One- versus two-electron reaction pathways in the electrocatalytic reduction of benzyl bromide at silver cathodes

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Abstract—The electrocatalytic reduction of benzyl bromide at a silver cathode has been investigated in acetonitrile in the absence and presence of acids, using cyclic voltammetry (CV) and controlled-potential electrolysis (CPE). CV gives rise to two reduction waves, which represent the dissociative $1e^-$ reduction of $PhCH_2Br$ to $PhCH_2^{\cdot}$ and Br^- followed by a further reduction of the benzyl radical to $PhCH_2^-$ at more negative potentials. The charge stoichiometry ($1e^-$ vs $2e^-$/molecule) and product distribution depend on the applied potential and reaction medium. In the absence of added acids, the reduction of $PhCH_2Br$ at potentials of the first wave is a $1e^-$ process mainly yielding bibenzyl, whereas toluene becomes the principal product at potentials beyond the second wave. The addition of acids strongly modifies the dependence of selectivity on the applied potential. The presence of a strong acid changes the mechanism of the process, which now becomes a $2e^-$ reduction to toluene, even at potentials corresponding to the first reduction wave.
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1. Introduction

The electrochemical activation of the C–X bond in organic halides is one of the most important reactions in organic electrochemistry.[1] The process has attracted much attention both from mechanistic and synthetic points of view. The electroreduction of RX to the corresponding hydrocarbon is also investigated as a promising method of treating halogenated wastes.[2] The mechanism of the reductive cleavage of the C–X bond is well established. It involves a pair of one-electron transfers occurring in two steps followed by various possible reactions of the ensuing carbanion, for example, protonation and nucleophilic substitution.

$$RX + e^- \rightarrow R^{\cdot} + X^- \quad E_1 \quad (1)$$
$$R^{\cdot} + e^- \rightleftarrows R^- \quad E_2 \quad (2)$$

The dissociative electron transfer (ET) (Eq. 1) may proceed via a stepwise mechanism with an intermediate formation of $RX^{\cdot-}$ or it may occur in a single step, the cleavage of the C–X bond being concerted with the ET.[3]

The voltammetric response as well as the chemistry underlying the reduction process depend on the relative values of E_1 and E_2. When $E_1 > E_2$, two successive $1e^-$ reduction waves are observed and the electrochemical process can be easily directed to radical or anionic chemistry by applying potentials corresponding to E_1 or E_2, respectively. Unfortunately, E_2 is often more positive than E_1, so that $R^{\cdot}$ is reduced as soon as it is formed. Thus, most organic halides, especially chlorides and bromides, exhibit a single $2e^-$ reduction wave in voltammetry and give products based on carbanion chemistry in preparative-scale electrolyses. A very limited number of examples of systems exhibiting two $1e^-$ reduction waves have also been reported.[4] In such cases, the distribution of the reduction products in electrolysis can be modulated by varying the applied potential.[4b–d]

The possibility of creating conditions for which the reduction of $R^{\cdot}$ occurs beyond that of RX, that is, $E_2 < E_1$, is of fundamental importance in electrosynthesis. As pointed out by Fry and Powers,[4d] the relative values of E_1 and E_2 depend on both the nature of the halogen atom and the structure of the compound. However, predicting the dependence of the values of E_1 and E_2 on the structure of RX is a difficult task. An alternative approach is to work on the choice of the cathode material. In fact, if catalytic surfaces, capable of significantly lowering the reduction overpotential for RX, are

used as cathode materials, E_1 may become more positive than E_2. It has been recently shown that silver has extraordinary electrocatalytic properties towards the reduction of organic halides in aprotic solvents.[5,6] We have recently shown that the $2e^-$ single wave observed for the reduction of benzyl bromide and benzyl iodide at an inert electrode is split into two waves at an Ag cathode.[6] In this letter, we wish to describe the results of a study on the potentialities of an Ag cathode in promoting either radical or anionic chemistry in the reduction of benzyl bromide. The process was investigated by varying both the applied potential and reaction medium. In particular, attention was focussed on the role of acids on the selectivity and charge stoichiometry of the process.
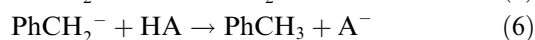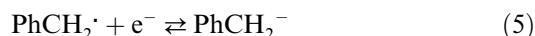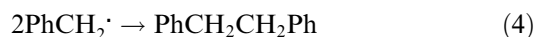
2. Results and discussion

