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ORIGINAL PAPER

Electrochemical homolytic and heterolytic coupling of activated olefins in the absence and presence of benzyl bromide in microemulsion

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Abstract Electrochemical reduction of four activated olefins namely cyclohexenone (CH), cyclopentenone (CP), methylmethacrylate (MMA), acrylonitrile (AN) in the absence and presence of benzylbromide (BBr) were investigated in CTAB/*n*-hexane/*n*-butanol/water based bicontinuous microemulsion (μE). Both cyclic voltammetric studies and galvanostatic preparative electrolysis were carried out. Cyclic voltammetric results in μE were also compared with those in N,N-dimehtylformamide (DMF) medium. Adsorption effects are observed both in DMF and μE. AN undergoes one electron reduction in aprotic solvent and two electron reduction in μE. CH, CP, BBr undergo one electron reduction and yield significant homolytic coupled products under galvanostatic conditions. AN and MMA lead to two electron reduction under identical conditions. In the presence of BBr, CH and CP alone yield significant heterolytic coupled products with simultaneous competitive resin formation. Reduction of AN leads to the formation of a identifiable quantity of propylamine and 3-phenylpropylamine in the absence and in the presence of BBr, respectively.

Keywords Coupling reactions · Benzyl bromide · Activated olefins · Microemulsions · Electrochemistry

1 Introduction

Electroreductive coupling of acrylonitrile (AN) to adiponitrile is one of the major successful industrial processes. This type of coupling process has received considerable attention and has been reviewed from time to time [1–3]. Mechanistic investigations have been carried out to understand the highly selective hydrodimerisation even in the aqueous medium in the presence of surfactants [4, 5]. Cross coupling or heterolytic coupling would be of significant interest in the carbon–carbon bond formation reactions. Successful electrochemical heterolytic coupling of activated olefins in the presence of organic halogen compounds have also been achieved in N,N-dimehtylformamide (DMF) media with vitamin B_{12} as catalyst [6]. Activated olefins like cyclohexenone (CH) [7, 8] and cyclopentenone (CP) [9] have led to reasonable yields of dimeric products in DMF. However in this medium the formation of polymeric by-products invariably occurs even under potentiostatic conditions. Activated olefins like methylmethacrylate (MMA) and AN mainly lead to polymer films in DMF and acetonitrile [10]. There are considerable challenges and opportunities in the synthetic chemistry of such coupling processes in aprotic solvents.

Microemulsions (μEs) are emerging as interesting greener synthetic media for a wide variety of organic processes [11, 12]. Rusling and coworkers have investigated some interesting electro organic processes in μEs [13, 14]. Inter and intra molecular coupling between activated olefins and alkyl halides have been the main reactions studied extensively [15–17]. Debromination [18] leading to the alkene formation in μE has been reported. Electrogeneration of carbene intermediate from dibromodihalomethane and subsequent coupling with activated olefins have also been investigated [19]. Apart from carbon electrodes used in the above reactions nano TiO_2 electrodes have also been employed [20]. Redox catalysts like vitamin B_{12} are invariably employed as a mediator in μE media. To facilitate product separation, these redox centers may also be covalently bonded to the electrode surface [21–25]. All the

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above synthetic investigations by Rusling and coworkers have been carried out under potentiostatic conditions. There is only one report from this group, which employs the galvanostatic method for such synthesis, where the yield was found to be low [26]. Further confirmation of the feasibility of electro organic synthesis in μEs is yet to emerge. Recently a report on the coupling reactions from ionic liquids has been published [27].

In some recent investigations from this laboratory the systematic physicochemical and electrochemical characterization of bicontinuous μEs [28], comparative voltammetric investigations of electro organic processes in aqueous, aprotic, micellar and μE media [29] and electrochemical detoxification processes [30] have been reported. In continuation a feasibility study of homolytic and heterolytic reductive coupling reactions in μE was taken up. Electroreduction of benzyl bromide (BBr), CH, CP, MMA and AN were studied. The heterolytic coupling processes of electrogenerated benzyl radical with all other activated olefins were also investigated. The main objective of this work was to study the possibility of carrying out these processes under galvanostatic conditions without employing any homogeneous or surface bound redox mediator, since such conditions would be ideal for practically feasible scaling up and process development. Cyclic voltammetric (CV) studies were also carried out in DMF and μE to compare the medium effect and identify the reaction pathways.

