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Electrochemical oxidation of *p*-*t*-butyltoluene to *p*-*t*-butylbenzaldehyde

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Electrochemical oxidation of *p*-*t*-butyltoluene (TBT) to *p*-*t*-butylbenzaldehyde (TBBZ) was carried out in a filterpress cell. Electrolysis was carried out galvanostatically at PbO_2 anode and Metcote ES1 cathode using sulfuric acid as electrolyte. The effect of different parameters such as acid concentration and current density was studied in order to optimize the yield of TBBZ. Electrolysis conditions were optimized for maximum current efficiency for TBBZ production. At optimum conditions at 41% conversion, a current efficiency of 73% with aldehyde to acid mole ratio of 13 was obtained.

Keywords: *p-t-butylbenzaldehyde*, *electrosynthesis*, *flow cell*, *p-t-butyltoluene oxidation*, *process optimization*, *electrochemical oxidation*

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1. Introduction

p-*t*-butylbenzaldehyde (TBBZ) is used as an intermediate for the manufacture of the perfumery compound called Lilial. Chemically it is prepared by oxidation of *p*-*t*-butyltoluene (TBT) using MnO_2 in concentrated sulfuric acid. However, use of stoichiometric quantities of MnO_2 produces large quantities of $MnSO_4$ which is not only expensive but also environmentally hazardous [1]. Electrochemical oxidation is a better alternative for such processes. Using indirect oxidation of TBT to TBBZ with the $Mn^{2+/3+}$–H_2O–H_2SO_4 system excellent yields of 96.2% have been obtained [2]. However, the principle disadvantages of indirect synthesis are large reaction volumes, poor space–time yields and problems with recycling of electrolyte [3].

TBT can be oxidized at a PbO_2 anode directly. Previous studies report the direct oxidation of TBT at a PbO_2 anode in sulfuric acid electrolyte [4] as well as in sulfuric acid–sulfonic acid electrolyte [5]. Electrochemical oxidation of TBT to TBBZ via methoxylation has also been studied at a carbon anode in acetic acid–methanol as electrolyte [6]. However, each process suffers from low selectivities, even at moderate conversion levels. Methoxylation of TBT in acetic acid–methanol at a graphite anode also produces *p*-*t*-butylbenzyl methyl ether. Further, methylal and methyl acetate are also formed [6]. Oxidation of TBT in sulfuric acid electrolyte at a PbO_2 anode produces *p*-*t*-butylbenzoic acid as a by-product. During electrolysis, in both processes tar and oligomers are also formed due to coupling of TBT and reported current efficiencies for TBBZ are of the order of 30% to 40%, which are very low to make direct oxidation of TBT to TBBZ economically attractive [3].

Previous researchers have used different approaches to maximize the process current efficiency for TBBZ. Tissot *et al.* [4] have used different anode materials out of which lead–antimony alloy was found to give maximum current efficiency. Acetates, chlorides or oxides of Cu, Co, Mn etc. have also been used to increase the efficiency for TBBZ [7]. Kato *et al.* [6] have used $NaBF_4$ to minimize energy consumption during methoxylation of TBT in a bipolar packed bed electrode cell. However, it appears that optimum conditions to obtain maximum current efficiency for TBBZ are not fully understood. Thus, a detailed investigation of the direct oxidation of TBT at PbO_2 electrode in sulfuric acid electrolyte was carried out with the view of optimizing operating conditions for maximum current efficiency for TBBZ.

2. Experimental details

The FM01-LC laboratory process package supplied by ICI Chemicals and Polymers, UK was used and details of the setup are given in earlier papers [8, 9]. All experiments were carried out with a PbO_2 on lead alloy electrode ($0.0064\,m^2$) as anode and Metcote ES1 electrode ($0.0064\,m^2$) as cathode with the interelectrode gap maintained at 6 mm. Analytical grade TBT was supplied by E. Merck, Germany, sulfuric acid, sodium bisulfite, sodium hydrogen carbonate were supplied by Loba Chemie, India.

