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Autoxidation of methoxytoluene in acetic acid; electrochemical assistance of the catalytic effect of cobalt

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Abstract

Liquid phase autoxidation of *p*-methoxytoluene to *p*-anisaldehyde in water–acetic acid medium (10–90% vol.) using cobalt acetate as a catalyst has been investigated under or not electrolysis between two graphite electrodes. The rate of formation of anisaldehyde is strongly increased under electrolysis condition: the maximum anisaldehyde yield occurs at $t = 70$ min whereas this maximum is reached only after $t = 5$ h 30 min without electrolysis.

1. Introduction

The direct oxidation of alkylated aromatic hydrocarbons by air or oxygen is the source of many products of commercial interest. The oxidation processes can be carried out in the liquid or gas phase. Oxidation in the liquid phase has the advantage of providing better yields and greater selectivity due to the mild conditions afforded by the use of salts of transition metals as catalysts.

Studies of the oxidation of alkylaromatics in the liquid phase by cobalt or manganese salts have shown that the reaction initiation period is reduced by the action of a cocatalyst such as sodium bromide or methyl ethyl ketone [1]. The mechanisms of oxidation in liquid acetic acid of an alkylaromatic into aldehyde in the presence of redox mediators such as Co^{III}/Co^{II} or Mn^{III}/Mn^{II} are represented in Fig. 1 in the absence and in the presence of oxygen respectively [2].

— In the absence of oxygen and in the presence of Co^{III} the oxidation of these alkylaromatics leads to the formation of acetates as the main products. This reaction stops when all the cobalt(III) has been consumed. Co^{III} must be prepared before its use either by a chemical method [3] or electrochemically [4].

— In the presence of oxygen, the autoxidation reaction occurs; the cobalt(III), although present initially, is not entirely consumed. There are two possible initial reaction pathways according to the conditions.

(i) If, to begin with, there is only oxygen and cobalt at oxidation state II, a period of latency of the order of some hours is generally observed; the addition of a promoter such as NaBr allows the reaction to start sooner (Mid Century Process [5]). Mechanism 3 shows that, in this case, the alkylaromatic is first of all attacked by the $Br^{\cdot}$ radical formed by the action of O_2 on Br^-.

The resulting benzyl radical reacts rapidly with the oxygen to lead to the benzyl peroxide radical

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$$\text{Ar-CH}_3 + \text{Co}^{\text{III}} \rightleftharpoons [\text{Ar-CH}_3]^{+\circ} + \text{Co}^{\text{II}} \tag{1}$$

$$[\text{Ar-CH}_3]^{+\circ} \rightarrow \text{Ar-CH}_2^{\circ} + \text{H}^+ \tag{2}$$

mechanism 1 : without O_2

$$\text{Ar-CH}_2^{\circ} + \text{Co}^{\text{III}} \rightarrow \text{Ar-CH}_2^{+} + \text{Co}^{\text{II}} \tag{3}$$

$$\text{Ar-CH}_2^{+} + \text{CH}_3\text{COOH} \rightarrow \text{Ar-CH}_2\text{-OOCCH}_3 + \text{H}^+ \tag{4}$$

mechanism 2 : with O_2

$$\text{Ar-CH}_2^{\circ} + \text{O}_2 \rightarrow \text{Ar-CH}_2\text{O}_2^{\circ} \tag{5}$$

$$\text{Ar-CH}_2\text{O}_2^{\circ} + \text{Co}^{\text{II}} \rightarrow \text{Ar-CH}_2\text{O}_2\text{Co}^{\text{III}} \tag{6}$$

$$\text{Ar-CH}_2\text{O}_2\text{Co}^{\text{III}} \rightarrow \text{Ar-CHO} + \text{HOCo}^{\text{III}} \tag{7}$$

$$\text{HOCo}^{\text{III}} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCo}^{\text{III}} + \text{H}_2\text{O} \tag{8}$$

$$2\ \text{Ar-CH}_2\text{O}_2^{\circ} \rightarrow \text{Ar-CHO} + \text{O}_2 + \text{ArCH}_2\text{OH} \tag{9}$$