2 Experimental

2.1 Reagents

The high purity chemicals cetyl trimethylammonium bromide (CTAB) (Aldrich), *n*-hexane (Merck), *n*-butanol (Merck) was used for the preparation of μE. Dimethylformamide (Merck) containing 0.1 M tetra-*n*-butylammonium iodide (TBAI) (SRL) served as the aprotic media. The other chemicals were purchased from standard manufacturers benzylbromide (Alfa-Aesar), cyclohexenone (Acros), cyclopentenone (Acros), methylmethacrylate (Merck) and acrylonitrile (Merck).

2.2 Preparation of microemulsion

Bicontinuous μE was chosen in the present investigation to ensure sufficient electrical conductivity (through continuous aqueous phase) and adequate radical stability for coupling (through continuous organic phase). The μE was prepared by mixing CTAB, n-hexane, *n*-butanol and water in the composition 17.5, 12.5, 35, 35 wt%, respectively and then stirred vigorously until a clear solution is obtained.

2.3 Voltammetric studies

The voltammetric measurements were carried out in an Autolab PGSTAT-30 potentiostat/galvanostat controlled with the GPES 4.9 software (Eco-Chemie B.V., The Netherlands). An H-type glass cell with 15 ml capacity in the working electrode compartment was used for the voltammetric studies. The working electrode was a glassy carbon disc of 5 mm diameter obtained from Tokai GC-A. The counter and the reference electrodes were a platinum foil and a saturated calomel electrode, respectively. The glassy carbon electrode was polished with 1/0–4/0 emery sheets, washed with water and trichloroethylene prior to every experiment.

2.4 Galvanostatic experiments

A single compartment cell of 12 ml volume was used for all the galvanostatic experiments. Both the cathode and anode (3.5 cm^2 each) were graphite electrodes. A constant current of 10 mA cm^{-2} was passed using a galvanostat. The charge corresponding to 2 F per mole was passed for AN and MMA, since clear indication of two electron reduction was obtained from CV experiments for these compounds. In other homolytic and heterolytic coupling reactions 1 F per mole was passed. In all cases 25% excess charge was also passed to ensure exhaustive electrolysis and enable product isolation. Constant stirring was given throughout the electrolysis. After electrolysis the reaction mixture was evaporated under vacuum and the surfactant was removed using ethylacetate/heptane in the ratio 7:3.

The product formed was characterized by High performance liquid chromatography (HPLC). An LC-10AT pump and an SPD-10A UV-detector (Shimadzu, Japan) at 254 nm with a Shim pack CLC ODS-18 column were used. A 70:30 (v/v) mixture of methanol/water was used as the mobile phase. The flow rate was 1.0 ml min^{-1}. IR spectrum was recorded as a liquid film (Perkin Elmer Paragon-500) and NMR spectrum was recorded using $CDCl_3$ as the solvent (Bruker—400 MHz).

Typically in the homolytic coupling reaction of BBr apart from the minor peak for the reactant a major peak corresponding to the product was obtained in HPLC. The coupled product bibenzyl was confirmed by IR (1,100–1,300 cm^{-1}, sharp peak due to $-CH_2Br$ absent) and NMR [7.4 (aromatic proton), 2.9 ($-CH_2-CH_2-$)]. In the heterolytic coupling of CH and BBr, the major peak corresponding to the coupled product was obtained in HPLC. The product was further confirmed by IR (1,600 cm^{-1} $-C{=}C-$ absent, reduction in the intensity of $-CH_2Br$ peak, 1,660 cm^{-1} $-C{=}O-$ present) and in NMR [7.2 (aromatic protons), 1–2 (alicyclic protons), 4.5 (proton adjacent to $-C{=}O$)]. The IR and NMR signals were also matched with standard spectrum.

3 Results and discussion

3.1 Voltammetric studies of individual compounds

Typical cyclic voltammograms of BBr in DMF and μE media are presented in Fig. 1. The peak current values after background correction vary within 10% in both the media. The cathodic peak potential in μE (−1.45 V) is more negative than in DMF (−1.25 V). This is quite contrary to the general trend of less negative potentials for a few molecules in the μE reported earlier [29] and for other organic molecules reported here Figs. 2, 3. This may be due to the presence of large concentration of Br^- ions from the surfactant (17.5 wt%) at the electrode-electrolyte interface exerting a negative influence for the production of additional bromide ions during the electro reduction of BBr.

