

Electrocarboxylation and related radical coupling processes of aryl and benzyl halides in microemulsion

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1 Introduction

Electrocarboxylation of aryl halides and benzyl halides in cetyltrimethylammonium bromide (CTAB) based bicontinuous microemulsion is reported. Benzyl halides exhibited higher conversion of coupling products between the benzyl radical and the phenyl acetate radical. Benzylphenylacetate is found to be the predominant product in galvanostatic electrolysis experiments.

Electrocarboxylation of aryl halides is conventionally carried out in dimethylformamide (DMF) using nickel cathode and magnesium or aluminium anodes [1, 2]. Further improvements in the electrocarboxylation processes employing redox mediators [3–5] and silver cathodes [6, 7] have been reported. Poly halogenated aromatic compounds [8], iodo aromatic compounds [9] and aliphatic halides [10, 11] also undergo facile electrocarboxylation. Al^{3+} ion generated at the anode appears to have a catalytic influence on the electrocarboxylation reactions [12]. Highly pure and moisture free DMF still remains the medium of choice for electrocarboxylation reactions [13]. Quite recently both cyclo addition of carbon dioxide to epoxides [14] and electrocarboxylation of cinnamate ester [15] were achieved in moisture free ionic liquid. In contrast to dimethylformamide and ionic liquids, bicontinuous microemulsions contain significant amount of water and are indeed much greener media for chemical and electrochemical processes [16]. Rusling et al. have reported free radical generation and coupling processes in bicontinuous microemulsion

[17–19]. Similar electro generated free radical reactions have also been reported [20, 21]. Electrochemical coupling of benzyl free radicals generated from benzyl bromide with active methylene compounds under galvanostatic experimental conditions in cationic microemulsions was reported from this laboratory [21]. The objective of this communication is to explore the possibility of another important coupling reaction, namely electrocarboxylation, involving the carbon dioxide and the electro generated aryl and benzyl free radicals in a bicontinuous microemulsion.

2 Experimental procedure

The bicontinuous microemulsion employed in the present work consisted of cetyltrimethylammonium bromide (CTAB) (17.5 wt%)/*n*-hexane (12.5 wt%)/*n*-butanol (35 wt%) and water (35 wt%). Cyclic voltammograms were recorded using nickel (5 mm dia) as working electrode, a Pt counter electrode and a SCE reference electrode at 25 ± 1 °C.

Preparative scale electrolysis was carried out in this microemulsion (50 mL) using a cylindrical nickel foam cathode (Area 33 cm²) and aluminium or magnesium dissolving anodes in an undivided cell at 25 ± 1 °C. Two grams each of benzyl bromide, benzyl chloride, chlorobenzene and *p*-chlorotoluene were reduced in independent experiments under galvanostatic conditions at a current density of 50 mA cm⁻². A charge of 2.5 F per mole was passed in each experiment. After electrolysis the electrolyte was vacuum distilled. After evaporation of solvents and low boiling products, the solid residue was repeatedly extracted with 3:7(v/v) mixtures of heptane and ethylacetate to recover the products. The liquid was vacuum distilled to obtain the product mixture which was analyzed

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Table 1 Product distribution in the galvanostatic reduction of aryl and benzyl halides in CTAB microemulsion

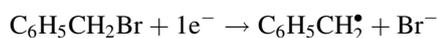
R-X	Products yield percentage			
	Weight of crude mass, g	Acid %	Ester %	Hydrocarbon %
C ₆ H ₅ CH ₂ Br	0.8123	7.15	19.02	15.13
C ₆ H ₅ CH ₂ Cl	0.9267	10.95	18.23	10.56
<i>p</i> -ClC ₆ H ₄ CH ₃	0.1502	–	4.47	–
C ₆ H ₅ Cl	0.5073	5.16	6.08	–

using HPLC, NMR and IR. The total weight of the crude product is given in Table 1.

HPLC gave three distinct peaks whose retention time coincided with phenyl acetic acid, toluene and benzylphenylacetate. The actual yields of these compounds were calculated from the crude weight of total products obtained and the percentage composition of the individual compounds obtained in HPLC analysis. Further confirmation of the products was done using FT-IR and NMR spectroscopy.

3 Results

Typical cyclic voltammogram recorded at a sweep rate of 20 mV s⁻¹ on a nickel electrode are shown in Fig. 1. The cathodic current obtained in the carbon dioxide saturated microemulsion (1b) is only slightly higher than that in the carbon dioxide free emulsion (Fig. 1a). Benzyl bromide reduction in the presence of carbon dioxide saturated microemulsion also occurs close to the background reduction potential regions. Benzyl bromide probably undergoes one electron reduction leading to the formation of a benzyl free radical [21].