mechanism 3 : with promoter

$$\text{NaBr} + \text{CH}_3\text{COOH} \rightleftharpoons \text{HBr} + \text{CH}_3\text{COONa} \tag{10}$$

$$\text{HBr} + \text{O}_2 \rightarrow \text{Br}^{\circ} + \text{HO}_2^{\circ} \tag{11}$$

$$\text{Ar-CH}_3 + \text{Br}^{\circ} \rightarrow \text{Ar-CH}_2^{\circ} + \text{HBr} \tag{12}$$

$$\text{Ar-CH}_2^{\circ} + \text{O}_2 \rightarrow \text{Ar-CH}_2\text{O}_2^{\circ} \tag{13}$$

$$\text{Ar-CH}_2\text{O}_2^{\circ} + \text{Co}^{\text{II}} \rightarrow \text{Ar-CHO} + \text{OHCo}^{\text{III}} \tag{14}$$

$$\text{Co}^{\text{III}} + \text{HBr} \rightarrow \text{Co}^{\text{II}} + \text{Br}^{\circ} + \text{H}^+ \tag{15}$$

Fig. 1. Oxidation mechanism.

which regenerates Co^{III} by action with the Co^{II}. The Co^{III} pursues the catalytic cycle by then reacting with HBr to regenerate $Br^{\cdot}$ and form Co^{II}. Unfortunately bromides are formidable corrosion agents requiring the use of special coatings on the internal walls of industrial reactors.

(ii) If there is only Co^{III} and oxygen, the alkylaromatic is first of all attacked by Co^{III}. The benzyl radical formed then reacts as above and the Co^{III} is regenerated for a further cycle of reactions leading to aldehyde (mechanism 2).

The study performed in our laboratory concerns oxidation by molecular oxygen of toluenes in solution in mixtures of acetic acid and water in the presence of the Co^{III}/Co^{II} redox couple. According to reactions (1), (2) and mechanism 2, it can be seen that the oxidation reaction will be all the faster, the greater the concentration of Co^{III}. The goal of our work was to increase the proportion of Co^{III} with a view to eliminating the use of a catalyzer promoter such as sodium bromide, on the one hand, and to modify the Co^{III}/Co^{II} ratio with a view to controlling better the overall kinetics of the autoxidation process, on the other hand. Bearing this in mind, an electrolysis device was inserted in the autoxidation reactor with a view to oxidizing the cobalt to state (III) on the anode.

2. Materials and method

The reagents used, *p*-methoxytoluene, cobalt(II) acetate, glacial acetic acid and sodium acetate, were supplied by Aldrich. The isothermal cylindrical reactor (Metrohm cell) had a capacity of 150 ml, and the solvent used was a mixture of water and acetic acid (10–90 vol.-%). The oxygen was bubbled into the liquid phase by means of a PTFE tube at a flow rate of 100 ml min^{-1} (240 mmol h^{-1}). This high oxygen flow rate compared to the maximum of the oxygen consumption rate (about 6 mmol h^{-1}) was chosen for improving the oxygen transfer rate into the liquid phase. Increasing the oxygen flow increases the mass transfer coefficient and the liquid–gas interfacial area. This reactor had two reflux devices placed in series on top of it: the first was thermostatted to 0°C and the second to − 30°C in order to limit the loss of methoxytoluene.

Electrolysis of the cobalt(II) acetate into cobalt(III) acetate during the chemical reaction was performed under galvanostatic conditions in this reactor with two graphite electrodes with a surface area of 21 cm^2 and 12 cm^2 for the anode and cathode, respectively. The area of the anode was chosen greater than that of the cathode in view to form more Co^{III} by oxidation than Co^{II} by the reverse reaction

The Faradaic yield R_f is defined as the ratio between the charge required to form the various products obtained by electrolysis: Q_{th} (calculated with Faraday's law) and the amount of effective charge supplied to the system: Q_{exp} ($Q_{exp} = It$).