CH and CP give two distinct reduction peaks in DMF. Typical CV along with the background current for CH in DMF is presented in Fig. 2a. CH gives two reduction peaks around −2.0 V and −2.75 V. The second cathodic reduction process occurs very close to the background reduction process. The exact quantification of this peak current thus becomes difficult. However if one assumes that the background current also increases exponentially in this peak region, we may at least qualitatively conclude that the first and the second cathodic peak currents are quite similar.

The background current due to the hydrogen evolution increases significantly at less negative potentials in μE Fig. 2ba. Hence only one cathodic peak (−1.65 V) is observed in μE. The peak current value in μE is similar to the first cathodic peak in DMF.

Typical CVs for MMA in DMF and μE media are shown in Fig. 3a. The cathodic peak currents are found to be similar in both the media. The cathodic peak potential in

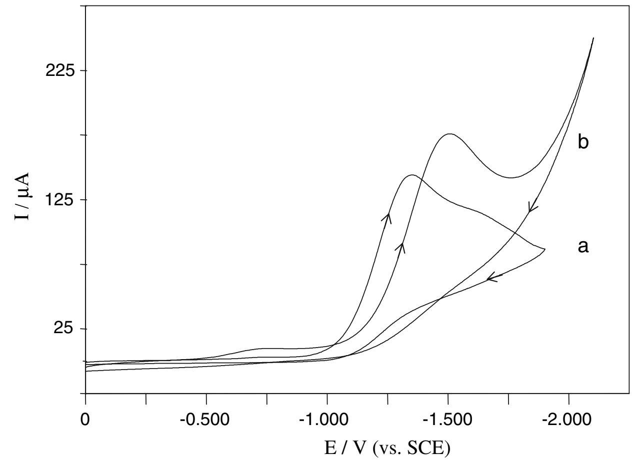


Fig. 1 Cyclic voltammograms for benzyl bromide reduction on GCE at 20 mV s^{-1}; 5.4 mM BBr in (**a**) DMF containing 0.1 M TBAI, (**b**) μE

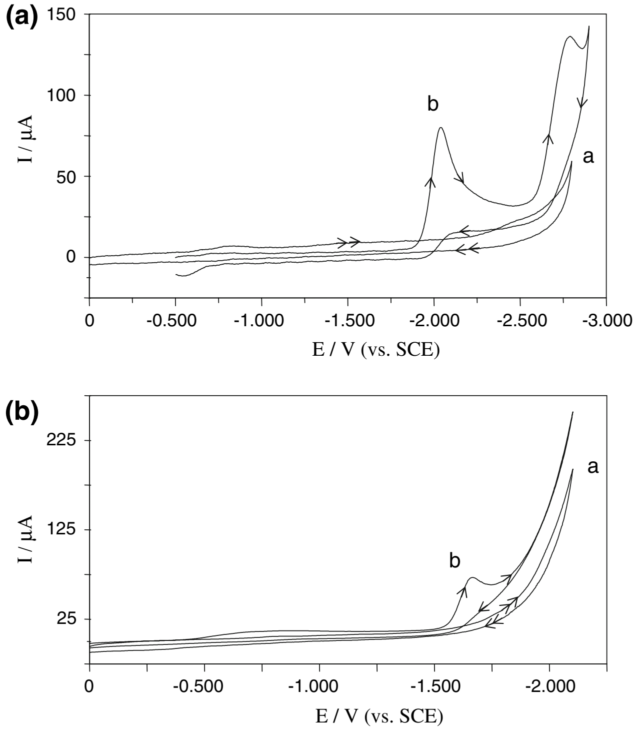


Fig. 2 Cyclic voltammograms for cyclohexenone reduction on GCE at 20 mV s^{-1}; (**a**a) Background, (**a**b) 2.7 mM CH in DMF containing 0.1 M TBAI, (**b**a) Background, (**b**b) 2.7 mM CH in μE

