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Anodic oxidation of *p*-methoxytoluene in acetic acid on graphite

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The direct oxidation of *p*-methoxytoluene in acetic acid medium was studied on a graphite anode for the preparation of *p*-anisaldehyde and *p*-anisyl acetate. The effect of the water contents of the solvent on the reaction selectivity was determined for solvent mixtures containing from 0 to 20 vol % water. In anhydrous medium *p*-anisyl acetate was the main product. When the water contents increased the yield of *p*-anisaldehyde increased. It was shown that the higher the proportion of water, the lower the *p*-methoxytoluene oxidation rate. The formation of products of consecutive oxidation steps decreased as the temperature increased from 60 to 90 °C.

Keywords: *anodic oxidation*, *direct oxidation*, *graphite anode*, *p-methoxytoluene*, *p-anisyl acetate*, *p-anisaldehyde*

1. Introduction

In general, the electrooxidation of alkylated aromatics is carried out in media which not only serve as solvents but also act as nucleophiles [1]. The anodic oxidation of *p*-phenoxytoluene on platinum in acetic acid [2] or of *p*-methoxytoluene on graphite in methanol [3] mainly gives the corresponding aldehydes or their acetals. Phenolic compounds, in which the hydroxyl group is protected, can be oxidized in methanol to obtain *p*-hydroxybenzaldehyde derivatives [4]. Wendt *et al.* studied the direct anodic oxidation of diverse toluenes in methanol and ethanol on a graphite anode [5, 6]. They reported that the oxidation of toluenes to acetal dimethyl benzaldehydes gives yields of 70 to 75% for the *p*-methoxytoluene and the *p*-chlorotoluene and only 30% for the toluene [6]. For the oxidation of toluene, they explained the low yield in acetal dimethyl benzaldehyde by a drop in the yield due to polymerization reactions at the anode. Kim *et al.* [7] also noticed the formation of oligomers during the oxidation of *p*-*tert*-butyltoluene on platinum anodes in acetic acid-methanol medium (90–10% by volume); they obtained the acetal dimethyl *p*-*tert*-butylbenzaldehyde with a yield of 84%.

The *p*-methoxytoluene is relatively easy to oxidize due to the electron donor effect of the methoxy group. Its oxidation has given rise to numerous electrochemical studies [1, 8–11]. Recently, it has been shown that the oxidation of *p*-methoxytoluene by molecular oxygen catalyzed by cobalt acetate in acetic acid can be enhanced by electrochemistry [12, 13]. The object of the present work was to study the direct anodic oxidation of *p*-methoxytoluene on graphite in acetic acid medium and to examine the competition between the formation of the main oxidation products: *p*-anisaldehyde as product of the 4e side chain oxidation and *p*-anisyl acetate as the product of 2e oxidation.

2. Materials and method

The *p*-methoxytoluene as well as the acetic acid, the acetic anhydride, and the sodium acetate were supplied by Aldrich and were used without further purification. The experiments on the oxidation of *p*-methoxytoluene were performed in a 150 cm^3 thermostatted Metrohm cell, a double walled cylindrical glass reactor.

The current–potential curves were plotted using the three electrode method. The working electrode was a 2 mm diameter platinum disc ($S = 3.14 \times 10^{-2}$ cm^2), the counter electrode was a large surface area platinum net. The reference was a saturated aqueous calomel electrode (SCE). The current–potential curves were plotted at a rotation rate of the platinum disc of 1000 rpm. The electrodes used for oxidation of the *p*-methoxytoluene at large scale were graphite rods: the area of the anode was 21 cm^2 and the area of the cathode was 8 cm^2. Electrolyses were performed in an individed cell in galvanostatic mode ($i_{\text{anode}} =$ 40 mA cm^{-2}).