Samples of the solution were taken and analyzed quantitatively with respect to time by HPLC (Hewlett-Packard 1050 series). The remaining reagent and the products formed were separated and assayed on an ODS C18 column (length: 10 cm; internal diameter: 4.6 mm); the eluent was a mixture of phosphate buffer (pH = 7) and methanol circulating at a rate of 1 cm^3 min^{-1}. The separation was accomplished by creating a methanol gradient from 10 to 77% in volume in 16 min. The cobalt(III) acetate was analyzed quantitatively with respect to time by UV/visible spectrophotometry at $\lambda = 610$ nm, a wavelength at which only the cobalt(III) absorbs.

3. Results

3.1. Chemical oxidation of methoxytoluene

3.1.1. Without promoter

Bubbling oxygen through a solution of methoxytoluene and cobalt(II) acetate in a mixture of acetic acid and water (90–10%) does not cause any reaction in the absence of a promoter and without electrolysis. This corresponds to the latency period generally observed for this reaction [5]. A nearly linear decrease in the methoxytoluene concentration is observed over time (curve a, Fig. 2). This is due to the loss of methoxytoluene by stripping under the oxygen flow. This evaporation was limited to approximately 10% of the initial amount of methoxytoluene after 5 h bubbling at 100 ml min^{-1}.

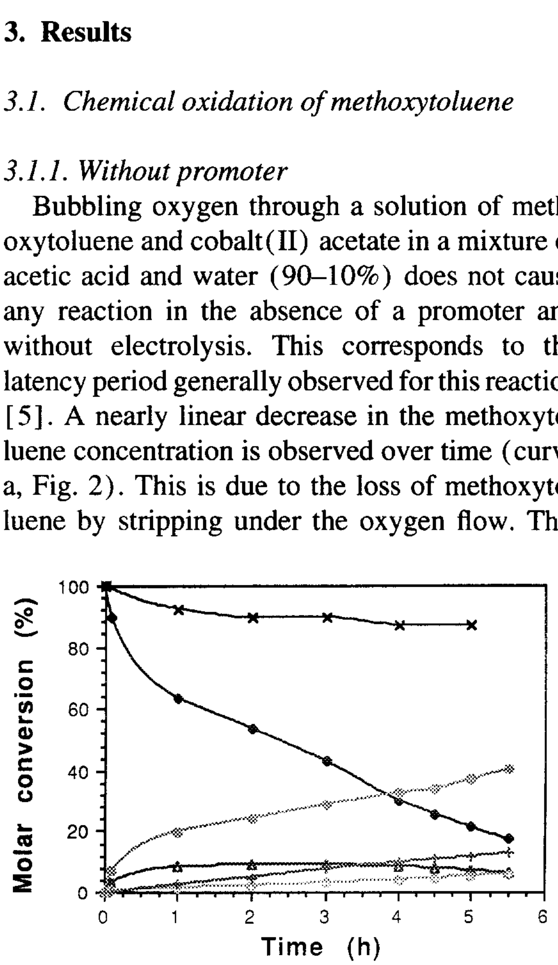

Fig. 2. Autoxidation of *p*-methoxytoluene. Solution: 150 ml of water–acetic acid (10–90% vol.) containing sodium acetate (0.5 mol l^{-1}) and methoxytoluene (0.10 mol l^{-1}). $T = 90°C$. Oxygen flow rate: 100 ml min^{-1}. $Co^{II} = 0.10$ mol l^{-1}; $Co^{II} = 0.064$ mol l^{-1} + Co(III) = 0.036 mol l^{-1}. (a) ×, *p*-Methoxytoluene; (b) ◆, *p*-methoxytoluene; △, anise alcohol; ●, *p*-anisaldehyde; ○, anisic acid; +, *p*-anisyl acetate.

3.1.2. With cobalt(III) acetate

In the presence of cobalt(III) acetate, the oxidation of methoxytoluene was immediate (Fig. 2; curves b). The main products obtained were 4-methoxybenzyl alcohol, anisaldehyde, anisic acid and acetate. The aldehyde formation was very fast during the first few minutes and subsequently stabilized. Right at the start of the reaction there was a short phase of direct oxidation of the methoxytoluene by the cobalt(III) and then the autoxidation reaction started. If the reaction had been stoichiometric, all the initial cobalt(III) would have been consumed according to the reactions:

$$\mathrm{Ar{-}CH_3 + 2Co^{III} + H_2O \rightarrow Ar{-}CH_2OH + 2Co^{II} + 2H^+} \quad (16)$$

$$\mathrm{Ar{-}CH_2OH + 2Co^{III} \rightarrow Ar{-}CHO + 2Co^{II} + 2H^+} \quad (17)$$

$$\mathrm{Ar{-}CHO + 2Co^{III} + H_2O \rightarrow Ar{-}COOH + 2Co^{II} + 2H^+} \quad (18)$$

