cleavage of carbon-halogen bonds plays a crucial role in many chemical processes. In particular, electrochemical reduction of organic halides is widely investigated for applications in synthesis[1,2] and pollution remedy,[3-8] and also for developing and testing dissociative electron transfer (DET) theories.[9-13] The reaction may proceed through either of two principal mechanisms: a stepwise mechanism involving the intermediate formation of $RX^{•-}$, followed by rupture of the carbon-halogen bond (Scheme 1a) and a concerted mechanism in which electron transfer (ET) and bond breaking occur in a single step (Scheme 1b). The competition between stepwise and concerted mechanisms depends on various parameters such as molecular structure, nature of the halide leaving ion, strength of the breaking bond and reaction free energy.[14] This competition can be expressed in terms of the difference between the standard potentials of the two reaction routes, which also defines the free energy of dissociation of the radical anion, $\Delta G_{RX^{•-}\rightarrow R^•+X^-}$ (eq. 1).

$$\Delta G_{RX^{•-}\rightarrow R^•+X^-} = F\left(E^\ominus_{RX/RX^{•-}} - E^\ominus_{RX/R^•+X^-}\right)$$
$$= FE^\ominus_{RX/RX^{•-}} + BDE_{R-X} - T\Delta S_{RX\rightarrow R^•+X^•} - FE^\ominus_{X^•/X^-} \qquad (1)$$

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where BDE_{R-X} is the dissociation energy of the R-X bond, F is the Faraday constant, and $E^\ominus_{RX/RX^{•-}}$, $E^\ominus_{RX/R^•+X^-}$ and $E^\ominus_{X^•/X^-}$ are the standard potentials of the subscript couples. Any combination of these parameters resulting in a more negative $\Delta G_{RX^{•-}\rightarrow R^•+X^-}$ favors the concerted pathway and vice versa. For example, the weaker the bond and the more negative the value of $E^\ominus_{RX/RX^{•-}}$ (and also the more positive the value of $E^\ominus_{X^•/X^-}$), the more favorable the concerted reaction route is. It is worth noting that all parameters might not vary in a class of organic halides, so that the competition is governed by one or two of them. Various examples of situations in which passage from one mechanism to the other primarily depends on one parameter are reported in the literature.[15-17]
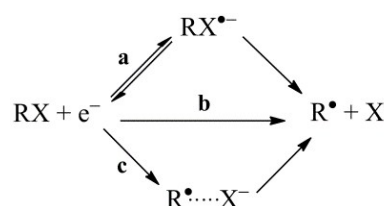
Scheme 1. General mechanism of dissociative electron transfer.

In view of the various parameters involved in equation (1), it is not always easy to predict which mechanism is preferred. However, based on the large body of literature data on the mechanism of DET to carbon-halogen bonds,[12,13,15-25] it is possible to classify organic halides into two categories: aromatic halides mainly following a stepwise mechanism and aliphatic halides preferring concerted DET. It is important to stress that there are some exceptions to this general

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classification and careful examination of the system should always be carried out before assigning one or the other mechanism to the ET reaction. For example, it has been shown that electrochemical reduction of iodobenzene and 3-methyl iodobenzene can occur by a concerted mechanism.[26] On the other hand, some alkyl halides bearing π-electron acceptors were found to follow the stepwise mechanism.[15,16,23,27]

A variant of the concerted pathway, known as sticky DET, is observed when the two fragments, R[•] and X[−], can give rise to ion-dipole interactions in the solvent cage before they diffuse apart (Scheme 1c). In this case, the dynamics of the electron transfer is strongly affected by the interaction energy of the fragments, which depends on the dipole moment of R[•] as well as on the charge density on X[−]. Many examples of alkyl halides following this DET mechanism have been reported.[11-13,23,25]

Very often, activation of C-X bonds requires electrocatalysis and indeed electrocatalytic reduction of RX has been a central topic in heterogeneous ET for the last few decades. The process has been mainly investigated in organic solvents such as CH_3CN and DMF, showing that a few metals such as Ag, Cu and Pd possess remarkable electrocatalytic properties.[28-33]

Room-temperature ionic liquids (RTILs) are receiving increasing interest as electrochemical solvents because they possess several desirable properties such as high thermal stability, non-volatility, high intrinsic conductivity and wide electrochemical window.[34,35] Although RTILs have been widely used as solvents for electrochemical processes, only a few studies pertaining to the reduction of organic halides are reported in the literature.[36-41] In particular, electrochemical reduction of organic halides in ionic liquids on catalytic electrodes such as Ag and Cu is almost completely missing. Herein we report on the dissociative electron transfer to a series of organic chlorides (Scheme 2) in 1-butyl-3-methylimidazolium tetrafluoroborate. Glassy carbon, used as a non-catalytic electrode material,[42] together with Ag and Cu, which are notoriously known for their electrocatalytic properties toward activation of carbon-halogen bonds, were used as cathodes. The principal scope of the study was to examine the mechanism of DET on different electrodes in a room-temperature ionic liquid. A special attention was devoted to the relation between mechanism and electrocatalysis and, for this scope, the selected compounds include both aromatic and aliphatic chlorides.
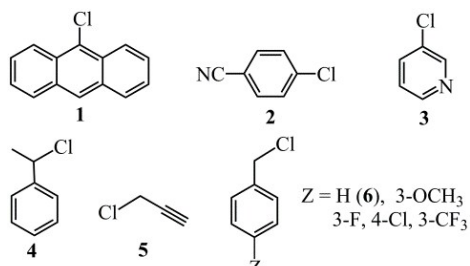
Scheme 2. Molecular structures of investigated compounds.

