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One-pot synthesis of benzoic acid by electrocatalytic reduction of bromobenzene in the presence of $\rm CO_2$

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A R T I C L E I N F O

ABSTRACT

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The electrocatalytic properties of Ag for the reduction of organic halides have been exploited for one-pot electrosynthesis of benzoic acid. Among various investigated dipolar aprotic solvents, only dimethylformamide gives good results. The process has been investigated both under potentiostatic and galvanostatic control. In both cases, the reaction smoothly proceeds under mild conditions and lasts in a few hours, giving benzoic acid yields of the order of 80%.

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1. Introduction

Carbon dioxide is a cheap, nontoxic and abundant C₁ source, which represents an ideal C₁ building block for organic synthesis [1]. Among the possible products that may be prepared by C-fixation of CO₂, arylcarboxylic acids represent an important class of compounds in organic synthesis [2]. However, practical use of CO₂ in synthetic processes leading to C—C bond formation is quite limited by the high thermodynamic stability and low reactivity of the molecule. Therefore, methods to catalytically activate CO₂ for C—C bond forming reactions have been extensively investigated. In particular, transition-metalcatalyzed addition of carbon nucleophiles to CO₂ has recently attracted much attention as a viable method of synthesis of arylcarboxylic acids [3–6]. These reactions use organozinc reagents [3,4] or organoboronic esters [5,6], which are both prepared starting from haloarenes. Although high yields have been reported in several cases, these catalytic systems have some disadvantages. The process involves at least two distinct stages of synthesis and requires highly expensive transition metal catalysts. In addition, reactions are often very slow, requiring reaction times as long as 12-36 h.

Some progress has recently been made to eliminate the use of expensive metal catalysts. Kobayashi and Kondo [4] have shown that organozinc reagents can be carboxylated with CO_2 in a transition-metal-free process by appropriately choosing the reaction medium. A different approach has been proposed by Correa and Martín [7], who report one-pot synthesis of carboxylic acids by catalytic carboxylation of aryl bromides. They use a Pd(0) complex as a catalyst and Et₂Zn as a reducing agent.

Herein, we report the electrocatalytic carboxylation of bromobenzene studied as a model system for the development of a simple method for the one-pot synthesis of functionalized benzoic acids under mild conditions. The method fully exploits the powerful electrocatalytic properties of Ag for the reduction of carbon–halogen bonds [8,9]. Although electrocarboxylation of organic halides has been extensively applied for the synthesis of many carboxylic acids [10–14], especially substituted acetic and propanoic acids, little attention has been devoted to the electrosynthesis of aromatic acids.

2. Experimental

2.1. Chemicals

N,N-dimethylformamide (DMF) and acetonitrile were purified as previously described [14]. THF was distilled in the presence of Na/ benzophenone under argon atmosphere. All other solvents (\geq 99.5%, extra dry) were used as received. Et₄NBF₄ and *n*-Bu₄NBF₄ (Fluka, 98%) were recrystallized from an ethanol/water mixture (2:1) and dried in a vacuum oven at 70 °C.

2.2. Instrumentation and procedures

Electrochemical experiments were carried out at 25 °C in a threeelectrode cell by using a computer-controlled EG&G PARC Model 273A potentiostat/galvanostat. The working electrodes used for cyclic voltammetry were glassy carbon and silver, fabricated and activated as reported previously [8], whereas the counter-electrode and the reference electrode were a Pt wire and Ag|AgI|0.1 M *n*-Bu₄NI in DMF, respectively. The latter was always calibrated against the ferrocenium/ferrocene couple for the conversion of the potentials to the SCE scale.

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Preparative scale electrolyses were performed at an Ag plate of 3.6 cm² in an undivided cell with a sacrificial Al anode. Analyses of the products were performed on untreated electrolyzed solutions by HPLC (JASCO 2075, equipped with a UV detector ($\lambda = 256$ nm) and a 15 cm, 4.6-mm Prevail organic acid column). The eluent was a mixture of MeCN and phosphate buffer at pH = 2.5. Identification and quantitative determination of the products were based on comparison with authentic compounds and the use of calibration curves. In a few cases the target product was isolated according to the following procedure. At the end of the electrolysis, the solvent was evaporated off under reduced pressure and the residue was treated with 20 mL of 1 M HCl and then extracted with Et_2O (5×15 mL). The ether was evaporated and the residue was re-dissolved in 20 mL of 1 M NaOH and extracted with Et_2O (5×10 mL). Finally, the aqueous fractions were acidified with 6 M HCl (5 mL) and extracted with Et₂O $(5 \times 15 \text{ mL})$. The ether was again evaporated and the residue was dried under vacuum for several hours to give a pale yellow solid, which was analyzed by HPLC and NMR. ¹H-NMR (250 MHz, DMSO) (ppm): 7.46–7.53 (m, 2 H), 7.59–7.66 (m, 1 H), 7.93–7.96 (m, 2 H), 10.73 (br, 1 H). ¹³C-NMR (250 MHz, DMSO) (ppm): 128.5, 129.2, 130.7, 132.8, 167.3.