As shown in Figure 1, the cyclic voltammetry of benzyl bromide at Ag gives rise to two irreversible reduction peaks with E_p values of -1.08 and -1.40 V versus SCE at $v = 0.2 \, \text{V s}^{-1}$.[7] The addition of proton donors such as acetic acid increases the first peak at the expense of the second one, which decreases up to disappearing, while the peak potentials are not significantly affected. Notice that the reduction of the acids at the electrode surface starts at potentials beyond the reduction peaks of $PhCH_2Br$ and, hence, does not contribute to the observed CV response. As we have shown in an earlier paper,[6] $PhCH_2Br$ is sequentially reduced to $PhCH_2^{\cdot}$ and Br^- and then to $PhCH_2^-$ at the first and second peaks, respectively. This process involves the adsorption of the starting compound as well as its reduction products, especially the bromide ion. The presence of a strong proton donor appears to modify the reaction mechanism. Now, a very sharp peak, which is typical of a process involving adsorbed species, is observed. Furthermore, the second peak due to the reduction of $PhCH_2^{\cdot}$ to $PhCH_2^-$ disappears. It is likely that, in the presence of an acid, the process becomes a $2e^-$ reduction of $PhCH_2Br$ to toluene.
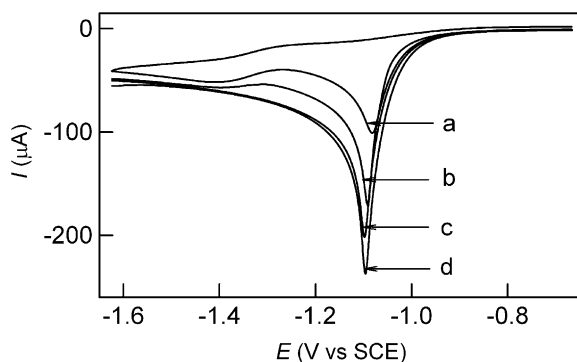
The results of the preparative-scale electrolyses of benzyl bromide in the absence and presence of proton donors are summarised in Table 1. As proton donors, we used dichloroacetic acid (DCA), acetic acid (AcOH), phenol (PhOH) and 2,2,2-trifluoroethanol (TFE). All experiments were conducted under potentiostatic conditions and were interrupted after the current decreased to ca. 5% of its initial value. In all cases, $PhCH_2Br$ conversion was greater than 95%. As can be seen, a mixture of toluene and bibenzyl, with a distribution strongly depending on both reaction medium and applied potential, E_{app}, is obtained.

The data obtained without added acid (Table 1, entries 1–3) can be rationalised according to the following reaction mechanism:

$$PhCH_2Br + e^- \rightarrow PhCH_2^{\cdot} + Br^- \quad (3)$$
$$2PhCH_2^{\cdot} \rightarrow PhCH_2CH_2Ph \quad (4)$$
$$PhCH_2^{\cdot} + e^- \rightleftarrows PhCH_2^- \quad (5)$$
$$PhCH_2^- + HA \rightarrow PhCH_3 + A^- \quad (6)$$

where the proton donor HA is the residual water or the solvent itself.[8] Reactions 3–6 may also involve adsorbed species, especially the starting halide and the products of the first ET. The process at -1.0 V involves $1e^-$ reduction of $PhCH_2Br$ to a benzyl radical, which then dimerises to give bibenzyl (Eqs. 3 and 4). The reduction potential of $PhCH_2^{\cdot}$ at a gold electrode has been reported to be -1.43 V versus SCE in acetonitrile.[9] Thus, at potentials more negative than this value, the reduction of the radical becomes fast, resulting in the formation of toluene as the principal product. It is important to stress that, even under such conditions (entry 3), only a modest yield of toluene can be obtained together with a significant quantity of bibenzyl. The latter is more likely to be formed via an S_N2 reaction between $PhCH_2^-$ and $PhCH_2Br$, rather than by radical–radical coupling. Thus, the selectivity of the process for toluene production is not very high, even at potentials as negative as -1.8 V versus SCE. Also the overall yield decreases with decreasing E_{app} and the process consumes ca. $1e^-$/molecule of $PhCH_2Br$, even at the most negative potential. This is due to side reactions consuming the starting halide, for example, the nucleophilic attack at $PhCH_2Br$ by $PhCH_2^-$ and conjugate bases $NCCH_2^-$ and OH^-, arising from the protonation step (Eq. 6).[10]