2. Experimental

2.1. Chemicals

1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF$_4$, Sigma-Aldrich ≥ 98%) contains acidic impurities mainly arising from hydrolysis of BF_4^-.[43] It was, therefore, always purified according to the following procedure. A mixture of H$_2$O/[BMIm]BF$_4$ (3:1, v/v) was titrated with 0.07 M KOH up to a neutral pH and then evaporated with a rotary evaporator until the water content was reduced to trace levels. The ionic liquid was then dissolved in CH_2Cl_2 and filtered to eliminate any insoluble residue. After eliminating CH_2Cl_2 by a rotary evaporator, the ionic liquid was dried at 80 °C under a reduced pressure of 0.03 mbar for 18 h. The pH of the initial ionic liquid, measured by preparing a 1% (v/v) aqueous solution, passed from ca 2 to ca 6, after treatment.

All other compounds, purchased from Sigma-Aldrich or Acros, were used without further purification.

2.2. Instrumentation

Cyclic voltammetry was performed with a PC-controlled PARC 273A potentiostat/galvanostat with positive feedback iR compensation. All experiments were carried out at 25 °C in a three-electrode cell with glassy carbon (a 3 mm diameter disc, Tokai GC-20), Ag and Cu (2 mm diameter discs) working electrodes and a Pt wire counter-electrode. The reference electrode was made of a silver wire (Alfa Aesar 99.999%) in 0.01 M AgCF$_3$SO$_3$ in [BMIm]BF$_4$ and was separated from the working electrode compartment by a glass frit and methyl cellulose gel. The potential of the reference electrode was always calibrated at the end of the experiment versus the ferrocenium/ferrocene (Fc$^+$/Fc) couple to which all potentials in the paper are referred. Prior to each experiment the working electrodes were cleaned by polishing with a 0.25-μm diamond paste (Struers) followed by ultrasonic rinsing in ethanol.

3. Results and discussion

3.1. Electroreduction of compounds 1-6

Cyclic voltammetry of compounds **1-6** in [BMIm]BF$_4$ is reported in Fig. 1. All compounds exhibit an irreversible reduction peak corresponding to the reductive cleavage of the carbon-chlorine bond, except 3-chloropyridine which requires potentials beyond the onset of the cathodic solvent discharge. It is important to underline that the viscosity, η, of RTILs is much higher than those of molecular solvents. In particular, for [BMIm]BF$_4$, η = 154 mPa s at 25 °C,[35] which is about 2 orders of magnitude greater than the typical value of η for many organic solvents. A consequence of the high viscosity is a considerable decrease of the rate of mass transport in RTILs, with diffusion coefficients, D, decreasing by about 2 orders of magnitude with respect to values measured in conventional organic electrolytes. For this reason, voltammetric peak currents measured in RTILs are much smaller than values from cyclic voltammetry performed in organic solvents. To compensate
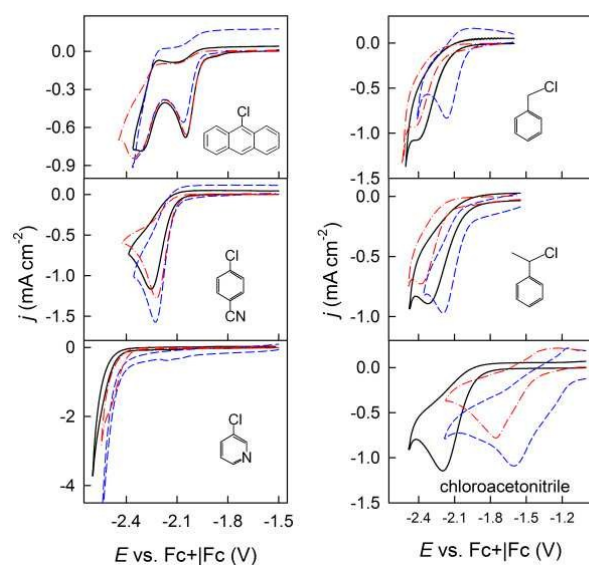
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Figure 1. Cyclic voltammetry of RCl (0.01 M) in [BMIm]BF$_4$, recorded at 0.2 V/s on (——) GC, (– – –) Ag and (–·–·–) Cu.

for the decrease of current due to reduced rate of mass transport, all CV experiments were carried out with a substrate concentration of 10^{-2} M rather than 10^{-3} M, which is commonly used in experiments in molecular solvents.

9-Chloroanthracene shows a second reversible cathodic peak attributable to one-electron reduction of anthracene, generated at the first reduction peak.[36] Since this study focuses on the dissociative electron transfer to the carbon-chlorine bond, the second reduction step of 9-chloroanthracene was not analyzed.

Analysis of the characteristics of the irreversible reduction peak observed in cyclic voltammetry offers an efficient way to distinguish between concerted and stepwise mechanisms.[44] One important parameter derived from the peak characteristics for this purpose is the transfer coefficient α defined as

$$\alpha = \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{\ominus}} = \frac{\partial \Delta G^{\ddagger}}{F\partial\left(E - E^{\ominus}\right)} \tag{2}$$

where $\Delta G^{\ominus}$, given by $F(E - E^{\ominus})$, is the free energy of the ET reaction and $\Delta G^{\ddagger}$ is the cathodic activation free energy, i.e., the activation free energy of the ET reaction in the direction of reduction.