Experiments were conducted galvanostatically. TBT was added to 600 ml, 1 M sulfuric acid used as electrolyte in a three necked flask fitted with a condenser. Because of the poor solubility of TBT in aqueous electrolyte, electrolysis was carried out using an emulsion of TBT in the electrolyte. Non-ionic surfactant (1.5 g) was added to the reaction mixture to maintain a stable emulsion. The flask was placed in an electromantle which was used for temperature

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variation. The reaction mixture from the flask was pumped into the electrolyser with a magnetically driven PTFE pump. The flow rate was monitored using a rotameter.

TBBZ was analysed by gas chromatography using dodecane as internal standard [4] and by Chemical analysis using sodium bisulfite method [10]. The aqueous phase was extracted with hexane to remove dissolved organics and was analysed for dissolved TBT, TBBZ and *p*-*t*-butylbenzoic acid (TBBA). TBBA was analysed as follows: after the reaction, the organic phase was separated. A known quantity of the organic phase was taken and extracted with sodium hydrogen carbonate to dissolve TBBA as sodium salt in the aqueous phase. The TBBA was precipitated by acidifying the aqueous phase, filtered, dried and weighed.

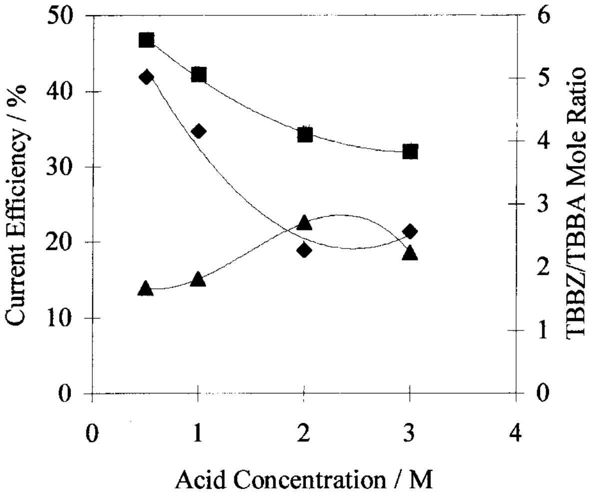

Fig. 1. Effect of acid concentration on current efficiency and mole ratio of TBBZ to TBBA. Key: (■) current efficiency for TBBZ, (▲) current efficiency for TBBA and (◆) TBBZ/TBBA mole ratio. Other parameters: current density 468 A m^{-2}; TBT 0.134 mol; temperature 60 °C; charge passed 6 A h; Reynolds number 2879.

3. Results and discussion

3.1. *Effect of acid concentration*

Previous studies by Tissot *et al.* [4] on oxidation of TBT at PbO_2 anode in sulfuric acid electrolyte indicated a drop in current efficiency for TBBZ with decreasing acid concentration. They found that, at pH 7, in the presence of Na_2SO_4, the yield of TBBZ is practically zero. According to them, the decrease in the TBBZ formation may be due to the different kind of oxide formed, since β-PbO_2, which has high oxygen overvoltage, is formed at very low pH [11]. Further, at high acid concentration, darkening of the solution due to tar and polymer formation was observed. However, in our studies, when oxidation of TBT was carried out at different acid concentrations, it was observed that current efficiency of TBBZ decreased with increasing acid concentration (decreasing pH). Also, at higher acid concentration of 2–3 M, tar formation was higher. Although sulfuric acid is a good electrolyte, at higher concentration it oxidizes or sulfonates the substrate [12]. TBBZ has three electron donating mythyl groups on the *t*-carbon atom which make it sensitive to oxidation compared to other organic aldehydes such as nitrobenzaldehyde, which has the electron withdrawing nitro group [13, 14]. Thus, decrease in the yield with increasing acid concentration may be due to the oxidation of TBBZ to TBBA. Thus, for change in acid concentration from 0.5 to 3 M, a drop in mole ratio of TBBZ/TBBA from 5 to 2 was observed. The results are shown in Fig. 1.