When good proton donors are added, the dependence of the product distribution on applied potential changes drastically. In the case of dichloroacetic acid, the process at -1.0 V becomes a $2e^-$ reduction of $PhCH_2Br$ to toluene. A remarkable increase of the yield of toluene at -1.0 V is also obtained with acetic acid and phenol. With these two acids, the process approaches a $2e^-$ reduction at potentials slightly more negative than -1.0 V. For instance at -1.4 V, toluene yields as high as 89% and 83% can be obtained with CH_3CO_2H and PhOH, respectively. Trifluoroethanol is less efficient than the above acids, but its effect is well evident if compared with the experiments performed in the absence of added proton donors. When Cl_2CHCO_2H

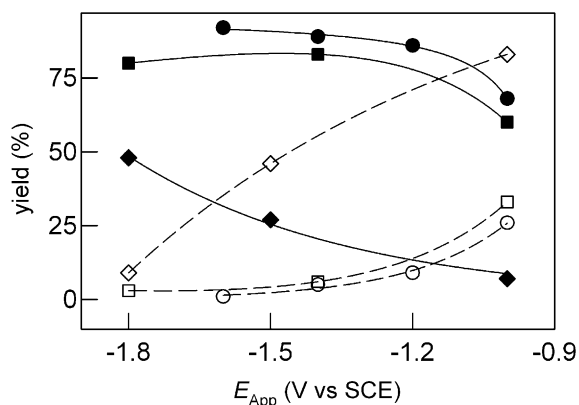**Figure 1.** Cyclic voltammetry of 3.02 mM benzyl bromide in $CH_3CN + 0.1$ M $(C_2H_5)_4NClO_4$ recorded at $v = 0.2 \, \text{V s}^{-1}$ in the absence (a) and presence of acetic acid, (b) $c_{AcOH} = 1.5$ mM, (c) $c_{AcOH} = 2.9$ mM, (d) $c_{AcOH} = 5.7$ mM.

Table 1. Electrolysis of benzyl bromide (20 mM) in CH_3CN + 0.1 M $(C_2H_5)_4NClO_4$ at a silver cathode

Entry	Acid	c_{acid} (mM)	E_{app}[a] (V)	n (F/mol)	RH[b] (%)	RR[b] (%)	Total[b] (%)
1			−1.0	1.0	7	83	90
2			−1.5	1.0	27	46	73
3[c]			−1.8	1.1	48	9	57
4	Dichloroacetic acid	40	−1.0	2.0	89	7	96
5	Acetic acid	41	−1.0	1.6	68	26	94
6	Acetic acid	41	−1.2	1.8	86	9	95
7	Acetic acid	41	−1.4	1.9	89	5	94
8	Acetic acid	41	−1.6	2.0	92	1	93
9	Phenol	40	−1.0	1.5	60	33	93
10	Phenol	40	−1.4	1.7	83	6	89
11	Phenol	40	−1.8	1.7	80	3	83
12	Trifluoroethanol	41	−1.0	1.1	15	80	95
13	Trifluoroethanol	41	−1.4	1.3	58	25	83
14	Trifluoroethanol	41	−1.8	1.4	65	4	69

[a] Applied potential versus SCE.
[b] Yield calculated with respect to converted $PhCH_2Br$.
[c] Hydrocinnamonitrile (19%) was also detected.