In the case of a stepwise mechanism, the ET step can be analyzed according to the Marcus-Hush theory of outer-sphere electron transfer,[45-47] which predicts a quadratic activation-driving force relationship:

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta G^{\ominus}}{4\Delta G_0^{\ddagger}}\right)^2 \tag{3}$$

where $\Delta G_0^{\ddagger}$ is the intrinsic barrier, i.e., the activation free energy at $\Delta G^{\ominus} = 0$. The intrinsic barrier is defined as $\Delta G_0^{\ddagger} = \lambda/4$, where λ is the reorganization energy. This model does not

consider rupture or formation of bonds during ET and therefore cannot be applied without appropriate correction when bond breaking is concerted with ET. A theory for concerted dissociative ET has recently been developed by Savéant who showed that a quadratic activation-driving force relationship holds also for this type of ET.[9,10] The Savéant model is based on a Morse potential energy for R-X and the assumption that the potential energy of the products R$^{\bullet}$ and X^{-} is identical to the repulsive part of the R-X Morse curve. In the early version of the model, possible interactions between R$^{\bullet}$ and X^{-} were neglected, but this aspect was later reconsidered leading to the sticky model of dissociative ET.[11] The Savéant model leads to a relationship between $\Delta G^{\ddagger}$ and $\Delta G^{\ominus}$ of the same form as eq. (3) with the only exception that the intrinsic barrier of the concerted mechanism contains an important contribution from the bond dissociation energy in addition to that of the reorganization energy. Additionally, the model shows that the bond elongation at the transition state is quite small, indicating that the transition state is in the parabolic region of the Morse curve..

Equations (2) and (3) predict a linear dependence of α on E (eq. 4), which, however, is rarely observed for concerted dissociative ET to carbon-halogen bonds. This is mainly due to the high value of $\Delta G_0^{\ddagger}$ combined with small variations of E under typical voltammetric investigations. It is therefore common practice to carry out voltammetric analysis on the basis of equations obtained by theoretical treatment of electron transfer according to the Butler-Volmer model of electrode kinetics,[48-50] which assumes constant α and hence a linear dependence of $\Delta G^{\ddagger}$ on $\Delta G^{\ominus}$.

$$\alpha = \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{\ominus}} = \frac{1}{2} + \frac{F\left(E - E^{\ominus}\right)}{8\Delta G_0^{\ddagger}} \tag{4}$$

Theoretical treatment of cyclic voltammetry of an irreversible electron transfer, according to Butler-Volmer kinetics, gives the following equations at 25 °C:[48,51,52]

$$\frac{\partial E_p}{\partial \log \upsilon} = -1.151\frac{RT}{\alpha F} = -\frac{29.6}{\alpha}\,\text{mV} \tag{5}$$

$$E_p - E_{p/2} = -1.857\frac{RT}{\alpha F} = -\frac{47.7}{\alpha}\,\text{mV} \tag{6}$$

where E_p and $E_{p/2}$ are the potentials at the peak and half-peak, respectively, υ is the scan rate, R is the universal gas constant, F is the Faraday constant and α is the electron transfer coefficient. The same equations have been derived by Savéant for a concerted dissociative ET by assuming a linear dependence of $\Delta G^{\ddagger}$ on $\Delta G^{\ominus}$ in the narrow region of potentials covered by a voltammetric peak.[9]

If the process follows a concerted mechanism (Scheme 1b), electron transfer and bond rupture occur in a single step with a high intrinsic barrier, $\Delta G_0^{\ddagger}$, arising mainly from the C-Cl bond energy.[44] The peak will be located at potentials much more negative than the standard potential, $E^{\ominus}$, of the process; that is, reduction occurs with a high overpotential. Therefore, concerted DET corresponds to an irreversible electron transfer

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Table 1. Voltammetric data for the electroreduction of organic chlorides **1-6** in [BMIm]BF$_4$ at 25 °C.

RCl	GC $E_p{}^a$ (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^b	Ag $E_p{}^a$ (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^c	$\Delta E_p{}^d$ (V)	Cu $E_p{}^a$ (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^c	$\Delta E_p{}^d$ (V)
1	-2.05	-0.034		-2.05	-0.032		0.00	-2.05	-0.032		0.00
2	-2.25	-0.046		-2.23	-0.038		0.02	-2.22	-0.044		0.03
3	< -2.55			< -2.50				< -2.50			
4	-2.32	-0.119	0.27	-2.20	-0.080	0.37	0.12	-2.38	-0.081	0.37	-0.06
5	-2.22	-0.105	0.30	-1.56	-0.095	0.31	0.66	-1.76	-0.087	0.34	0.46
6	-2.41	-0.110	0.30	-2.16	-0.084	0.35	0.25	-2.44	-0.080	0.37	-0.03

$^a E_p$ vs. Fc$^+$/Fc measured at υ = 0.2 V/s. ^{b}Average of the values calculated from eqs. (5) and (6). ^{c}calculated from eq. (5). $^d \Delta E_p = E_{p,M} - E_{p,GC}$, difference between the peak potentials measured at GC ($E_{p,GC}$) and Ag or Cu ($E_{p,M}$).

and equations (5) and (6) can be used to calculate α, which is significantly smaller than 0.5 because the process occurs with a high overpotential and hence $E_p \ll E^\ominus$.

If instead the reaction occurs according to a stepwise mechanism (eqs. 7 and 8), two possibilities are to be considered.[44]

$$RCl + e^- \rightleftharpoons RCl^{\bullet-} \qquad (7)$$
$$RCl^{\bullet-} \longrightarrow R^\bullet + Cl^- \qquad (8)$$

If reaction (7) is very fast (reversible electron transfer), the process is kinetically controlled by the bond rupture and a plot of E_p versus $\log\upsilon$ gives a straight line with slope $\partial E_p/\partial\log\upsilon$ = -29.6 mV at 25 °C.[48] In addition, $E_p - E_{p/2}$ = -47.5 mV. In the opposite situation, the bond cleavage is faster than electron transfer (eq. 7), which becomes the rate-determining step. The characteristics of the peak are those of an irreversible electron transfer and equations (5) and (6) can be applied. In particular, in the case α = 0.5, as is often assumed for aromatic halides,[36,53] $\partial E_p/\partial\log\upsilon$ = -59.2 mV and $E_p - E_{p/2}$ = -95.4 mV. If, in the examined range of scan rates, reactions (7) and (8) have comparable rates, the system is in a mixed kinetic regime and both $\partial E_p/\partial\log\upsilon$ and $E_p - E_{p/2}$ show values lying somewhere between those expected for kinetic control by electron transfer and bond rupture.

