

Anodic oxidation of *p*-*t*-butyltoluene in sulphuric acid solution

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The electrochemical oxidation of *p*-*t*-butyltoluene has been investigated. From several anode materials studied, Pb-Sb alloys give the best yields of *p*-*t*-butylbenzaldehyde at 60°C in 1 M H₂SO₄.

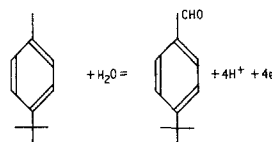
1. Introduction

The usual method of preparing *p*-*t*-butylbenzaldehyde (TBB) from *p*-*t*-butyltoluene (TBT) uses MnO₂ in concentrated sulphuric acid: the selectivity is quite high and the formation of *p*-*t*-butylbenzoic acid (TBBA) is low. The principal disadvantage of this process is the large quantity of MnSO₄ formed. We have previously studied [1] an alternative process in which the MnSO₄ is electrochemically oxidized to MnO₂ and recycled into the chemical reactor. However, we did not succeed in obtaining a good selectivity in a one-reactor process, where the chemical and the electrochemical oxidation proceed in the electrolysis cell. Several publications on this subject have appeared [2-5].

In this work we have studied the electrochemical oxidation of TBT without addition of metal salts. The oxidation of an alkyl group fixed to an aromatic ring was reported very early [6] and has recently been re-examined [7, 8]. When a Pb anode is used, the latter authors support the mechanism based on the electrochemical formation of PbO₂, followed by a chemical reaction of this with the substrate, rather than the other, purely electrochemical, mechanism which was previously proposed.

0.5 dm³ volume, equipped with a stirrer, a thermometer and a reflux condenser. The anode had an area of 14 or 100 cm² and the electrolyte consisted of 120 cm³ of 1 M H₂SO₄ with a suspension of TBT (from 4 to 50 vol%) maintained with good mechanical stirring. The reference electrode was Hg/Hg₂SO₄ and all potentials are referred to this system.

At the end of the electrolysis, the organic layer was separated or extracted with pentane, and analysed by vapour-phase chromatography (stationary phase: 0 V 101, temperature: 160-200°C), with dodecane as internal standard. The TBBA was methylated with dimethylformamide dimethylacetal in order to increase its volatility. According to the overall reaction



4 *F* are necessary to oxidize 1 M of TBT in TBB, and 6 *F* to obtain TBBA. The reproducibility of the results was not very good and all yields indicated are the mean value of more than three trials and are stated with a ±20% accuracy.

2. Experimental

The electrolytic cell consisted of a thermostatted cylindrical reactor (without diaphragm) of

3. Results and discussion

Table 1 shows the chemical yield and the selectivity of TBB and TBBA obtained with several

Table 1. Yield and selectivity of TBB and TBBA with different anodes. Electrolyte: 1 M H_2SO_4 at 60° C with Pt cathode; anodic current density: 4 A dm^{-2} ; quantity of electricity: 4 F mol^{-1}

Anode	Chemical yield		Selectivity	
	%TBB	%TBBA	%TBB	%TBBA
Pb-5%Sb	35	7	74	15
Pb-20%Sb	38	10	72	19
Pb	15	11	48	35
Pb-5%Ag	8	13	30	50
PbO ₂ (on Ti or C)	12	4	57	19
MnO ₂ (on Pb)	8	7	40	35
Pt	7	3	47	20
C	7	6	39	33
Au	2	—	29	—
TiO ₂ -RuO ₂ (on Ti)	2	—	29	—
Ta ₂ O ₅ -IrO ₂ (on Ti)	2	—	29	—

anodes under the same experimental conditions. Generally the total quantity of TBT, TBB and TBBA recovered was of the order of 95% of the TBT introduced. It appears from Table 1 that the selectivity for TBB formation is highest at the Pb-Sb alloy anodes.

The high oxygen overvoltage on PbO₂ [9, 10] cannot alone explain the good yields obtained with the Pb-Sb alloys, which are better than those obtained with pure lead. As a matter of fact, Sb lowers the oxygen overvoltage [9]. It seems that antimony plays an important role during the oxidation of the alkyl group, perhaps in giving stronger oxidizing properties to the PbO₂ [9-13]. As a result, for further studies we used the Pb-5% Sb anode, which gives the best yield and selectivity of TBB.