The variations of the concentration of the *p*-methoxytoluene and of its oxidation products during the electrooxidation reaction with time were followed by HPLC (Hewlett Packard model 1050) on a C18 ODS column (length: 10 cm, internal diameter: 4.6 mm) with UV–visible detection at variable wavelength. The eluent was a mixture of phosphate buffer and of methanol circulating at a flow rate of 1 cm^3 min^{-1}. The aqueous solution of phosphate buffer was made of sodium hydroxide ($C_{\text{NaOH}} = 0.03$ mol dm^{-3}) and potassium dihydrogenophosphate ($C_{\text{KH}_2\text{PO}_4} =$ 0.05 mol dm^{-3}. The separation was achieved by per-

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forming a methanol gradient from 10% to 77% by volume in 16 min. The products were identified by coupling the retention time measurement and the recording of the absorption spectrum of each species, at a given wave length, using a diode array detector.

3. Results

Figure 1 shows that oxidation of the *p*-methoxytoluene at 0.01 mol dm^{-3} on a graphite anode begins at approximately 1.2 V in acetic acid–water mixtures (90–10% by volume). The voltammogram shows a plateau at around 2 V vs SCE. Direct electrooxidation of the *p*-methoxytoluene on a graphite anode in the water-acetic acid mixtures yields mainly *p*-anisyl acetate, *p*-anisyl alcohol, *p*-anisaldehyde and *p*-anisic acid as reaction products. As an example Fig. 2 shows the results of a preparative electrolysis conducted at 90 °C in a solution formed by a mixture of acetic acid and water (90–10% by volume respectively) containing sodium acetate as supporting electrolyte and *p*-methoxytoluene at an initial concentration of 0.2 mol dm^{-3}.

3.1. *Influence of the solvent composition*

The influence of the solvent composition on the chemical yield in *p*-anisaldehyde and in *p*-anisyl acetate was studied in mixtures of which the acetic acid composition varied from 80 to 100% by volume. When the solvent consists of glacial acetic acid and of acetic anhydride (96–4% by volume), the conversion of *p*-methoxytoluene is 84% for a charge of 4 F mol^{-1} of initial reactant at 70 °C (Fig. 3, curve a). The maximum yield in *p*-anisyl acetate then reaches 60% (Fig. 4, curve a) and the yield of *p*-anisaldehyde is 5% (Fig. 5, curve a) for a charge of 4 F mol^{-1}. At 6 F mol^{-1} (step of acid) the oxidation is not total: with depleted *p*-methoxytoluene concentration, the mass transfer rate is no longer sufficient. The electrolysis being carried out galvanostatically, oxygen evolution takes place on the anode. The conversion of *p*-methoxytoluene is 100% for a charge of 8 F mol^{-1} at 70 °C (Fig. 3, curve a). For the mixtures 99.8–0.2% acetic acid-water by volume and 95–5% acetic acid–water by volume, the rate of consumption of the *p*-methoxytoluene is identical with that in a solvent of 100% acetic acid (Fig. 3, curve b); on the other hand, the yield of *p*-anisyl acetate for a charge of 4 F mol^{-1} is much lower (36%) while that of *p*-anisaldehyde was higher (20%) (Figs 4 and 5, curves b).

At 60 °C, when the proportion of water increases from 5% to 20% by volume the yield of *p*-anisyl acetate decreases from 36% to 20% (Fig. 4, curves c and d) while the yield of *p*-anisaldehyde increases from 15% to 30% for a charge of 4 F mol^{-1} (Fig. 5, curves c and d).

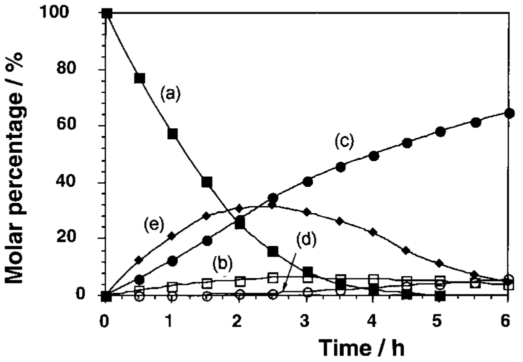


Fig. 2. Variation of the molar percentage of *p*-methoxytoluene and of the yield of different products as functions of time. 150 cm^3 of acetic acid-water solution (90–10% by vol.) containing sodium acetate at 1.0 mol dm^{-3}. Initial concentration of *p*-methoxytoluene 0.20 mol dm^{-3}. $T = 90$ °C. Electrolysis under galvanostatic condition: $I = 0.90$ A; graphite electrodes: anode 21 cm^2, cathode 8 cm^2, without separator. Curves: (a) *p*-methoxytoluene, (b) *p*-anisyl alcohol, (c) *p*-anisaldehyde, (d) *p*-anisic acid, (e) *p*-anisyl acetate.