The results of voltammetric analysis on all compounds are reported in Table 1. On GC, both aromatic and aliphatic chlorides show well-defined reduction peaks that are amenable to E_p vs. $\log\upsilon$ and $E_p - E_{p/2}$ analyses. In the investigated range of scan rates (0.05 – 5 V/s), all compounds show linear variations of E_p vs. $\log\upsilon$ and $E_p - E_{p/2}$ values independent of scan rate. The values of $\partial E_p/\partial\log\upsilon$ found for **1** and **2** are -34 mV and -46 mV, respectively, whereas the corresponding $E_p - E_{p/2}$ values (not reported in the table) are -55 mV and -73 mV. The $\partial E_p/\partial\log\upsilon$ and $E_p - E_{p/2}$ values of **1** agree well with a reversible electron transfer followed by a relatively slow first-order chemical reaction such as bond rupture, whereas the values obtained for **2** indicate a mixed

kinetic regime. These results point to a stepwise DET mechanism for both compounds in good agreement with a previous report by Lagrost et al,[36] who showed that the reductive cleavage of **1** in different ionic liquids occurs according to a stepwise mechanism with the intermediate formation of a radical anion decomposing with a rate constant of 4×10^2-10^3 s^{-1}. A similar analysis could not be carried out for **3** as its reduction peak is overshadowed by the solvent discharge. Considering that aromatic chlorides are known to undergo stepwise mechanism, which is here confirmed for **1** and **2**, we assume the same type of DET mechanism also for **3**.

Similar analysis for the reduction of **4-6** on GC showed $\partial E_p/\partial\log\upsilon$ and $E_p - E_{p/2}$ values lower than -105 mV and -146 mV, respectively, indicating that DET to these compounds is kinetically controlled by a slow electron transfer. The electron transfer coefficient α was therefore calculated according to equations (5) and (6). The two methods gave values in close agreement with each other and the average values are reported in Table 1 (column 4). For all three aliphatic compounds, α is significantly lower than 0.5, pointing to a concerted mechanism. Again this result is in agreement with the general framework of DET to organic halides, where alkyl halides prefer a concerted mechanism.

Voltammetric analysis of RCl reduction on Ag and Cu led to the same conclusions described for GC. In the case of the aromatic chlorides **1** and **2**, values of $\partial E_p/\partial\log\upsilon$ between -32 mV and -44 mV were found, whereas the $E_p - E_{p/2}$ values were in the range from -55 mV to -65 mV. These values clearly indicate a stepwise mechanism for DET to these aromatic compounds. As in the case of GC, reduction of **3** could not be observed on Ag and Cu.

Concerning the aliphatic chlorides, it should be noted that the CV responses on Ag and Cu were not as well-defined as those of the aromatic compounds. In particular, CV of chloroacetonitrile shows a broad peak with a shoulder, which

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Table 2. Voltammetric data for the electroreduction of substituted benzyl chlorides Z-$C_6H_4CH_2Cl$ in [BMIm]BF_4 a 25 °C.

Z	σ^a	GC E_p^b (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^c	$10^7\times$D (cm^2/s)	Ag E_p^b (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^d	ΔE_p^e (V)	Cu E_p^b (V)	$\partial E_p/\partial\log\upsilon$ (V)	α^d	ΔE_p^e (V)
H	0	-2.41	-0.110	0.30	5.0	-2.16	-0.084	0.35	0.25	-2.44	-0.080	0.37	-0.03
3-OCH$_3$	0.12	-2.40	-0.111	0.30	4.7	-2.17	-0.082	0.36	0.23	-2.40	-0.077	0.38	0.0
4-Cl	0.23	-2.30	-0.116	0.28	4.6	-2.15	-0.091	0.33	0.15	-2.33	-0.075	0.39	-0.03
3-F	0.34	-2.33	-0.100	0.32	3.7	-2.16	-0.072	0.41	0.17	-2.34	-0.072	0.41	-0.01
3-CF$_3$	0.43	-2.29	-0.093	0.33	3.3	-2.14	-0.080	0.37	0.15	-2.27	-0.077	0.38	0.02

^{a}Hammett substituent constants from ref [60]. ^{b}E_p vs. Fc$^+$|Fc measured at υ = 0.2 V/s. ^{c}Average of the values calculated from eqs. (5) and (6). ^{d}calculated from eq. (5). $^e\Delta E_p = E_{p,M} - E_{p,GC}$, difference between the peak potentials measured at GC ($E_{p,GC}$) and Ag or Cu ($E_{p,M}$).

makes unreliable determination of $E_p - E_{p/2}$. For this reason, the voltammetric analysis on the reduction of compounds **4-6** on Ag and Cu was limited to the variation of E_p as a function of scan rate. Plots of E_p vs. $\log\upsilon$ gave straight lines with slopes between -95 mV and -80 mV, corresponding to α values in the range of 0.31 – 0.37. These values are well below 0.5 and are indicative of a concerted mechanism.