To convert 1 mole of methoxytoluene into aldehyde, 4 moles of cobalt(III) are required. Therefore for 0.036 mol l^{-1} of initial Co^{III}, the maximum concentration of anisaldehyde that it would be possible to obtain would be 0.009 mol l^{-1}, representing a 9% conversion rate. This is what can be observed after 9 min on the anisaldehyde curve in Fig. 2. After 5 h of reaction, the aldehyde yield reached 40%; in which case autoxidation occurred, in other words oxidation by the oxygen and regeneration of the Co^{III} from the Co^{II} according to mechanism 2 in Fig. 1.

3.2. Electrochemical oxidation of the methoxytoluene

3.2.1. With nitrogen

The indirect electrochemical oxidation of the methoxytoluene by the Co^{III} acetate (Fig. 3) in a de-oxygenated medium gave, after 2 h, acetate

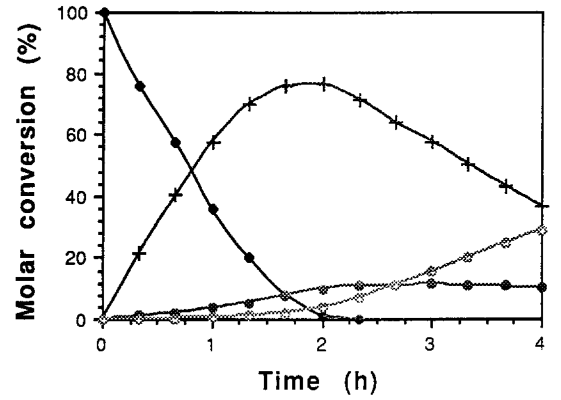

Fig. 3. Indirect electrochemical oxidation of *p*-methoxytoluene under nitrogen. Solution: 150 ml of water–acetic acid (10–90 vol.-%), containing sodium acetate (0.5 mol l^{-1}) and methoxytoluene (0.10 mol l^{-1}). $Co^{II} = 0.10$ mol l^{-1}; $T = 90°C$. Electrolysis under galvanostatic condition: $I = 0.85$ A. Graphite electrodes: anode = 21 cm^2, cathode = 12 cm^2, without separator. ◆, *p*-Methoxytoluene; ●, *p*-anisaldehyde; ○, anisic acid; +, *p*-anisyl acetate.

(80% molar) as the main product (Fig. 1, mechanism 1). The other products obtained were anisaldehyde and anisic acid. If the reaction was allowed to continue, this acetate oxidized into the following acid:

$$Ar\text{–}CH_2OOCCH_3 + 2Co^{III} + H_2O \rightarrow Ar\text{–}CHO + 2Co^{II} + 2H^+ \qquad (19)$$

$$Ar\text{–}CHO + 2Co^{III} + H_2O \rightarrow Ar\text{–}COOH + 2Co^{II} + 2H^+ \qquad (20)$$

Monitoring of the Co^{III} concentration over time by UV-visible spectrometry (Fig. 4) showed that it increases very slightly at the start of the reaction (2 to 3% conversion of Co^{II} into Co^{III}) and then much faster after one and a half hours to stabilize around 15 to 17% after two and a half hours. This increase in the Co^{III} concentration shows at $t = 2$ h a change of direction that corresponds to the appearance of the maximum benzyl acetate yield (Fig. 3). This can be explained by the fact that the Co^{III} reacts with greater difficulty with the acetate than with the methoxytoluene. Consequently, the concentration of Co^{III} tends to increase when the concentration of methoxytoluene decreases.