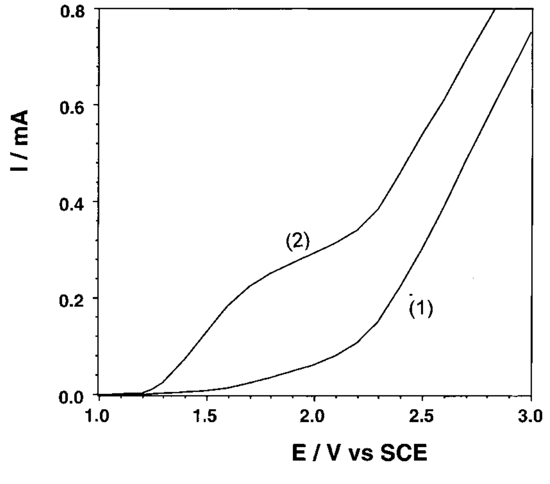


Fig. 1. Voltammogram of *p*-methoxytoluene on a platinum rotating electrode ($\Omega = 1000$ rpm, $S = 3.14 \times 10^{-2}$/cm^2). Key: (1) residual for acetic acid-water (90–10% by vol.) + sodium acetate (0.5 mol dm^{-3}). (2) residual + *p*-methoxytoluene (0.01 mol dm^{-3}).

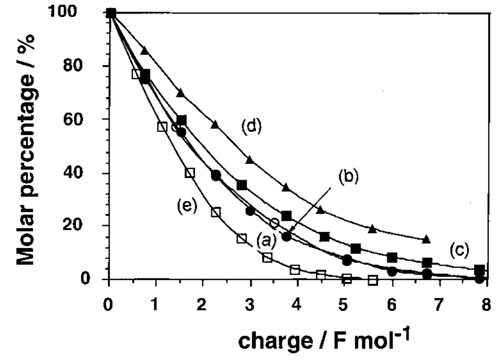


Fig. 3. Variation of *p*-methoxytoluene molar percentage as a function of charge during its oxidation. Solution: 150 cm^3 containing 1.0 mol dm^{-3} sodium acetate. $I = 0.90$ A; graphite electrodes: anode 21 cm^2, cathode 8 cm^2, without separator. Curves: (a) acetic acid–acetic anhydride (96–4% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, $T = 70$ °C; (b) acetic acid–water from 99.8–0.2% by vol. to 95–5% by vol., *p*-methoxytoluene 0.1 mol dm^{-3}, $T = 70$ °C; (c) acetic acid–water (95–5% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, $T = 60$ °C; (d) acetic acid–water (80–20% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, $T = 60$ °C; (e) acetic acid–water (90–10% by vol.), *p*-methoxytoluene 0.2 mol dm^{-3}, $T = 90$ °C.

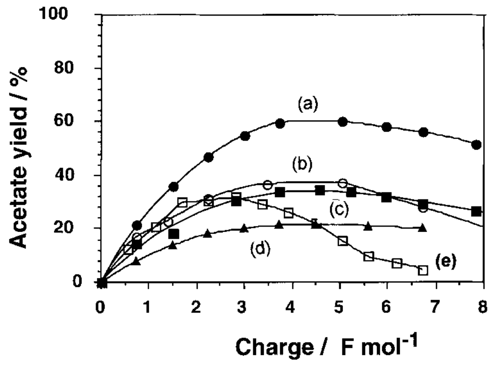


Fig. 4. Variation of *p*-anisyl acetate yield as a function of charge during oxidation of *p*-methoxytoluene. Solution: 150 cm^3 containing 1.0 mol dm^{-3} sodium acetate. I = 0.90 A; graphite electrodes: anode 21 cm^2, cathode 8 cm^2, without separator. Curves: (a) acetic acid–acetic anhydride (96–4% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (b) acetic acid–water (99.8–0.2% by vol.)-(95–5% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (c) acetic acid–water (95–5% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 60 °C; (d) acetic acid–water (80–20% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 60 °C; (e) acetic acid-water (90–10% by vol.), *p*-methoxytoluene 0.2 mol dm^{-3}, T = 90 °C.