Sulfuric acid has a detrimental effect on aldehyde stability; hence, it was decided to add sulfuric acid periodically during electrolysis. In the experiments using varying acid concentrations, maximum current efficiency was obtained at 0.5 M (16.7 ml of 98% sulfuric acid in 583.3 ml of water) of sulfuric acid (Fig. 1). Therefore, the corresponding quantity of acid was split into two equal parts. Thus, 8.33 ml of acid in 583.3 ml of water were taken at the start of the electrolysis. After 60 min, the next 8.33 ml of acid was added to the electrolyte. It is evident from the results (Fig. 2) that, stepwise addition of acid increases the current efficiency for TBBZ from 46% to 73% and the TBBZ/TBBA molar ratio increases from 5 to 13.

3.2. *Effect of hydrodynamic conditions*

Experiments were carried out at different flow velocities to determine whether the reaction is under mass transfer control. A turbulence promoter in the form of a Teflon mesh was used in all the experiments. The variation was made in the upper possible flow range of flow rates and was relatively narrow. Lower flow rates were avoided since they could

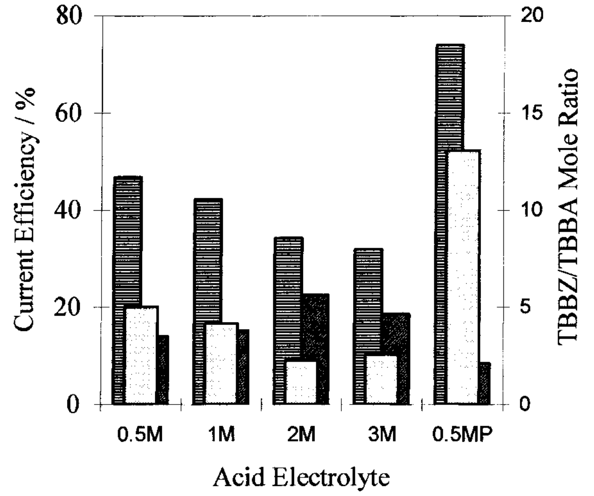

Fig. 2. Effect of periodic addition of sulfuric acid on current efficiency and molar ratio of TBBZ to TBBA. 0.5, 1, 2, 3 M represents molar acid concentration; 0.5 MP represents periodic addition of acid for total acid concentration of 0.5 molar. Key: (▤) current efficiency for TBBZ, (☐) TBBZ/TBBA mole ratio and (▨) current efficiency for TBBA. Other parameters: temperature 60 °C; current density 468 A m^{-2}; charge passed 6 A h; TBT 0.134 mol, Reynolds number 2879.

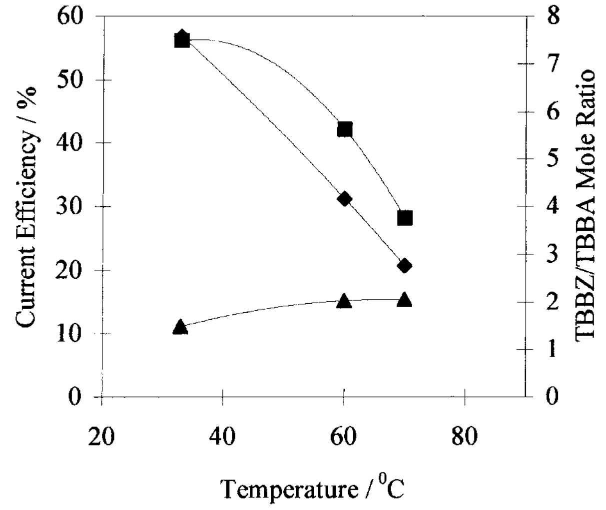

Fig. 3. Effect of temperature on current efficiency and mole ratio of TBBZ to TBBA. Key: (■) current efficiency for TBBZ, (◆) TBBZ/TBBA mole ratio and (▲) current efficiency for TBBA. Other parameters: current density 468 A m^{-2}; charge passed 6 A h; TBT 0.134 mol; sulfuric acid 1 M; Reynolds number 2879.

reduce the overall turbulence and cause de-emulsification. The results indicated a negligible effect of Reynolds number on the current efficiency for 2879 $< Re < 3187$. It is therefore evident that there is no mass transfer limitation.