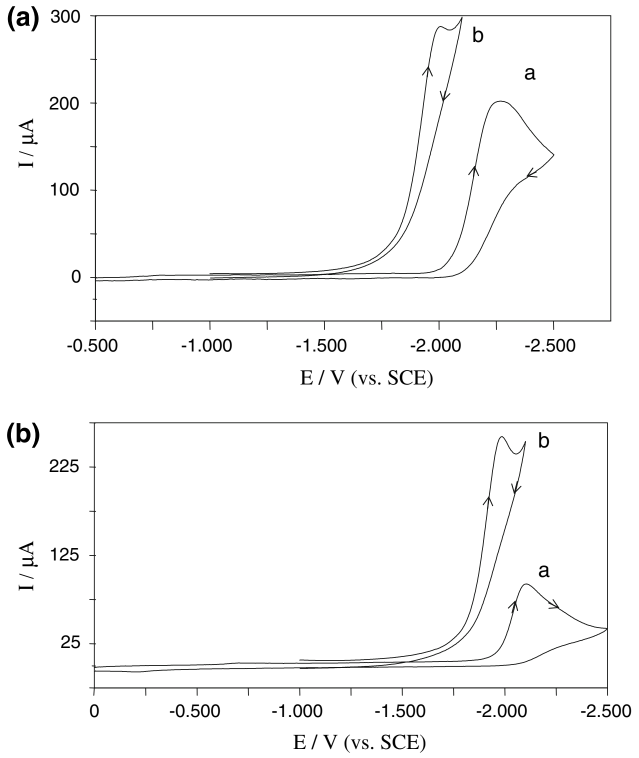


Fig. 3 Cyclic voltammograms for the reduction of (**a**) 4.17 mM MMA in (a) DMF containing 0.1 M TBAI, (b) μE; (**b**) 4.86 mM AN in (a) DMF containing 0.1 M TBAI, (b) μE at 20 mV s^{-1}

μE (−2.0 V) is found to be less negative when compared to DMF (−2.2 V).

The cathodic peak current for AN in DMF (Fig. 3ba) is found to be almost half the peak current value observed for the same compound in μE. The cathodic peak potential value is found to be lower in μE.

The first cathodic peak current value per unit concentration (Ip/C) at a constant sweep rate for all the individual compounds in DMF and μE are compared in Fig. 4a and b, respectively. For simple reductive processes without adsorption effects Ip/C value should remain constant. In the present work BBr, CH, CP in μE and BBr in DMF exhibit this behavior. The Ip/C value for CH in DMF show a slight decrease with increase in concentration, indicating weak adsorption effects especially at higher concentrations. In other cases Ip/C value decreases with increasing reactant concentration. This is a clear indication of weak adsorption of reactants on the electrode surface for AN, MMA in μE and DMF, CP in DMF.

The Ip/C values vary within a narrow range for BBr, CH, CP and AN in DMF medium. The Ip/C values for MMA at all concentrations investigated are found to be significantly higher than the Ip/C values for other compounds. It appears that in DMF, MMA undergoes two electron reductions, while all the other compounds undergo one electron reduction.

$$\text{Ar-CH}_2\text{-Br} + 1e^- \rightarrow \text{Ar-CH}_2^{\bullet} + \text{Br}^- \quad (1)$$

$$\text{Ar-CH}_2^{\bullet} + \text{Ar-CH}_2^{\bullet} \rightarrow \text{ArCH}_2\text{CH}_2\text{Ar} \quad (2)$$

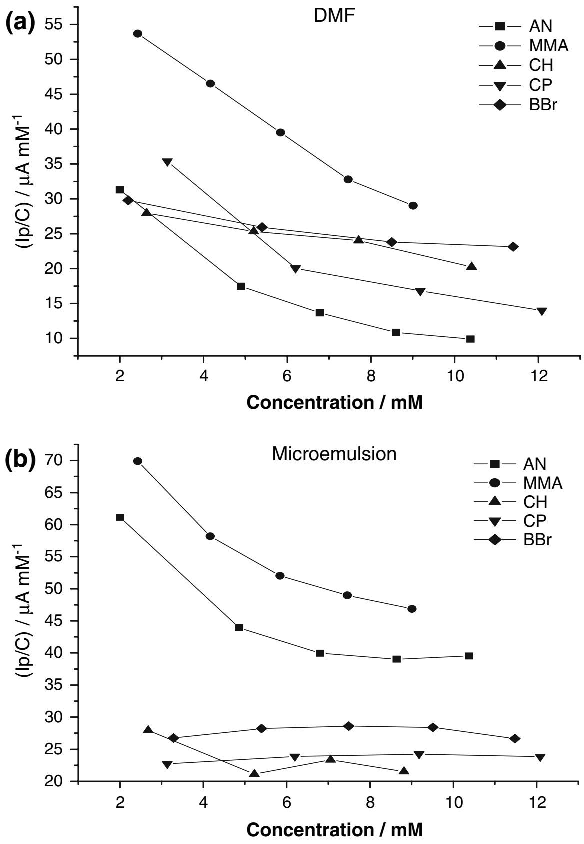
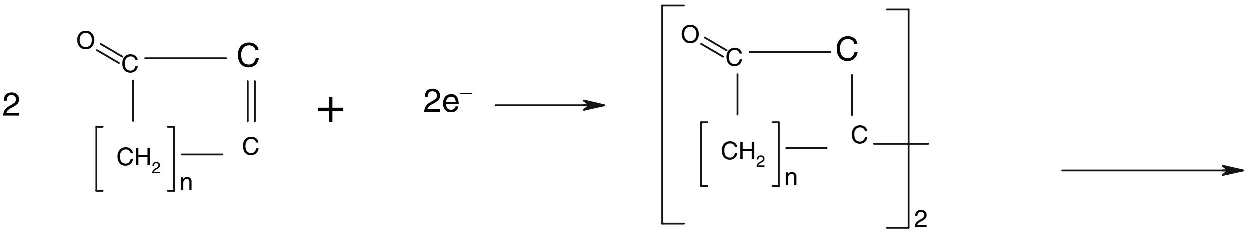