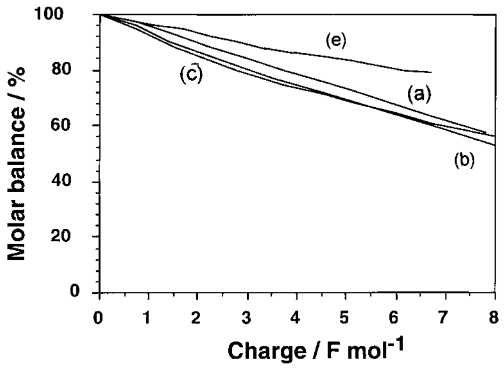


Fig. 6. Variation of molar balance as a function of charge during oxidation of *p*-methoxytoluene. Solution: 150 cm^3 containing 1.0 mol dm^{-3} sodium acetate. I = 0.90 A; graphite electrodes: anode 21 cm^2, cathode 8 cm^2, without separator. Curves: (a) acetic acid–acetic anhydride (96–4% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (b) acetic acid–water (99.8–0.2% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (c) acetic acid–water (95–5% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 60 °C; (d) acetic acid–water (90–10% by vol.), *p*-methoxytoluene 0.2 mol dm^{-3}, T = 90 °C.

3.2. *Temperature effect*

A material deficit was observed during the electrolysis (Fig. 6). This loss represent about 40% of the initial *p*-methoxytoluene for a charge of 8 F mol^{-1} in pure acetic acid and mixtures of acetic acid and water for experiments made at temperatures of 60–70 °C (Fig. 6, curves a, b and c). This is mainly due to the formation of secondary products, some of which (probably oligomers and polymers [5, 6, 13, 14]) were detected but not identified by HPLC. The temperature increase reduces the formation of secondary products: for the mixtures acetic acid–water (95–5% by volume) at 60 °C and acetic acid-acetic anhydride at 70 °C, the mass balance (calculated from the remaining *p*-methoxytoluene, the *p*-anisyl alcohol, the *p*-anisaldehyde, the *p*-anisic acid, and the *p*-anisyl acetate) is only 70% for a charge of 6 F mol^{-1}, while for a temperature of 90 °C for an acetic acid–water mixture (90–10% by volume) it is 84% (Fig. 6, curve e).

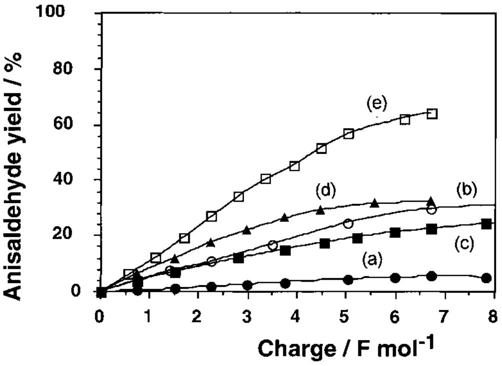


Fig. 5. Variation of *p*-anisaldehyde yield as a function of charge during oxidation of *p*-methoxytoluene. Solution: 150 cm^3 containing 1.0 mol dm^{-3} sodium acetate. I = 0.90 A; graphite electrodes: anode 21 cm^2, cathode 8 cm^2, without separator. Curves: (a) acetic acid–acetic anhydride (96–4% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (b) acetic acid–water from 99.8–0.2 to 95–5% by vol., *p*-methoxytoluene 0.1 mol dm^{-3}, T = 70 °C; (c) acetic acid–water (95–5% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 60 °C; (d) acetic acid–water (80–20% by vol.), *p*-methoxytoluene 0.1 mol dm^{-3}, T = 60 °C; (e) acetic acid–water (90–10% by vol.), *p*-methoxytoluene 0.2 mol dm^{-3}, T = 90 °C.