3.3. *Effect of temperature*

With increase in temperature, the current efficiency for TBBZ decreased. As stated in Section 3.1, TBBZ being very prone to oxidation, may be converted to TBBA at higher temperatures. The mole ratio of TBBZ/TBBA decreased from 7 to 2 with rise in temperature from 33 to 70 °C. It was also observed that increase in temperature darkened the colour of the organic phase, and also increased formation of tarry substances. The results are shown in Fig. 3.

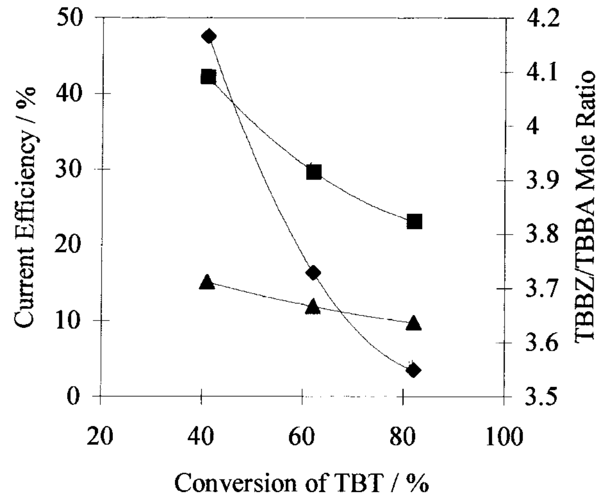

Fig. 4. Effect of conversion on current efficiency and molar ratio of TBBZ to TBBA. Key: (■) current efficiency for TBBZ, (◆) TBBZ/TBBA mole ratio and (▲) current efficiency for TBBA. Other parameters: current density 468 A m^{-2}; TBT 0.134 mol; sulfuric acid 1 M; temperature 60 °C; Reynolds number 2879.

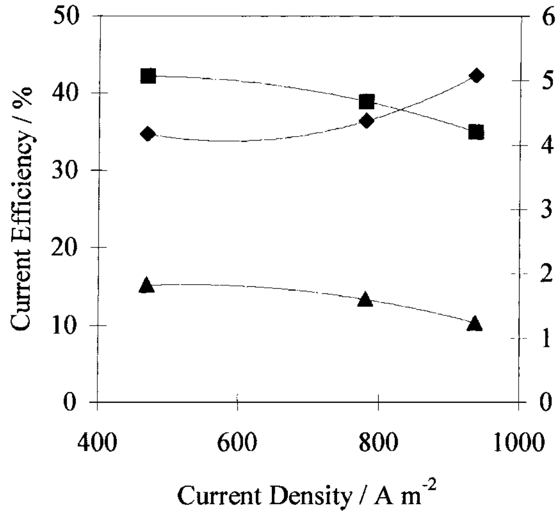

Fig. 5. Effect of current density on current efficiency and mole ratio of TBBZ to TBBA. Key: (■) current efficiency for TBBZ, (◆) TBBZ/TBBA mole ratio and (▲) current efficiency for TBBA. Other parameters: temperature 60 °C; charge passed 6 A h; TBT 0.134 mol; sulfuric acid 1 M; Reynolds number 2879.

3.4. *Effect of conversion*

Experiments carried out at increasing conversions from 41% to 82% resulted in a gradual decrease in current efficiency from 42% to 23% for TBBZ. Current efficiency for acid was also found to decrease from 13% to 9%. Thus, the current may be utilized for tar/polymer formation and oxygen evolution as conversion is increased. The results are shown in Fig. 4.

3.5. *Effect of current density*

Experiments were also carried out at different current densities for the same amount of charge passed. It was observed that current efficiency for TBBZ, as well as for TBBA, decreased with increase in current density. However, there was a slight increase in the TBBZ/TBBA ratio from 4 to 5. This may be because of the decrease in the electrolysis time, thus reducing the residence time of exposure of the aldehyde formed to the acid electrolyte and also to higher temperatures. The results are shown in Fig. 5.

4. Conclusion

A study of the effect of various operating variables on the electrochemical oxidation of TBT to TBBZ has indicated that low acid concentration in the electrolyte and lower operating temperature favour high current efficiency for TBBZ. Periodic addition of acid to the electrolyte yields a substantially higher current efficiency for TBBZ.

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