3. Results and discussion

The success of electrocarboxylation relies on the selective reduction of RX to generate R⁻, which immediately captures CO₂. Therefore, we started the study by examining the redox properties of bromobenzene and CO₂ in different solvents at Ag and GC electrodes to check whether reduction of CO₂ overlaps that of the substrate. In cyclic voltammetry each of the two compounds shows a single, irreversible cathodic peak. The peak potentials measured at $v = 0.2 \text{ V s}^{-1}$ in all solvents are collected in Table 1. These data show that Ag has extraordinary electrocatalytic properties for the reduction of bromobenzene. The peak potentials of PhBr are more than 0.6 V more positive at Ag than at GC, except in THF and DMSO. What is more important is that at Ag, E_p of PhBr is always considerably more positive than that of CO₂. The data show that selective reduction of PhBr at Ag can be carried out in the presence of CO₂ in all investigated solvents.

A series of controlled-potential electrolyses (CPEs) was performed in CO₂-saturated solvents containing 95 mM PhBr. As a rule, the applied potential (E_{app}) was chosen to be slightly more negative than E_p of PhBr and the electrolysis was interrupted after a charge consumption of 2.1 e⁻/molecule of PhBr. At the end of the electrolysis the solution was analyzed by HPLC for the quantitative determination of the products, benzene and benzoic acid, and the results are summarized in Table 2. Neither fouling of the Ag electrode during electrolysis in most solvents nor any weight loss at the end of the experiment has been observed. Both the distribution of the products and the overall conversion of PhBr are strongly affected by the nature of the solvent. In particular, the process in MeCN and DMSO gives

Table 1
Voltammetric data for the reduction of PhBr and CO ₂ in different solvents at 25 °C. ^a

Solvent	$E_{\rm p}^{\rm (GC)}$ (V)		$E_{\rm p}^{\rm (Ag)}$ (V)		$\Delta E_{\rm p}~({\rm V})^{\rm b}$
	PhBr	CO ₂	PhBr	CO ₂	
MeCN THF ^c PC DMF DMSO NMP	-2.58 -2.05 -2.32 -2.71 -2.27 -2.53	$-2.48 \\ <-2.8 \\ -2.45 \\ <-3 \\ -2.47 \\ -2.49$	-1.78 -1.80 -1.69 -1.79 -1.81 -1.63	-2.37 -2.68 -2.26 -2.35 -2.33 -2.27	0.80 0.25 0.63 0.92 0.46 0.90

^a Background electrolyte: 0.1 M Et₄NBF₄; E_p (vs SCE) measured at v = 0.2 Vs⁻¹. ^b ΔE_p is the difference between the reduction peak potentials of PhBr at Ag and GC cathodes ($\Delta E_p = E_p^{(AS)} - E_p^{(GC)}$).

^c 0.1 M Bu₄NBF₄ was used as base electrolyte.

Table 2

Electrocarboxylation of PhBr in different CO2-saturated solvents.^a

Entry	Solvent	E_{app}^{b}	$j^{\mathbf{b}}$	Conversion	PhH	PhCO ₂ H				
		(V vs SCE)	(mA/cm ²)	(%)	(%) ^c	(%) ^c				
Controlled-potential electrolysis										
1	MeCN	-1.85		93	94	6				
2	DMSO	-1.85		67	89	6				
3	PC	-1.85		75	8	18				
4 ^d	NMP	-1.85		46	64	36				
5	NMP	-2.25		84	67	31				
6 ^e	THF	-2.40		72	41	59				
7 ^f	DMF	-1.85		67	16	83 (74) ^g				
8	DMF	-1.85		80	20	79 (71) ^g				
9 ^h	DMF	-1.85		70	21	78 (68) ^g				
10	DMF	-2.00		73	17	83				
11	DMF	-2.20		70	14	85				
Galvanostatic electrolysis										
12	DMF		11	77	15	83				
13	DMF		17	70	13	86				
14	DMF		22	65	14	86				

^a Unless otherwise stated, other conditions were: 0.1 M Et₄NBF₄ background electrolyte, C_{PhBr} = 95 mM; T = 25 °C, Ag cathode, Al sacrificial anode.