Fig. 4 Plot of Ip/C vs. C for all the compounds in (**a**) DMF containing 0.1 M TBAI, (**b**) μE at 20 mV s^{-1}



(3)

$$\text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 + 2e^- \rightarrow \text{R}_1\text{R}_2\text{CH-CHR}_3\text{R}_4 \quad (4)$$

The relative peak current values in μE media are compared in Fig. 4b. In this medium BBr, CH and CP appear to undergo one electron reduction. The Ip/C values for MMA in μE as well as DMF remain similar, indicating that this compound also undergoes a two electron reduction in μE. Relatively lower peak currents in DMF when compared to μE may be due to blocking type adsorption effects. The relative Ip/C values for An in DMF and μE once again indicate one electron reduction in DMF and two electron reduction in μE.

3.2 Voltammetric studies of activated olefins in the presence of BBr

Typical cyclic voltammograms obtained for different concentrations of AN in the presence of 2.2 mM BBr in DMF media are presented in Fig. 5. There is a slight decrease in the peak current in the peak potential region corresponding to benzylbromide reduction, probably due to blocking adsorption with increase in total concentration of organic reactant (2.2 mM BBr + AN). The peak current due to the reduction of AN continues to increase with increase in concentration. Similar trends were noticed for CH, CP and

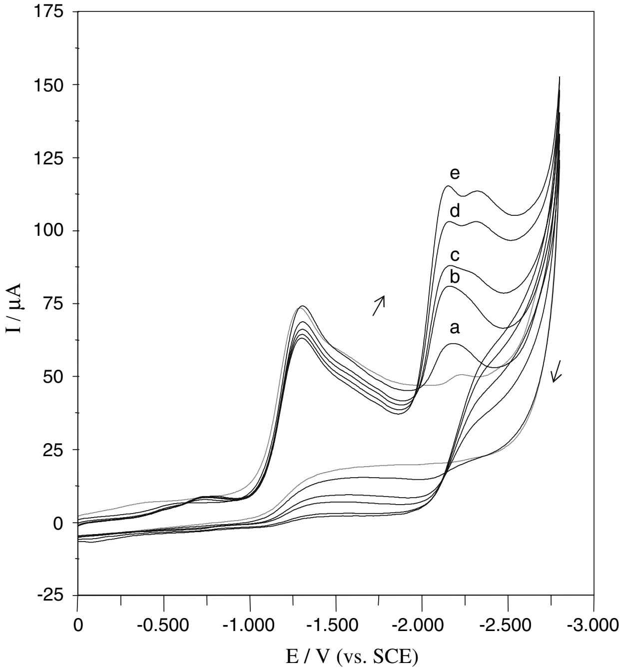


Fig. 5 Cyclic voltammograms for AN reduction on GCE at 20 mV s−^{1} in the presence of 2.2 mM BBr with varying AN Concentrations (a) 1.97 mM, (b) 4.77 mM, (c) 6.6 mM, (d) 8.38 mM, (e) 10.12 mM in DMF containing 0.1 M TBAI

MMA in DMF medium. There is also an interesting split in the cathodic peak especially at higher concentrations of AN indicating stronger adsorption effects.