3.1. Cathodic material and addition of metallic salts

At the beginning we used a Pb cathode. Although this material is stable when used as the cathode in 1 M H_2SO_4 at 60° C, it became corroded in the presence of TBT. Lead sulphate is formed and the yield of TBB is about one-third of that obtained with a Pt cathode. The yield of TBBA is not reduced.

Stainless steel was also tried as a cathodic material but yields of TBB and TBBA were very low (5 and 2% respectively under the same conditions as indicated in Table 1). These results are attributed to the presence of metallic cations in the electrolyte due to the corrosion of the steel; as a matter of fact, we have found, by atomic absorption analysis, 34 mg dm^{-3} of Ni²⁺, 53 mg dm^{-3} of Cr³⁺ and 263 mg dm^{-3} of Fe³⁺ in the electrolyte after 4 h of electrolysis. It is known [9, 14] that cations such as Co²⁺, Ag⁺, Fe³⁺ and Ni²⁺ lower the oxygen overvoltage and also the oxidizing power of PbO₂. We obtained a low yield, too, in the presence of salts generally used as O₂ carriers [4, 5, 15-17], e.g. CoSO₄, Ce(SO₄)₂, MnSO₄ and Cr₂O₃.

In Table 2 we list the results obtained during the main trials.

3.2. Concentration of H_2SO_4 (runs 1, 2 and 4)

The decrease of the yield at low sulphuric acid concentration is probably due to the different kind of oxide formed. Indeed, β -PbO₂, which has a high oxygen overvoltage, is formed especially at very low pH [9, 18]. At pH 7, in the presence of

Table 2. Yields of TBB and TBBA. Cathode material: Pt; anode material: Pb-5%Sb

Run	H_2SO_4 concentrations (M)	T (° C)	Current density (A dm^{-2})	F mol^{-1}	Chemical yield (%)			Faradaic yield (%)
					TBB	TBBA	TBT	
1	0.1	60	4	4	5	3	5	
2	5	60	4	4	14	4	14	
3	1	25	4	4	11	6	11	
4	1	60	4	4	35	7	35	
5	1	80	4	4	40	20	40	
6	1	60	2	4	32	24	32	
7	1	60	8	4	38	12	38	
8	1	60	4	2	11	5	22	
9	1	60	4	6	38	10	25	
10	1	60	4	8	43	31	21.5	

Na_2SO_4 , the yield of TBB is practically zero. In a 5 M H_2SO_4 solution, the yields are also not very high; moreover, we observe a darkening of the solution due to tar and polymer formation.

3.3. Temperature (runs 3, 4 and 5)

A temperature of 60°C is the most favourable with respect to the selectivity of TBB. At 25°C the yield of TBB diminishes and, at 80°C, the quantity of TBBA rises; at this temperature, the quantity of tar is also higher.

3.4. Anodic current density (runs 4, 6 and 7)

Generally [19] an increase in current density favours oxygen evolution to the detriment of the other oxidations. Here we observe a slight increase of the yield of TBB with the current density between 2 and 8 A dm^{-2} .

3.5. Duration of the electrolysis (runs 4, 8, 9 and 10)

The chemical yields of TBB and TBBA increase with the duration of the electrolysis. However, the optimum ratio with respect to the Faradaic yield of TBB, is 4 $F \text{ mol}^{-1}$.

4. Conclusions

During the electrolysis performed at constant current density, the anodic potential remains between 1.25 and 1.35 V (versus Hg/HgSO_4). These potentials correspond to the evolution of O_2 (Fig. 1). This figure shows the potentiostatic curves obtained with Pb-5%Sb with and without TBT. The anode was polarized at 0.9 V for 2 min before each curve. After the formation of the PbO_2 layer, the current decreases before the evolution of O_2 . When TBT is added, the current is slightly greater.

We carried out an oxidation at 1.2 V (same conditions as run 4, Table 2, except for the current density) and obtained a chemical yield of 30 and 26% for TBB and TBBA respectively. The mean current density was 1.5 A dm^{-2} . The direct transfer of an electron to the TBT can be excluded, the anodic potential being much too low for such a mechanism. The intermediate formation of oxide