The accumulated Faradaic yield monitored over time for this reaction (Fig. 5) passed from 92% at $t = 30$ min to 50% at $t = 4$ h. The fact that the Faradaic yield was lower than 100% shows that the reaction between the methoxytoluene and the Co^{III} is stoichiometric and follows mechanism 1 (Fig. 1). The decrease in Faradaic yield over time is due to the fact that during the reaction, the products formed are more difficult to oxidize than the methoxytoluene; since the current supplied remained constant throughout the experiment, an increasing part of it was consumed by the oxidation of the solvent (oxygen evolution at the anode).

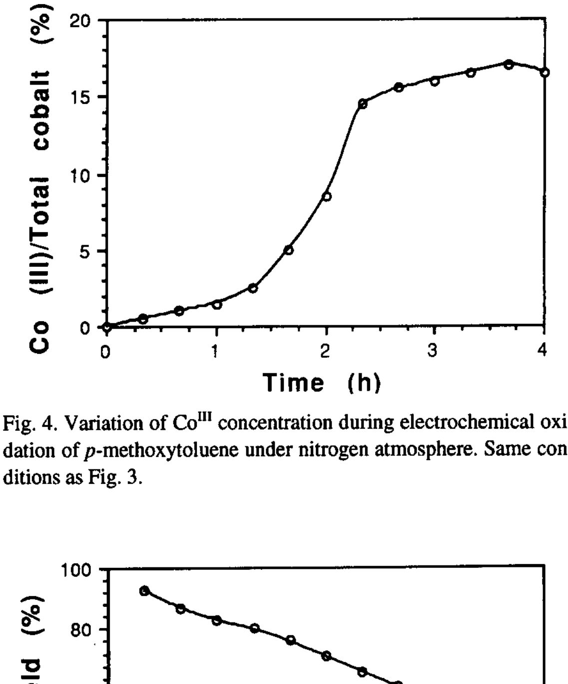

Fig. 4. Variation of Co^{III} concentration during electrochemical oxidation of *p*-methoxytoluene under nitrogen atmosphere. Same conditions as Fig. 3.

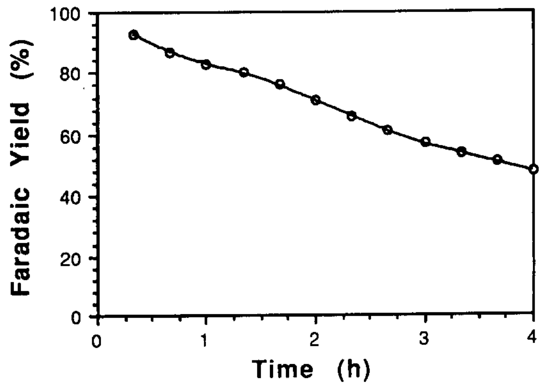

Fig. 5. Variation of faradaic yield during electrochemical oxidation of *p*-methoxytoluene under nitrogen atmosphere. Same conditions as Fig. 3.

3.2.2. *With oxygen*

The experimental procedure represented in Fig. 6 is the same as that in Fig. 2b with, in addition, continuous in situ electrolysis at a constant current ($I = 0.9$ A). The products obtained in this case were the same as those obtained with chemical autoxidation. Furthermore, the overall kinetic mechanism was similar to the one that did not involve continuous electrolysis. Fig. 6 shows that the maximum anisaldehyde yield (40%) occurred after 1 h 15 min. In the same conditions, without any current applied, the 40% aldehyde yield occurred at $t = 5$ h 30 min (Fig. 2b).

If the evolution in the Faradaic yield is monitored over time for this reaction (Fig. 7), it can be seen that this yield is higher than 100% for the first two hours, in other words until the anisaldehyde has practically disappeared. This Faradaic yield higher than 100% shows that a greater amount of products has been obtained than allowed by the charge supplied by the system. This shows that the Co^{III} acetate is not only regenerated by electrolysis of the Co^{II} acetate:

$$\mathrm{Co^{II}(CH_3COO)_2 + CH_3COO^-} \rightarrow \mathrm{Co^{III}(CH_3COO)_3 + e} \quad (21)$$

but also by the autoxidation phenomenon (mechanism 2, Fig. 1).