The voltammetric responses were also similar in μE medium. Typical cyclic voltammograms of different concentrations of CH in the μE containing 5.4 mM BBr are shown in Fig. 6. Again there is a slight decrease in cathodic peak current in the BBr reduction region. The cathodic peak current due to CH reduction continues to increase with increasing concentration of this compound. The voltammetric responses of CP, MMA, AN were found to be quite similar.

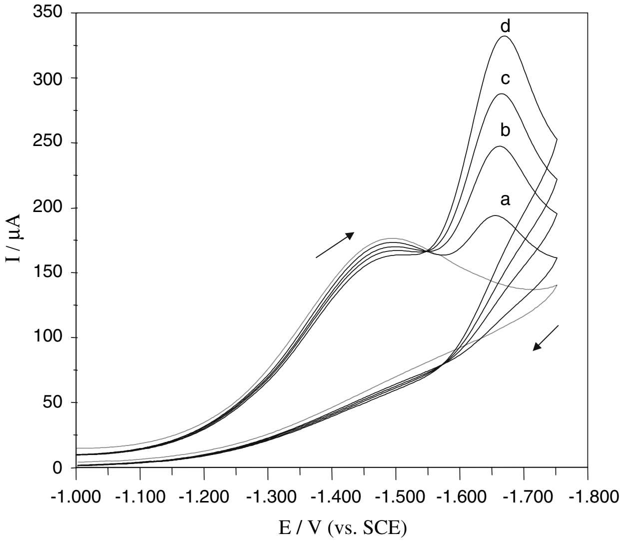


Fig. 6 Cyclic voltammograms for CH reduction on GCE at 20 mV s^{-1} in the presence of 5.4 mM BBr with varying CH concentrations (a) 2.6 mM, (b) 5.07 mM, (c) 6.85 mM, (d) 8.56 mM in μE

The general trend noticed for all the four activated olefins indicate that the electro reduction process in the BBr reduction region is not significantly influenced by the addition of activated olefins. The benzyl radical generated in this potential region however may be available for the coupling in the reduction potential regions of activated olefins. The results of coupling between these molecules can only be ascertained by constant potential or constant current electrolysis and product characterization.

The Ip/C values for all the four activated olefins in the absence and in the presence of BBr in both μE and DMF media are compared in Figs. 7 and 8, respectively. The same scale for Ip/C values is employed in both the figures to enable easier differentiation of Ip/C values for individual compounds. In this comparison one may encounter variations in Ip/C values, either due to the variation in the overall number of electrons transferred (one electron versus two electron) or due to other effects such as weak adsorption, variation in diffusion coefficient, transfer coefficient. It may be however be presumed that the variations due to the latter factors may be lower whereas the effect of the number of electrons involved would be substantially higher;

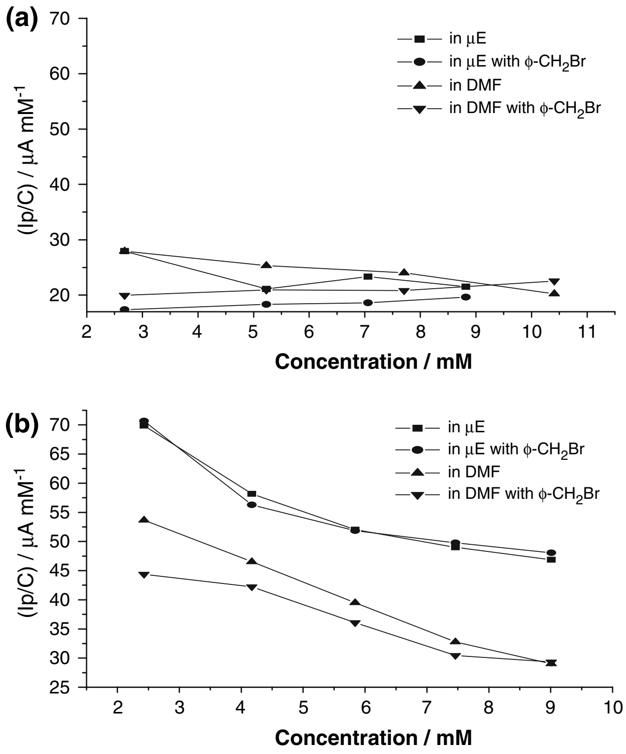


Fig. 7 Plot of Ip/C vs. C for (**a**) CH in the absence and presence of 5.4 mM BBr; (**b**) MMA in the absence and presence of 5.4 mM BBr in DMF containing 0.1 M TBAI and μE at 20 mV s^{-1}