and CH_3CO_2H are used, the total yield is very high (ca. 95%) and does not depend on E_{app} or on the yield of toluene. Conversely, when the alcohols PhOH and F_3CCH_2OH are used as proton donors, the total yield decreases with decreasing E_{app}, that is, increasing toluene yield. This trend is similar to that observed when no acids are added and can be attributed to the nucleophilic reaction between the conjugate bases of the proton donors and benzyl bromide.
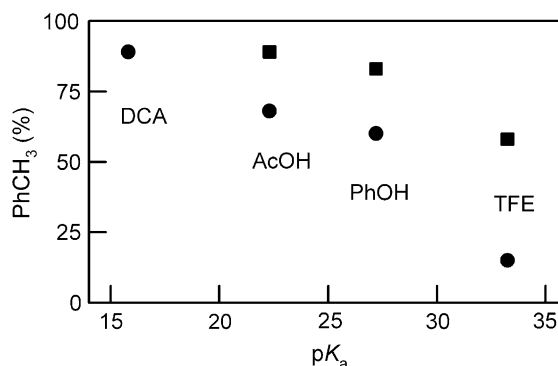
The influence of the acids on the product distribution is shown in Figure 2, which compares data obtained in the absence and presence of CH_3CO_2H and PhOH. The data obtained using F_3CCH_2OH as a proton donor show a similar trend, but were omitted for the sake of clarity. As can be clearly seen, high yields (>75%) of toluene can be obtained with both acids at $E_{app} \approx -1.1$ V, whereas very negative potentials should be applied to obtain a modest yield of toluene if no acid is added. The variation of the product distribution as a function of E_{app} depends on the nature of the acid, stronger acids favouring formation of toluene. This is better illustrated in Figure 3 in which the yields of toluene obtained at −1.0 and −1.4 V versus SCE are plotted versus pK_a of the acids in acetonitrile.[11]

The most striking result of the electrolyses with added acids is that the $2e^-$ reduction of $PhCH_2Br$ to $PhCH_3$ can be achieved at potentials that are more than 0.4 V more positive than the reduction potential of the benzyl radical. In principle, the added acids may facilitate the reduction of $PhCH_2\cdot$ by increasing the rate of protonation of $PhCH_2^-$ (Eq. 6). There are, however, at least two observations against such an interpretation. Firstly, the reduction potential of $PhCH_2\cdot$ is not affected by the addition of strong acids as evidenced by CV investigations with CH_3CO_2H. Secondly, the maximum effect of a chemical reaction following an ET (EC process) is known to be a positive shift of E_p of ca. 0.3 V.[12] Moreover, the reduction of $PhCH_2\cdot$ follows an EC mechanism with a fast chemical reaction, even without added acids.[8] Therefore, added acids would not cause significant shift of the reduction potential of the radical if their role were merely that of protonating $PhCH_2^-$ in place of H_2O or CH_3CN.

Figure 2. Distribution of electrocatalytic reduction products of benzyl bromide at Ag in the absence ((◆) RH, (◇) RR) and presence of acetic acid ((●) RH, (○) RR) or phenol ((■) RH, (□) RR). The lines were drawn to show the trends.

Figure 3. Electrocatalytic reduction of benzyl bromide at Ag in the presence of acids: dependence of toluene yield, obtained at −1.0 V (●) and −1.4 V (■), on pK_a of the acids in CH_3CN.

Table 2. Electrolysis of benzyl bromide (20 mM) in CO_2-saturated CH_3CN + 0.1 M $(C_2H_5)_4NClO_4$ at a silver cathode

| Entry	E_{app}[a] (V)	n (F/mol)	RH[b] (%)	RR[b] (%)	RCO_2H[b] (%)
1	−1.0	1.1	10	80	6
2	−1.2	1.4	15	60	20
3	−1.4	1.8	10	32	55
4	−1.5	1.8	15	21	60
5	−1.7	2.0	14	13	71

[a] Applied potential versus SCE.
[b] Yield calculated with respect to converted $PhCH_2Br$.