Carbon dioxide apparently is not reduced in this potential region. Hence, carboxylation can proceed through the

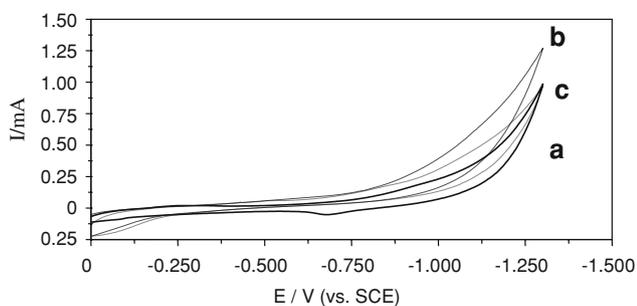
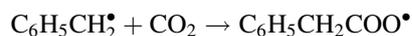


Fig. 1 **a** Cyclic voltammograms of background electrolyte (Bicontinuous microemulsion) on nickel cathode at 20 mV s⁻¹. **b** Cyclic voltammograms of background electrolyte saturated with carbon dioxide at 20 mV s⁻¹. **c** Cyclic voltammograms of background electrolyte saturated with carbon dioxide + Benzyl bromide (2 mM) at 20 mV s⁻¹

reaction of carbon dioxide with benzyl radical and subsequent one electron electro reduction.

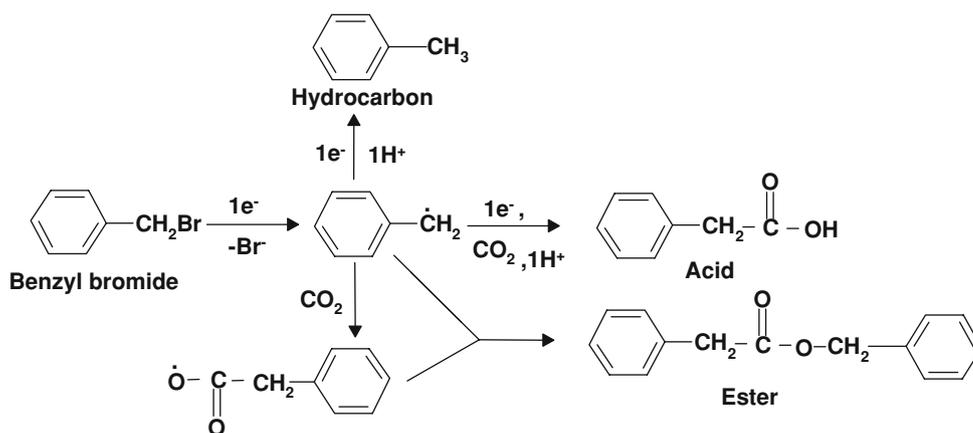


In the cyclic voltammetry time scale no increase in the reduction current in the benzyl bromide reduction region was noticed in the presence of excess carbon dioxide, indicating that the carboxylation process is slow (Fig. 1c)

During galvanostatic electrolysis using magnesium anodes, significant magnesium dissolution and inorganic salt formation were noticed in CTAB microemulsion, irrespective of the starting material employed. The cyclic voltammetry observations on nickel clearly suggest that the aryl halides, as well as the carbon dioxide do not give distinct cathodic peaks corresponding to free radical generation. This is in sharp contrast to the voltammetric behavior of benzyl bromide reported earlier in the same microemulsion on glassy carbon [21], where a distinct cathodic peak was observed around -1.5 V. Hence on nickel the reduction of aryl and benzyl halides, as well as carbon dioxide can only occur along with background hydrogen evolution with significantly low current efficiency. This was indeed found to be the case in the preparative experiments under galvanostatic conditions.

The product yield percentage reported in Table 1 corresponds to galvanostatic experiments using an aluminium anode alone. Even in this case the *p*-chlorotoluene and the chlorobenzene gave relatively low yields of the products. However, benzyl bromide and benzyl chloride gave a mixture of phenylacetic acid (noted as acid in Table 1) benzylphenylacetate (noted as ester) and toluene (noted as hydrocarbon). Interestingly benzylphenylacetate was found to be the major product, as shown in Scheme 1. This is formed by coupling of the benzyl radical and the phenyl acetate radical. The above experiments indicated that benzyl radicals show substantial stability as well as reactivity towards carbon dioxide in CTAB based bicontinuous microemulsion. The coupling between these two radicals was also found to be a faster competitive process. Earlier electrocarboxylation studies in aprotic as well as ionic liquids have shown that the formation of such esters is significantly lower (less than 10%) [6]. Thus microemulsion may provide

Scheme 1



higher selectivity towards such coupling processes; this deserves further investigation.

4 Conclusions

In this work CTAB based bicontinuous microemulsion was used for the first time to achieve electrocarboxylation of aromatic halides. The coupling product, namely ester, is formed in moderately higher yield compared to aprotic solvents and ionic liquids. The compositions and nature of other bicontinuous microemulsions for this coupling reaction to give higher product yield have to be standardized. Further work on this aspect is under progress.

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