The electrooxidation of *p*-methoxytoluene in solution in the acetic acid–water mixture (90–10% in volume) at 90 °C shows that the *p*-anisaldehyde yield reaches 65% for a charge of 7 F mol^{-1} at 90 °C (Fig. 2, curve c and Fig. 5, curve e). For this last experiment the faradaic yield goes from 95% at the beginning to 50% at the time the charge reaches 7 F mol^{-1}. The decrease in the faradaic yield during the electrolysis in galvanostatic mode can be explained by the fact that the oxidation products of the *p*-methoxytoluene are more difficult to oxidize at the anode and that the concentration of *p*-methoxytoluene decreases during the electrolysis, a part of the current is thus being used to oxidize the solvent water.

4. Discussion

It can be seen that the higher the proportion of water, the lower the rate of oxidation of the *p*-methoxytoluene (Fig. 3, curves c and d). The addition of water to the acetic acid increases the relative yield of *p*-anisaldehyde to the detriment of the *p*-anisyl acetate, but it also markedly decreases the rate of *p*-methoxytoluene conversion.

A mechanism which involves the formation of a radical can be envisaged. This radical was detected by electronic paramagnetic resonance for the oxidation of toluene [15]. The oxidation of this radical leads to the formation of the benzylic carbocation:

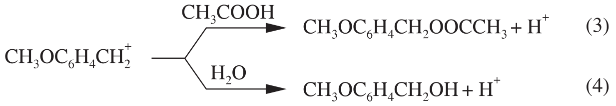
$$CH_3OC_6H_4CH_3 \rightarrow CH_3OC_6H_4CH_2^{\circ} + H^+ + e^- \quad (1)$$

$$CH_3OC_6H_4CH_2^{\circ} \rightarrow CH_3OC_6H_4CH_2^+ + e^- \quad (2)$$

Figure 2 shows that for a solvent containing 10% by volume of water the aldehyde is formed to the detriment of the anisyl acetate for a charge beyond

3 F mol^{-1}. This corresponds to the direct electrooxidation of the acetate. Let us notice that, in acetonitrile, the oxidation potential of benzyl acetate (1.9 V vs Ag^{+}/Ag) is near that of the benzyl alcohol (2.0 V) [16].

In the presence of acetic acid, the formation of the carbocation could lead to the formation of *p*-anisyl acetate (Reaction 3). In the presence of water, the *p*-anisyl alcohol is obtained at the first stage (Reaction 4) which would be oxidized to *p*-anisaldehyde (Reaction 5) and eventually to *p*-anisic acid (Reaction 6).



$$CH_3OC_6H_4CH_2^{+} \xrightarrow{CH_3COOH} CH_3OC_6H_4CH_2OOCCH_3 + H^{+} \quad (3)$$

$$CH_3OC_6H_4CH_2^{+} \xrightarrow{H_2O} CH_3OC_6H_4CH_2OH + H^{+} \quad (4)$$

$$CH_3OC_6H_4CH_2OH \rightarrow CH_3OC_6H_4CHO + 2\,H^{+} + 2\,e^{-} \quad (5)$$

$$CH_3OC_6H_4CHO + H_2O \rightarrow CH_3OC_6H_4COOH + 2\,H^{+} + 2\,e^{-} \quad (6)$$

One of the secondary products observed could be the *m* or *o*-acetoxy-*p*-methoxytoluene which would be obtained by the oxidation of the isomer forms of *p*-methoxybenzyl radical ($CH_3OC_6H_3^{+}CH_3$) in the acetic acid medium [17]. The *m* or *o*-acetoxy-*p*-methoxytoluene would seem to be a relatively stable product.

5. Conclusion

The composition of the medium and temperature parameters have an important effect on the products of the oxidation of the *p*-methoxytoluene:

(i) when the reaction occurs in anhydrous acetic acid, the *p*-anisyl acetate is the primary product; its yield can reach 60%;
(ii) when the proportion of water increases, the conversion into *p*-anisaldehyde increases but the speed of its formation decreases;
(iii) at 60 °C the electrolysis of the *p*-methoxytoluene leads to the formation of secondary products and/or of polymers; and
(iv) for higher temperatures (90 °C), the formation of secondary products or of polymers is less important and the *p*-anisaldehyde is thus obtained with yield reaching 70%.

Acknowledgements

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