To sum up, reduction of aromatic chlorides on all electrodes follows a stepwise mechanism with the formation of a radical anion intermediate, just as in molecular solvents such as CH_3CN and DMF. Also DET to aliphatic chlorides on both GC and metallic electrodes confirms the concerted mechanism previously found in organic solvents. However, the nature of the electrode material may significantly affect the reduction potential. The difference between E_p values measured at GC ($E_{p,GC}$) and at each metal ($E_{p,M}$) is reported in Table 1 as $\Delta E_p = E_{p,M} - E_{p,GC}$. This parameter is often used to evaluate the catalytic activity of metallic electrodes toward RX reduction.[32,42,54] It was found that $\Delta E_p \approx 0.0$ V for **1** and **2** both at Ag and Cu, clearly indicating that these metals do not show any catalytic activity for the reduction of RCl when the process follows a stepwise mechanism. The situation completely changes for the reduction of **4-6**, which follow a concerted mechanism. In this case, Ag shows remarkable catalytic effects with positive E_p shifts in the range 0.12 – 0.66 V, depending on molecular structure. Also Cu shows some catalytic activity, although not as good as that of Ag. A strong relationship between DET mechanism and electrocatalysis on various metals has previously been found for the reduction of organic chlorides in CH_3CN: catalysis is possible only when the reaction follows a concerted mechanism.[55-57] Overall, the results reported here confirm this relationship in [BMIm]BF_4.

Comparing Ag and Cu, both similar and significantly different catalytic activities have previously been reported for the two metals, depending on the reaction medium and molecular structure of RCl.[3,24,56,58] In general, the electrocatalytic activity of Cu for the reduction of organic halides in organic solvents is always less than or equal to that of Ag. The data reported here in [BMim]BF_4 confirm the general superiority of Ag over Cu as an electrocatalytic electrode material. At moment neither the origin of the electrocatalytic property of these metals nor the factors governing it are well-understood. Therefore, any attempt to rationalize the difference of activity of the two metals would be a matter of speculation.

3.2. Electroreduction of substituted benzyl chlorides

Substituted benzyl chlorides (Z-$C_6H_4CH_2Cl$, Z = H, 3-OCH$_3$, 3-F, 4-Cl and 3-CF$_3$) exhibit a single irreversible reduction peak on all three electrodes and an example of their voltammetric pattern is reported for $C_6H_5CH_2Cl$ in Fig. 1. The characteristics of the peak were analyzed as previously described for **1-6** and the results are reported in Table 2. All compounds show low electron transfer coefficients, indicating a concerted DET mechanism:
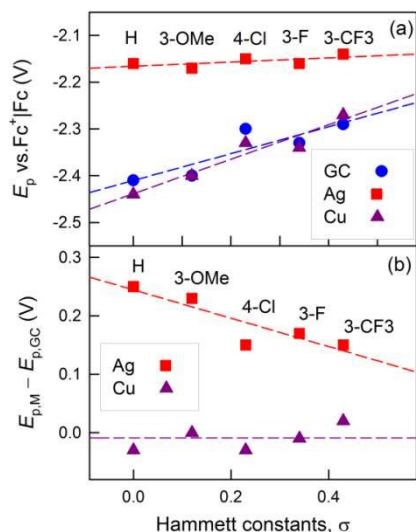
$$Z\text{-}C_6H_4CH_2Cl + e^- \longrightarrow Z\text{-}C_6H_4CH_2^\bullet + Cl^- \qquad (9)$$
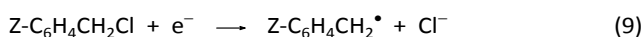
The peak current, i_p, for an irreversible one-electron transfer is given by equation (10)[48]

$$i_p = \left(2.99\times10^5\right)\alpha^{1/2}ACD^{1/2}\upsilon^{1/2} \qquad (10)$$

where A is the area of the electrode, C and D are the concentration and diffusion coefficient of RCl, respectively. Values of i_p were measured at different scan rates for each Z-$C_6H_4CH_2Cl$ at a GC electrode of area A = 0.074 cm^2. Plots of i_p vs. $\upsilon^{1/2}$ gave straight lines. The slopes of these lines, obtained by linear regression analysis of the data, were used to calculate D according to eq. (10) and the results are reported in Table 2 (column 6). The values of D measured in [BMIm]BF_4 are about 2 orders of magnitude lower than values found for

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molecules of similar bulkiness with $Z\text{-}C_6H_4CH_2Cl$ in organic solvents such as acetonitrile.[59] This lowering of D in $[BMIm]BF_4$ is due to its high viscosity.

Figure 2 shows plots of E_p and $E_{p,M} - E_{p,GC}$ vs. Hammett substituent constants (σ). On GC and Cu, E_p shifts to more positive values as the electron-withdrawing ability of the substituent increases. Plots of E_p vs. σ give roughly straight lines. Moreover, similar E_p values were obtained for each compound on these two electrodes. This is more evident in Fig. 2b, where a plot of $E_{p,Cu} - E_{p,GC}$ vs. σ shows values scattered around zero, without any clear trend. Cu does not show any catalytic activity for the reduction of benzyl chlorides. In contrast, all substituted benzyl chlorides have the same reduction potential on Ag, i.e., E_p is independent of σ (Fig. 2a). In addition, Ag shows appreciable catalytic activity, which decreases with increasing electron-withdrawing ability of the substituent (Fig. 2b).