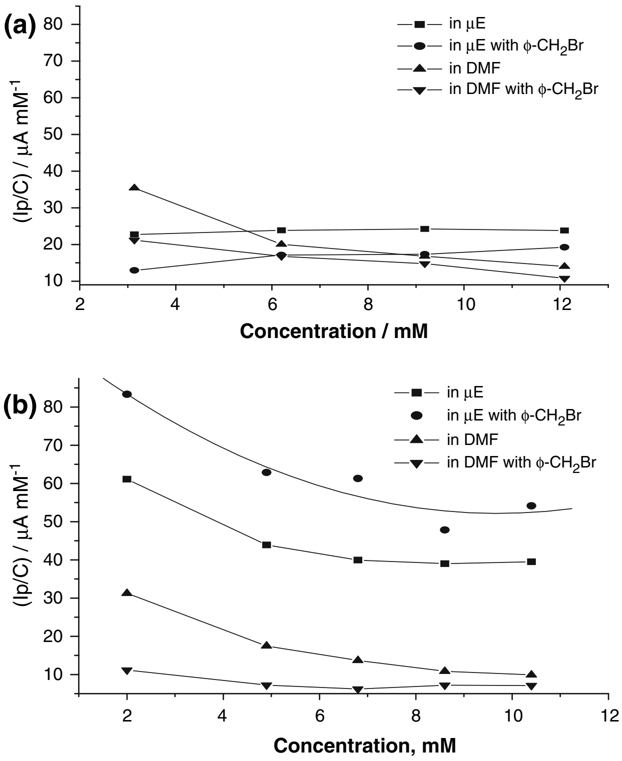
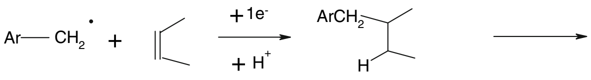


Fig. 8 Plot of Ip/C vs. C for (**a**) CP in the absence and presence of 5.4 mM BBr; (**b**) AN in the absence and presence of 5.4 mM BBr in DMF containing 0.1 M TBAI and µE at 20 mV s^{-1}

accordingly in the comparative work the Ip/C value below 30 µA mM^{-1} in the entire concentration range is considered as one electron process and the Ip/C value substantially higher than 30 µA mM^{-1}, at least in the lower concentration range, is considered to be a two electron reduction process.

As shown in Figs. 7a and 8a, the peak current values for CH and CP do not change significantly in both media, before and after addition of BBr. The relative Ip/C values also suggest that the cathodic reduction in this potential region correspond to an overall one electron reduction leading to homolytic or heterolytic coupling.



(5)

The Ip/C values for MMA in DMF are found to be significantly lower when compared to the same data in µE (Fig. 7b). In the presence of BBr the Ip/C value in DMF decreases further. Despite these differences the Ip/C value in all the four cases are found to be higher than 45 µA mM^{-1} in the lower concentration range, suggesting overall two electron reduction for this compound.

Ip/C values in AN exhibit some interesting variations as shown in Fig. 8b. In the absence of BBr the Ip/C value in µEs under identical concentration are at least twice the Ip/C values obtained in DMF, this indicates that one electron and at least two electron reductions occur in DMF and µE, respectively. On addition of BBr, Ip/C values decrease substantially in DMF suggesting significant blocking effects. In contrast, Ip/C values increase significantly in the presence of BBr in µE media suggesting partial reduction of the cyano group in addition to the double bond reduction.

$$\text{Ar-CH}_2^{\bullet} + \text{CH}_2 = \text{CH-CN} \xrightarrow[+\text{H}^+]{+1\text{e}^-} \text{Ar-[CH}_2]_3\text{-CN} \quad (6)$$

$$\text{Ar-[CH}_2]_3\text{-CN} \xrightarrow[+4\text{H}^+]{+4\text{e}^-} \text{Ar-[CH}_2]_3\text{-NH}_2 \quad (7)$$

Some of the observations regarding product distribution, blocking effects and polymerization were further confirmed by galvanostatic preparative electrolysis.