^b Applied potential (E_{app}) or current density (j).

^c Yield calculated with respect to converted PhBr after a charge consumption of 2.1 e⁻/molecule.

^d Electrolysis interrupted after charge consumption of 1.18 e⁻/molecule.

e 0.25 M Bu₄NBF₄ was used as base electrolyte.

^f $C_{\text{PhBr}} = 53 \text{ mM}.$

g Isolated yield.

^h $C_{PhBr} = 210 \text{ mM}.$

almost exclusively benzene. A slightly better result is obtained in PC and NMP with an acid yield of 18% and 31–36%, respectively. When the electrolysis was performed at -1.85 V in NMP (Table 2, entry 4), good conversion could not be achieved because of passivation of the Ag electrode. This problem of passivation could be avoided by shifting E_{app} to more negative values (Table 2, entry 5).

The best results are obtained in THF and DMF. It is worth noting, however, that THF is characterized by a high resistivity, which represents a severe drawback to its use in preparative electrochemistry. In fact, the electrolysis in THF had to be carried out using a high concentration of background electrolyte and $E_{app} = -2.40$ V instead of -1.85 V to achieve a satisfactory current. The effective value of E_{app} is not precisely known, but is certainly much more positive than -2.40 V because of the contribution of the uncompensated ohmic drop. DMF, which like all other polar solvents does not present these problems, shows good results both in terms of conversion and acid yield (Table 2, entries 7–11).

Fig. 1A shows variations in the quantity (n) of PhBr and its reduction products during the course of a controlled-potential electrolysis in DMF. As the consumed charge increases, both conversion of PhBr and formation of PhH and PhCO₂H smoothly increase, so that the yield of the acid remains constant (*ca* 80%). Almost complete conversion of bromobenzene is achieved with *ca* 30% excess charge with respect to the theoretical 2 e⁻/molecule. Some control experiments performed in DMF and MeCN in the absence of CO₂ show complete conversion of PhBr into PhH with the consumption of only 2 e⁻/molecule. The excess charge consumed in the electrocarboxylation experiments is therefore to be attributed to a partial involvement of CO₂ reduction in the process. Isolation of benzoic acid after electrolysis results in a decrease of its yield from *ca* 80% to *ca* 71% (Table 2, entries 7–9).

The effects of E_{app} and C_{PhBr} on the performance of the process have been investigated in DMF. As shown in entries 7–11 of Table 2, neither of these parameters significantly affects the yield of the target acid. However, decreasing E_{app} to more negative values lowers the conversion from 80% to 70%, possibly because of a greater involvement of CO₂ reduction at very negative potentials.



Fig. 1. Electrocarboxylation of 95 mM PhBr in CO₂-saturated DMF + 0.1 M Et₄NBF₄ at Ag. Dependence of the amount of unreacted PhBr and its reduction products on consumed charge during (A) controlled-potential electrolysis at -1.85 V or (B) galvanostatic electrolysis with j = 17 mA cm⁻²: PhBr (O), PhH (\Box), PhCO₂H (Δ). (C) Variation of PhCO₂H yield (\diamond) and current efficiency (∇) with consumed charge during galvanostatic electrolysis.

The reaction is found to be sensitive to the nature of the solvent, hydrodehalogenation of PhBr to PhH being strongly favored over electrocarboxylation in most investigated solvents, especially MeCN and DMSO, whereas formation of benzoic acid is favored in DMF. A similar trend has previously been reported for the electrocarboxylation of 2-amino-5-bromopyridine [14] and, more recently, for the reaction of phenylzinc iodide with $CO_2[4]$. The role of the solvent on the electrocarboxylation process cannot be easily rationalized. For example, the observed trend does not correlate with the solubility of CO_2 , which increases in the following order: DMSO<NMP<DMF<THF<MeCN [15,16]. Perhaps several parameters including CO_2 solubility, acidity of the residual water in the solvent, H-atom donor and proton donor abilities of the solvent, etc., should be taken into consideration.