Figure 2. Electroreduction of $Z\text{-}C_6H_4CH_2Cl$ (0.01 M) in $[BMIm]BF_4$ on GC, Ag and Cu. Dependence of (a) E_p and (b) catalytic effects, measured at υ = 0.2 V/s, on Hammett substituent constants.
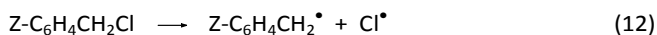
A close look at the mechanism of the DET to $Z\text{-}C_6H_4CH_2Cl$ may provide a rationale for the contrasting results observed on GC (or Cu) and Ag. The peak potential of an irreversible electron transfer is related to the standard potential, $E^{\ominus}$, and some kinetic parameters according to equation (11):[51,52]

$$E_p = E^{\ominus} - \frac{RT}{\alpha F}\left[0.780 + \ln\left(\frac{D^{1/2}}{k^{\circ}}\right) + \ln\left(\frac{\alpha F \upsilon}{RT}\right)^{1/2}\right] \quad (11)$$

in which k° is the standard electron transfer rate constant (k at $E = E^{\ominus}$). This equation is valid also for a concerted dissociative electron transfer.[9] For all substituted benzyl chlorides, the validity of eq. (11) has been confirmed by the linear variation of E_p vs. $\log\upsilon$, which allowed determination of α according to eq. (5); note that eq. (5) is the derivative $\partial E_p/\partial \ln\upsilon$ of eq. (11).

As shown in Table 2, on each electrode, α is roughly constant for the series of substituted benzyl chlorides, whereas D varies from 3.3×10^{-7} cm^2/s to 5.0×10^{-7} cm^2/s. It can

be calculated from eq. (11) that the maximum variation of E_p due to the observed variation of D is lower than 0.02 V, if α is assumed constant. Therefore, neglecting the effects of α and D, E_p will vary through the series only if $E^{\ominus}$ or k° or both parameters change with the molecular structure. The standard reduction potential of $Z\text{-}C_6H_4CH_2Cl$ can be calculated by separating reaction (9) into two steps: homolytic dissociation of the carbon-chlorine bond, followed by one-electron reduction of $Cl^{\bullet}$ to Cl^-.

$$Z\text{-}C_6H_4CH_2Cl \longrightarrow Z\text{-}C_6H_4CH_2{}^{\bullet} + Cl^{\bullet} \quad (12)$$

$$Cl^{\bullet} + e^- \rightleftharpoons Cl^- \quad (13)$$

Considering the Gibbs free energies of reactions (12) and (13), the standard potential, $E^{\ominus}$, of half-cell reaction (9) can be calculated as:

$$E^{\ominus} = E^{\ominus}_{Cl^{\bullet}/Cl^-} - \frac{BDE_{R\text{-}X}}{F} + \frac{T\Delta S^{\ominus}}{F} \quad (14)$$

where $BDE_{R\text{-}X}$ and $\Delta S^{\ominus}$ are the bond dissociation energy and entropy.

The activation free energy, $\Delta G^{\ddagger}$, of a concerted dissociative electron transfer is related to the reaction free energy, $\Delta G^{\ominus}$, according to the following equation:[9,44]

$$\Delta G^{\ddagger} = \frac{BDE_{R\text{-}X} + \lambda_o}{4}\left(1 + \frac{\Delta G^{\ominus}}{BDE_{R\text{-}X} + \lambda_o}\right)^2 \quad (15)$$

where λ_o is the solvent reorganization energy. The intrinsic barrier, $\Delta G_0^{\ddagger}$, is given by:

$$\Delta G_0^{\ddagger} = \frac{BDE_{R\text{-}X} + \lambda_o}{4} \quad (16)$$

This parameter provides the standard rate constant of electron transfer through the following equation:

$$k^{\circ} = Z_{el}e^{-\Delta G_0^{\ddagger}/RT} \quad (17)$$

where Z_{el} is the collision frequency at the electrode surface.

$BDE_{R\text{-}X}$ of C–Cl in benzyl chloride is 299.9 ± 4.3 kJ/mol,[61] but neither $\Delta S^{\ominus}$ nor $E^{\ominus}_{Cl^{\bullet}/Cl^-}$ in the ionic liquid is known, which precludes calculation of the exact value of $E^{\ominus}$. However, in this discussion, knowledge of the relative values of $E^{\ominus}$ is more important than determination of the single values. Analyzing the three parameters of eq. (14), $E^{\ominus}_{Cl^{\bullet}/Cl^-}$ is fixed for the series of substituted benzyl chlorides, whereas $\Delta S^{\ominus}$ of the homolytic bond rupture can be assumed to be constant. In fact, high level ab initio molecular orbital calculations on C-Cl bond dissociation of various organic chlorides has recently shown that $\Delta S^{\ominus}$ is not greatly affected by molecular structure.[62] On the other hand, both experimental and theoretical works on an extended series of substituted benzyl halides have shown that $BDE_{R\text{-}X}$ is not appreciably influenced by substituent.[63-65] Therefore, the observed variation of E_p is not due to substituent effects on $E^{\ominus}$ of $Z\text{-}C_6H_4CH_2Cl$.

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If the substituent effect on E_p does not come from $E^{\ominus}$, then perhaps it is related to the kinetics of the reaction. However, according to equations (15)-(17), k^o is not expected to show any significant dependence on substituent. $\Delta G_0^{\ddagger}$ substantially comes from BDE_{R-X}, which is expected to be constant throughout the series, together with a relatively small and constant contribution from λ_o.[10,16]

When the two fragments from concerted DET are able to give rise to ion-dipole interactions (formation of a weak adduct, $R^{\bullet}\cdots X^-$) in the solvent cage, the activation-driving force relationship is better described by the following equation, rather than by eq. (15):[11,44]

$$\Delta G^{\ddagger} = \frac{\left(\sqrt{BDE_{R-X}} - \sqrt{D_p}\right)^2 + \lambda_o}{4}\left(1 + \frac{\Delta G^{\ominus} - D_p}{\left(\sqrt{BDE_{R-X}} - \sqrt{D_p}\right)^2 + \lambda_o}\right)^2 \quad (18)$$

where D_p is the ion-dipole interaction energy. The intrinsic barrier is now given by:

$$\Delta G_0^{\ddagger} = \frac{\left(\sqrt{BDE_{R-X}} - \sqrt{D_p}\right)^2 + \lambda_o}{4} \quad (19)$$

This new model of electron transfer is known as the sticky model of dissociative electron transfer and, taking into account ion-dipole interactions, it predicts $\Delta G_0^{\ddagger}$ values that can be significantly smaller than predicted by eq. (16). The sticky model has been successfully applied to DET to many organic halides that produce in-cage ion-radical adducts.[11-13,25] In all such systems, while the kinetics were considerably faster than the predictions of eq. (15), the experimental data were found to fit eq. (18) very well.