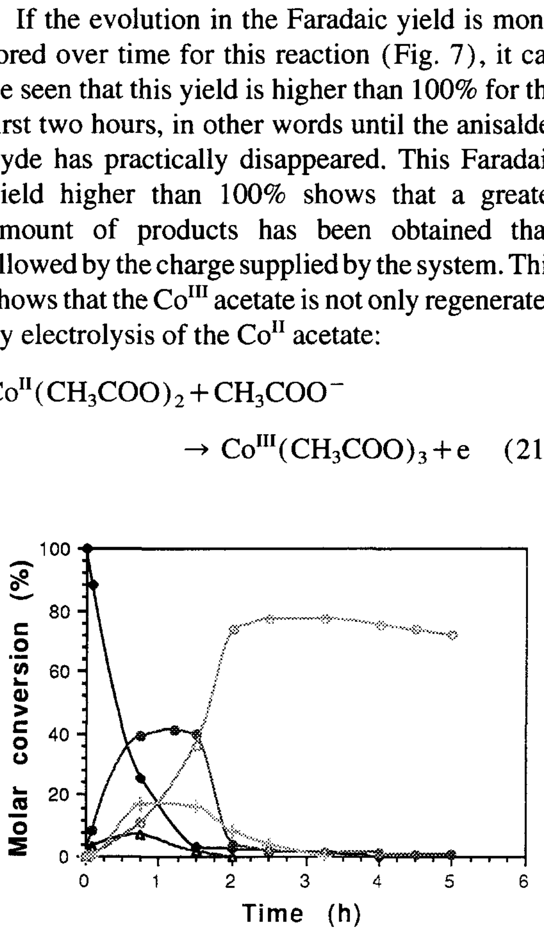

Fig. 6. Autoxidation of *p*-methoxytoluene under electrolysis conditions. Solution: 150 ml of water–acetic acid (10–90 vol.-%) with sodium acetate (0.5 mol l^{-1}) and methoxytoluene (0.10 mol l^{-1}). $T = 90$°C. Oxygen flow rate = 100 ml min^{-1}. Initial concentrations: Co^{II} = 0.064 mol l^{-1} + Co^{III} = 0.036 mol l^{-1}. Electrolysis under galvanostatic condition : $I = 0.90$ A. Graphite electrodes: anode = 21 cm^2, cathode = 12 cm^2, without separator. ◆, *p*-Methoxytoluene; △, anise alcohol; ●, *p*-anisaldehyde; ○, anisic acid; +, *p*-anisyl acetate.

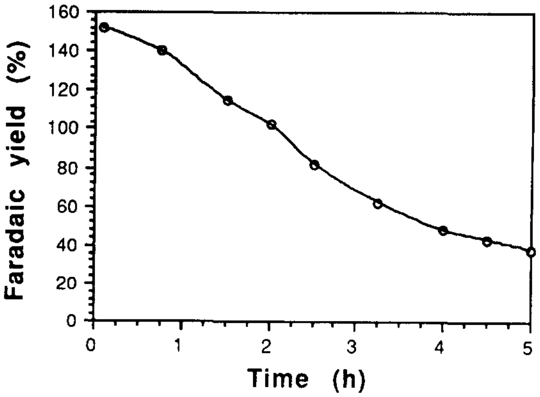

Fig. 7. Variation of Faradaic yield during electrochemical oxidation of *p*-methoxytoluene under nitrogen atmosphere. Same conditions as in Fig. 6.

4. Conclusion

This work shows that the autoxidation reaction catalyzed by the cobalt acetate can be favorably assisted by an electrochemical reaction that regenerates the oxidised form of the mediator. Continuous electrolysis of the cobalt(II) acetate into cobalt(III) acetate ensures maximum aldehyde yield after 1 h 15 min as against 5 h 30 min under the same conditions but without electrolysis. The role of electrolysis is not only to convert the alkylaromatic by a Faradaic reaction as in direct or indirect electrosynthesis where the maximum Faradaic yield that can be obtained is 100%, but also to control better the proportion of each of the concentrations of the two forms of the mediator that acts as catalyst of the autoxidation by oxygen (in this case, the Faradaic yield is higher than 100%). The aim of further work will be to adjust the ratio Co^{III}/Co^{II} to the optimum value according to the reagents, the oxygen transfer rate and the degree of reaction progress.

Acknowledgements

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