It appears, therefore, that in the presence of a strong acid a new reaction pathway comes into play, in competition with the reaction sequence 3–6. The formation of toluene may be achieved by an ET to $PhCH_2\cdot$ concerted with a proton transfer (Eq. 7), instead of two separate steps. Although concerted proton–electron transfers are not very common in the electrochemical literature, a few examples have recently been reported.[13] The rate of reaction 7 depends on pK_a of the acid HA. It is therefore in competition with reactions 5 and 6 and becomes important only with strong acids capable of releasing easily protons.

$$PhCH_2\cdot + e^- + HA \rightarrow PhCH_3 + A^- \qquad (7)$$
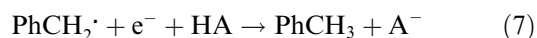
Another possible reaction pathway explaining the role of acids may be proposed in analogy with the behaviour of some organometallic complexes, which undergo hydrolysis with the heterolytic rupture of carbon–metal bonds.[14] If we assume that the dissociative ET reaction 3 involves adsorbed intermediates, an adsorbed benzyl-silver species, which is liable to protonation, would be formed. The protonation step involves a heterolytic rupture of the silver–carbon bond and an ET to the positively charged Ag site on the electrode surface. The process may be considered to occur either in a stepwise manner or in a single step. The overall hydrolysis reaction may be represented as follows:

$$(Ag{-}CH_2Ph)_{surf} + e^- + HA \rightarrow Ag_{surf} + PhCH_3 + A^- \qquad (8)$$
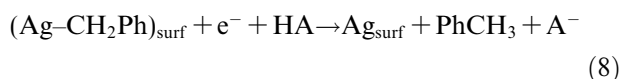
where the subscript surf stands for species bound to the electrode surface.

Although the above two reaction pathways are formally equivalent, both involving protonation accompanied by an ET, they are very different from the mechanistic viewpoint. However, it is not possible to discriminate between these two possibilities on the basis of the data so far available.

The role of a good anion scavenger such as CO_2 was also investigated. Controlled-potential electrolyses were performed in an undivided cell, using an Ag cathode and an Al sacrificial anode, and the results are reported in Table 2. Unlike the strong proton donors, CO_2 does not significantly change the reaction mechanism. The data obtained at different E_{app} values are in line with the reaction sequence 3–6 with an additional reaction between CO_2 and $PhCH_2^-$. At potentials more positive than the reduction potential of the benzyl radical, the

principal reaction pathway involves a $1e^-$ reduction with radical–radical coupling. As E_{app} becomes more negative, the charge consumption tends towards the $2e^-$/molecule of $PhCH_2Br$ with a high production of phenylacetic acid. The electrocarboxylation of organic halides is an interesting method of synthesis of carboxylic acids. In this respect, Ag is a good cathode material, even if E_{app} values more negative than the reduction potential of the radical are to be applied in order to obtain satisfactory yields of carboxylate.

In conclusion, the results obtained from the electrocatalytic reduction of benzyl bromide at an Ag cathode show that it is possible to control the selectivity of the reduction process by varying parameters such as E_{app} and composition of the reaction medium. Thanks to the remarkable electrocatalytic properties of the Ag surface, the reduction of $PhCH_2Br$ occurs at potentials well positive of the reduction potential of the benzyl radical. Thus, $1e^-$ or $2e^-$ reduction of the halide to bibenzyl or toluene, respectively, can be achieved by appropriately choosing the E_{app} value. The radical process at −1.0 V is quite selective (RH to RR yield ratio is smaller than 0.1) and results in a high yield of dimer. In contrast, neither the yield nor the selectivity of the $2e^-$ reduction process at more negative potentials is so good. However, a $2e^-$ process with a very high yield of toluene can be achieved, even at the least negative potentials, if a good proton donor such as a carboxylic acid is added. The electrocarboxylation of benzyl bromide at $E_{app} <$ −1.50 V versus SCE gives phenylacetic acid with satisfactory yields. Overall, the results reported in this paper put into evidence the importance of the catalytic role of silver surface in the electroreduction of benzyl bromide, which makes Ag a promising cathode material for dehydrohalogenation of organic halides as well as electrosynthesis processes involving such compounds.

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diately before use, by immersing in HNO_3 for a few seconds followed by washing in double-distilled water and acetone. The products of the electrolyses were analysed by using a JASCO HPLC model PU-2080, equipped with a JASCO UV detector and a 25 cm × 4.6 mm Discovery HS C18 Supelco column. The eluent was a mixture of CH_3CN and H_2O containing 5 g/L of CH_3CO_2H.

8. Since the pK_a of toluene is more than 10 orders of magnitude greater than that of CH_3CN or residual water, $PhCH_2^-$ is protonated to toluene as soon as it is formed. See: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

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