Dissociative electron transfer to substituted benzyl chlorides can produce ion-radical adducts ($R^{\bullet}\cdots Cl^-$), with D_p increasing with the dipole moment of the $Z-C_6H_4CH_2^{\bullet}$ radical fragment. Although $E^{\ominus}$ does not vary for the investigated series of benzyl chlorides, D_p changes with the substituent and therefore different compounds have different $\Delta G_0^{\ddagger}$ and k^o values. In particular, k^o increases with increasing electron-withdrawing ability of the substituent. Increasing the σ Hammett constant of the substituent increases the polarity of the radical, resulting in a higher D_p and therefore a higher k^o. In terms of reduction potential, this will result in a positive shift of E_p. This effect is well clear on GC, which acts as an outer-sphere electron donor without any interactions with $Z-C_6H_4CH_2Cl$ as well as its reduction products, $Z-C_6H_4CH_2^{\bullet}$ and Cl^-. It appears also that Cu behaves as an inert electrode for the DET to substituted benzyl chlorides inasmuch as it does not show any catalytic effects. Additionally, just like GC, E_p on Cu shifts to more positive potentials on increasing σ.

It has been shown that D_p in the sticky model arises from electrostatic interactions between a dipole and an anion.[13] Therefore, if in a series of reactions the ion is fixed as in the case of the substituted benzyl chlorides, D_p should increase with the dipole moment, μ, of the radical or, in other words, an increase of μ of $Z-C_6H_4CH_2^{\bullet}$ must result in a positive shift of E_p. A correlation between E_p and μ in this sense, may be

considered a further support of the existence of ion-dipole adducts in the ionic liquid. Values of μ for the radicals are not available in the literature, but it is reasonable to approximate $Z-C_6H_4CH_2^{\bullet}$ to the corresponding toluene $Z-C_6H_4CH_3$. Unfortunately, values for the dipole moments of all substituted toluenes were not found. The values reported for Z = H, 3-F and 4-Cl are 0.375, 1.82 and 2.21 D, respectively.[66] Plots of E_p vs. μ for these three substrates are reported in Fig. 3. As expected, for GC and Cu, there is a good correlation between the two parameters, with E_p shifting to more positive potentials on increasing dipole moment.

In contrast to GC and Cu cathodes, which do not possess catalytic activities for the reductive cleavage of benzyl
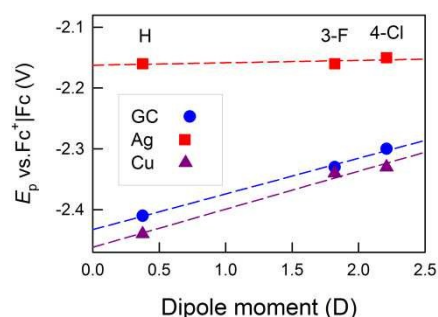
Figure 3. Dependence of E_p of 0.01 M $Z-C_6H_4CH_2Cl$, measured at υ = 0.2 V/s in [BMIm]BF$_4$, on the dipole moment of $Z-C_6H_4CH_2^{\bullet}$.

chlorides, there is no appreciable substituent effect on Ag (Fig. 2a), which instead exhibits good catalytic properties. It is important to note that even a remarkable variation of $Z-C_6H_4CH_2^{\bullet}$ dipole moment (1.84 D on changing Z from H to 4-Cl) does not produce any significant variation of E_p on Ag (Fig. 3). It appears that fragment clustering becomes negligible when the dissociative electron transfer is carried out on an Ag surface.
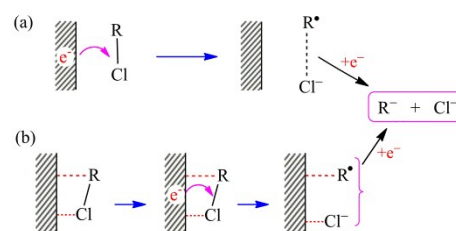
Figure 4. Schematic representation of dissociative electron transfer to $Z-C_6H_4CH_2Cl$ in [BMIm]BF$_4$ at (a) non-catalytic and (b) catalytic electrodes.

The observed contrast between electrocatalysis and substituent effects suggests the existence of distinct reaction pathways on catalytic and non-catalytic electrodes. A possible reaction mechanism highlighting this distinction is schematically represented in Fig. 4. At non-catalytic electrodes such as GC, there is no specific interaction between the electrode and the reagents and/or products, and therefore the reaction takes place at the Outer-Helmholtz Plane, which is the distance of closest approach to the electrode for non-specifically adsorbed species (Fig. 4a). Concerted dissociative electron transfer produces two fragments closed in a solvent

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cage and if the dipole moment of radical $R^{\bullet}$ is high enough, an ion-dipole adduct held together by electrostatic interactions may be formed. In this circumstance, substituents on $R^{\bullet}$ able to modulate its dipole moment will manifest tangible effects on reaction kinetics and hence on E_p. This is what happens in the reduction of $Z\text{-}C_6H_4CH_2Cl$ at GC and Cu electrodes.