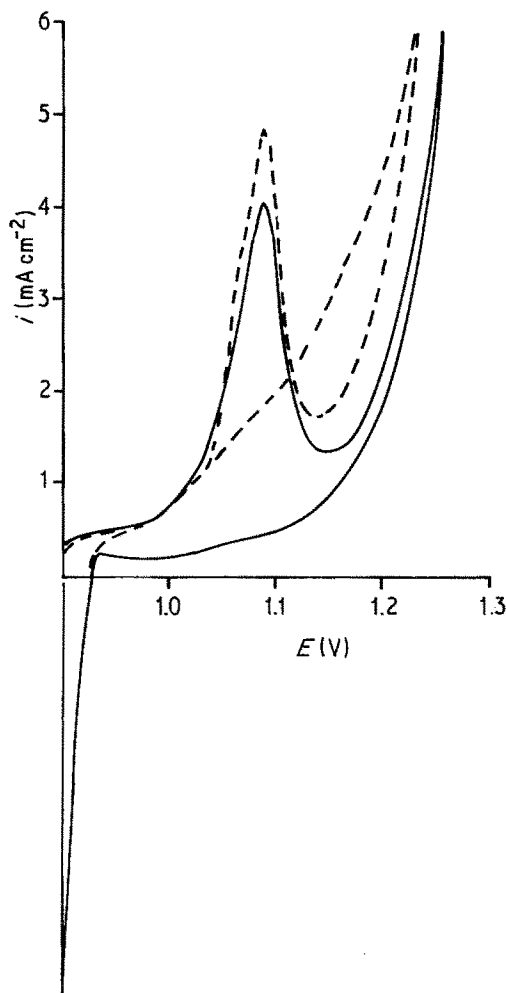


Fig. 1. Potentiostatic curves on Pb-5%Sb. —, 1 M H_2SO_4 ; ----, 1 M H_2SO_4 + TBT. Scan rate: 0.1 mV s^{-1} under stirring; temperature: 60°C.

or adsorbed species like O or OH at the electrode surface has been postulated [20, 21] to explain the oxidation of alkyl groups in aqueous media. Our results are in good agreement with this type of mechanism, more especially as the chemical oxidation of TBT by PbO_2 gives TBB and TBBA. However, this chemical oxidation proceeds with very low yield in 1 M H_2SO_4 (3% of TBB in 24 h at 25°C). The role of Sb is quite difficult to understand. One can, in fact, see in Fig. 2 that Pb and Pb-Sb give very similar polarization curves. Contrarily, Pb-Ag shows a lower oxygen evolution potential which can explain the low yields obtained with this material.

The problem of the formation of TBBA, which

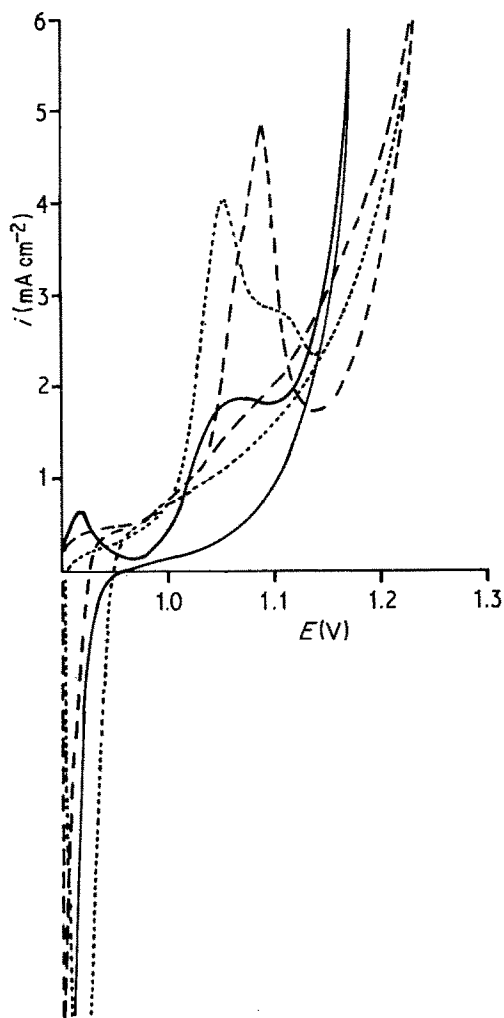


Fig. 2. Potentiostatic curves on different anodes. —, Pb-5%Ag; ----, Pb-5%Sb, Pb. Electrolyte: 1M H₂SO₄ + 20 vol% TBT; scan rate: 0.1 mV s⁻¹; temperature: 60°C.

lowers the selectivity of the TBB, is now under study and a 50 A bipolar cell is under construction.

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