3.3 Galvanostatic preparative electrolysis

The experimental conditions employed for the reduction of BBr and all the four activated olefins in µE and the main products obtained for each reactant are summarized in Table 1. BBr gave 45.6% yield of the dimer bibenzyl. CH and CP gave dimeric products with 28% and 27% yields. As suggested by voltammetric studies it appears that MMA undergoes a two electron reduction to methyl isobutyrate in µE. AN also undergoes two electron reduction to propionitrile as indicated by CV. IR and NMR data have also indicated the formation of an identifiable quantity of propylamine under galvanostatic conditions. Since all these products are low boiling they could not be quantitatively traced out in the residual portion after vacuum concentration.

In the homolytic coupling process discussed above the yield of the product was low. However, no significant quantities of polymeric or resinous material were detected either in the bulk solution or on the electrode surface as a film. The cross coupling products obtained for all the four activated olefins under galvanostatic conditions and their yields are summarized in Table 2.

Significant polymerization and resinous material formation was observed during the electrochemical reduction of CH and CP, correspondingly the yield of heterolytically coupled products was found to be around 10% and 19% for

Table 1 Homolytic reductive coupling of the compounds in µE

Reactant	Charge passed/F	Product	Yield %
Benzyl bromide	1.25	Bibenzyl	45.6
Cyclohexenone	1.25	Dimer	28.08
Cyclopentenone	1.25	Dimer	26.98
Acylonitrile	2.5	Propylamine	–
Methylmethacrylate	2.5	Methyl isobutyrate	–

Temperature: 25 °C, Current density 10 mA cm^{-2}

CTAB µE: 17.5 wt% CTAB + 12.5 wt% *n*-hexane + 35 wt% *n*-butanol + 35 wt% water

Table 2 Heterolytic coupling of activated olefins in the presence of BBr in μE

Reactant	Ratio of activated olefin: BBr	Product	Yield %
Cyclohexenone	5:1	2-Benzyl cyclohexanone	9.85
Cyclopentenone	5:1	2-Benzyl cyclopentanone	19.07
Acrylonitrile	5:1	3-Phenylpropylamine	14.88
Methylmethacrylate	5:1	3-Phenylmethylbutyrate	<2

Temperature: 25 °C, Current density: 10 mA cm^{-2}, Charge passed: 1.25 F

CTAB μE: 17.5 wt% CTAB + 12.5 wt% *n*-hexane + 35 wt% *n*-butanol + 35 wt% water

these two compounds. The competitive two electron reduction in the case of AN and MMA lead to low boiling volatile products as discussed above. Hence no resinous material was obtained during the galvanostatic electrolysis of these compounds in the presence of BBr. The yields of heterolytic coupling products obtained in these two cases were also quite low especially in the case of MMA. It is interesting to note that in the case of AN the coupled product was 3-phenylpropylamine rather than 3-phenylpropionitrile.

4 Conclusions

The present investigation brings out some insights into the scope and limitations of electrochemical coupling processes in μEs. CV data indicate that Ip/C values generally decrease with increase in reactant concentration indicating blocking effects at higher concentrations required for electro synthesis. This is probably one of the reasons for the success of electrochemical coupling processes in μEs in the presence of redox mediators like Vitamin B_{12} [21–25].

CVs indicate that even the number of electrons transferred during electrode processes can show variation between aprotic and μE media. For example AN undergoes one electron reduction in DMF and two electron reduction in μE.

BBr (−1.45 V) and other activated olefins (−1.7 to −1.9 V) undergo electro reduction in different distinct potential regions separated by approximately 300 mV. Constant potential electrolysis can be carried out in the BBr reduction region or in the reduction region of redox mediator (for e.g. −0.75 V for Vitamin B_{12}). Under galvanostatic conditions electro reduction of BBr and activated olefin group can occur simultaneously leading to poor selectivity.

Despite the above limitations homolytic coupling process of BBr, CH and CP, which show one electron reduction peaks in CV, also leads to significant yields of coupled products under galvanostatic conditions. AN, MMA exhibit direct two electron reduction behavior both in CV and galvanostatic preparative electrolysis.

One electron reduction leading to free radical formation of the activated olefin (CH, CP) appears to be an important determining factor for achieving heterolytic coupling. Under galvanostatic conditions both benzyl radicals and reduced activated olefin radicals would be present. It appears that simultaneous formation of resinous products also occurs to a significant extent in these conditions.

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