The situation drastically changes on Ag because the electrocatalytic activity of this electrode material requires a direct contact of the surface with the reagent and/or the products. It is likely that both $Z\text{-}C_6H_4CH_2Cl$ and its reduction products, $Z\text{-}C_6H_4CH_2^{\bullet}$ and Cl^-, are adsorbed on Ag. Adsorption of benzyl halides, benzyl radicals and halide ions on Ag has already been reported in molecular solvents.[67-70] Figure 4b shows a simplified reaction scheme for the reduction of RCl at catalytic electrodes such as Ag, whereby adsorption of reagents, intermediates and products plays a fundamental role. In particular, adsorption of $Z\text{-}C_6H_4CH_2^{\bullet}$ and Cl^- has a deep impact on the role of fragment clustering in the reaction kinetics. According to Fig. 4b, concerted dissociative electron transfer to adsorbed $Z\text{-}C_6H_4CH_2Cl$ produces two adsorbed fragments that are only partially solvated. Although in principle the two fragments can still give rise to ion-dipole interactions, both species are already involved in more important interactions with the surface. The separate interaction of $Z\text{-}C_6H_4CH_2^{\bullet}$ and Cl^- with the metal surface strongly weakens the possible ion-dipole adduct, which is by nature very weak even in the absence of surface interactions. The complete absence of substituent effects on E_p at Ag suggests that fragment clustering does not occur at this electrode for the investigated benzyl chlorides.

The constancy of E_p of $Z\text{-}C_6H_4CH_2Cl$ on Ag does not mean that eqs. (14)-(16) can be used to analyze the kinetics of the reaction at this electrode. The detailed reaction mechanism is much more complicated than the simplified scheme in Fig. 4b.[70] The adsorption free energy, $\Delta G^{\ominus}_{ads}$, of RCl and its reduction intermediates and products has to be taken into account. The observed negligible substituent effect may be read as follows: besides negligible fragment clustering, neither $E^{\ominus}$ nor $k^{\ominus}$ is affected by the substituents investigated in this study; alternatively, both parameters change but their combined effect on E_p is constant.

Although E_p of $Z\text{-}C_6H_4CH_2Cl$ at Ag does not depend on the nature of Z, the catalytic activity of the metal is affected by the substituent (see Fig. 2b). In particular, the catalytic effect, measured as $E_{p,Ag} - E_{p,GC}$, decreases with increasing dipole moment of $Z\text{-}C_6H_4CH_2^{\bullet}$ or substituent Hammett constant. Electroreduction of $Z\text{-}C_6H_4CH_2Cl$ at Ag involves two contrasting effects: surface interactions of reagents, intermediates and products, which enhance the reaction rate, and avoided fragment clustering, which instead lowers the reaction rate. The first effect appears to be independent of the substituent, whereas the second strongly depends on μ of $Z\text{-}C_6H_4CH_2^{\bullet}$ and is, therefore, affected by the nature of Z. The overall substituent effect is a decrease of the catalytic activity of Ag with increasing electron-withdrawing ability of Z.

4. Conclusions

Dissociative electron transfer to organic chlorides in 1-butyl-3-methylimidazolium tetrafluoroborate at both inert and catalytic electrodes shows results in general agreement with the reductive cleavage of carbon-chlorine bonds in molecular solvents such as CH_3CN. Reduction of aromatic chlorides follows a stepwise mechanism, with a radical anion intermediate, $RCl^{\bullet-}$, whereas bond-breaking and electron transfer are concerted in the case of alkyl and benzyl chlorides. As in CH_3CN,[55,56] a strict link between electrocatalysis and DET mechanism exists also in $[BMIm]BF_4$: there is electrocatalysis only when the process follows a concerted mechanism. Cu shows a good catalytic activity only for the reduction of chloroacetonitrile, in contrast to its well-generalized catalytic properties observed in organic solvents.[3,56,57] Unlike Cu, whose catalytic property becomes drastically scaled down in the ionic liquid, Ag exhibits good catalytic activities for the reduction of all alkyl chlorides. In general, however, Ag is less active in $[BMIm]BF_4$ than in CH_3CN.

Analysis of DET to a series of substituted benzyl chlorides ($Z\text{-}C_6H_4CH_2Cl$, Z = H, 3-OCH$_3$, 3-F, 4-Cl, 3-CF$_3$) provides some insight into the reaction mechanism. Only Ag shows catalytic activities for this series of compounds, all of which undergo reductive cleavage by a concerted mechanism. Although $E^{\ominus}$ is constant for the whole series, E_p on GC and Cu is significantly affected by the molecular structure, shifting to more positive potentials with increasing electron-withdrawing ability of the substituent. In contrast, E_p at Ag does not change with the substituent. This discrepancy of behavior is due to the fact that the mechanism of the process is strongly dependent on the nature of the electrode material. At non-catalytic electrodes, the process evolves through the formation of a weak ion-dipole adduct, which has tremendous repercussions on reaction kinetics. The process at Ag, on the other hand, involves adsorbed reagents, intermediates and products.
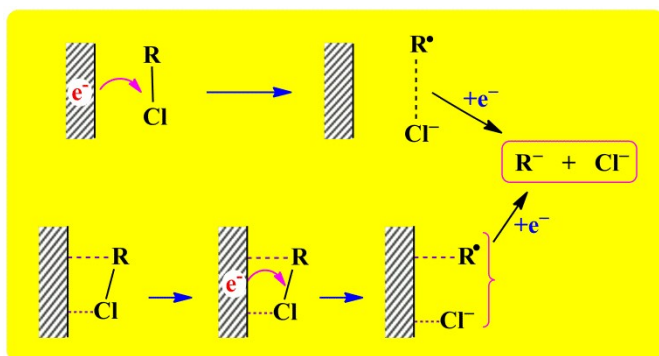
Acknowledgements

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Graphical Abstract

Silver shows good electrocatalytic activity for the reduction of organic chlorides only when the dissociative electron transfer follows a concerted mechanism.

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