Galvanostatic electrolysis is often more simple and more preferable than the potentiostatic one, especially when large scale applications are considered. We therefore checked the efficiency of the electrosynthesis under galvanostatic conditions. Some electrolyses were performed with different current densities under otherwise the same conditions used for the potentiostatic experiments. The course of the reaction was monitored during electrolysis, which was interrupted, as usual, after a charge consumption of 2.1 e^- /molecule. The results are reported in Table 2 (entries 12–14). These electrolyses give slightly better acid yields (*ca* 85%) than the experiments performed under potential control. The overall conversion is smaller than that of the controlledpotential electrolysis and is significantly affected by the current density. Increasing the charge consumption to 2.7 e⁻/molecule slightly increases the conversion of PhBr to 79, 79 and 77% for j = 11, 17 and 22 mA cm⁻², respectively. It is important to note that neither the current density nor the amount of consumed charge affects the yield of the target acid.

An example of the trends of PhBr disappearance and product formation during a galvanostatic electrolysis is shown in Fig. 1. The figure shows also the dependence of PhCO₂H yield and current efficiency (CE) on the consumed charge. CE is defined as the ratio between the charge consumed for the production of benzoic acid and the total charge (Q_{PhCOOH}/Q_{total}). The trends are similar to those observed for the CPEs; during electrolysis formation of PhCO₂H and PhH smoothly increases with increasing PhBr conversion. As shown in Fig. 1C CE decreases as the reaction proceeds and PhBr conversion increases, while the yield remains high and constant (*ca* 85%).

4. Mechanistic considerations

Based on the known electrochemistry of aromatic bromides both at inert [17] and catalytic electrodes [9], we propose the general mechanism shown in Scheme 1 for the reduction of bromobenzene at Ag in the presence of CO₂. The initial step is adsorption of PhBr followed by dissociative electron transfer, according to either a concerted or a stepwise mechanism, leading to adsorbed products. In a previous study on the electrocatalytic activation of bromobenzenes at Ag we have shown that the process involves surface bound species and the concerted mechanism is more likely for PhBr [9].

Different reaction pathways can be distinguished in Scheme 1. Ph•ads may either leave the electrode surface and abstract a H atom from the solvent or get reduced to a carbanion. The reaction route involving dissolved Ph• is very unlikely because reduction of the radical ($E^{\Theta} = 0.05 \text{ V}$ vs SCE [18]) is much easier than that of PhBr $(E_p = -1.79 \text{ V vs SCE in DMF at } v = 0.2 \text{ V/s})$. This means Ph•_{ads} will be immediately reduced to Ph⁻_{ads}, which could be less prone to adsorption because of an unfavorable electrostatic interaction with the negatively charged electrode surface. However, very recently it has been shown that, in the case of the reduction of benzyl chloride at Ag, the interaction between the carbanion and silver is very similar to the formation of an organometallic intermediate PhCH₂-Ag⁻[19]. Thus, Ph⁻_{ads} in Scheme 1 could stand for a phenyl-silver anionic adduct that can react with electrolphiles such as CO₂ or H₂O. Two reaction channels can be envisaged for Ph-ads and Ph- after desorption, both involving nucleophilic attack on CO₂ and any proton



Scheme 1. Possible mechanism of electrocarboxylation of PhBr at Ag.

donor HA available in the reaction medium. Since CO_2 is the best electrophile present in solution, carboxylation of desorbed Ph⁻ is expected to be much faster than its protonation. Indeed, this is what is observed for the electrocarboxylation of a large number of organic halides in DMF and MeCN [10–13]. In these cases high yields of carboxylated products are obtained. The other reaction route involves Ph⁻_{ads}, which is engaged in the same competition as before. In this case, however, the nucleophilic center suffers steric hindrance from its interaction with the electrode surface and this may drastically affect the competition in favor of the protonation. We may therefore speculate that the solvent plays a crucial role in the fate of Ph⁻_{ads} in terms of both its reactivity with the electrophiles and its adsorption/desorption behavior.

5. Conclusions

In conclusion, we report an efficient method of synthesis of benzoic acid, which offers some advantages over methods based on transition-metal catalysis. Among these, short reaction time (*ca* 3 h), no need for expensive metal catalysts and/or preparation of reactive organometallic intermediates, and simplicity of the electrolysis procedure may be mentioned. Both galvanostatic and potentiosatic electrolyses in DMF give good acid yields, whereas higher PhBr conversions approaching 100% can be achieved in the case of CPE without a significant decrease of current efficiency. Further investigations are underway to understand the role of the solvent and also to define better the scope and limitations of the method, with

particular attention to the tolerance to reducible functional groups such as ketones, nitriles, halogen atoms, etc.

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