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Liquid-phase *p-t*-butyltoluene autoxidation enhanced by electrochemistry: Activation of the catalytic effect of cobalt acetate

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Abstract

The autoxidation of *p-t*-butyltoluene (TBT) at 80 °C in the liquid phase is carried out with an initial mixture of cobalt(III) and cobalt(II) acetate in an acetic acid solution. The autoxidation kinetics of TBT is appreciably accelerated by electrolysis with a anodic current density of 62.5 A m^{-2}. The electrolysis increases the concentration of cobalt(III) acetate, the actual catalyst of the autoxidation reaction. The end product of oxidation is *p-t*-butylbenzoic acid (TBBA). *p-t*-Butylbenzaldehyde (TBBZ) is an intermediary whose concentration passes through a maximum. The oxidation experiments with TBT were performed with total cobalt acetate concentrations ranging from 0.0188 to 0.169 mol dm^{-3}. An increase in total cobalt acetate concentration favours the electrochemical regeneration of Co^{III} and slightly improves the TBBZ selectivity. The duration of TBT oxidation into TBBA is reduced by a factor of 5 compared with a reaction without electrolysis.

1. Introduction

In the chemical industry, the catalytic oxidation of organic compounds in the liquid phase is performed by various processes to manufacture many commercial products. In the case of alkylaromatics $ArCH_3$, the oxidation of the methyl group is a direct way of preparing the corresponding alcohols, aldehydes and acids: $ArCH_2OH$, ArCHO and ArCOOH. Our work on the oxidation of substituted toluenes by electrochemical techniques [1–3] led us to study the oxidation of *p-t*-butyltoluene (TBT). *p-t*-Butylbenzaldehyde (TBBZ), one of the products of TBT oxidation, is used in perfumery. The end product of TBT oxidation, *p-t*-butylbenzoic acid (TBBA), is used as a modifier for resins and as a polymerisation regulator for polyesters.

Two electrochemical approaches can be implemented to achieve the oxidation of alkylaromatics. In the technique of indirect electrolysis, a metal cation, under a higher state of oxidation, chemically oxidises the organic substrate dissolved in an aqueous solution. The reduced form of the cation is oxidised in an electrochemical reactor and is recycled in the chemical reactor. The concentration of the alkylaromatic, generally weakly soluble in the aqueous phase, is maintained at a sufficiently high value by forming an emulsion with the aqueous solution. The redox couples Mn^{III}/Mn^{II} and Ce^{IV}/Ce^{III} in acid medium are often used as oxidation mediators. The process requires a high concentration of the mediator in order to optimise its electrochemical oxidation. The indirect oxidation of the TBT by manganese sulphate in aqueous solution of sulphuric acid made it possible to reach a TBBZ selectivity of 84% [4]. Torii et al. [5] obtained a TBBZ yield of about 90% with cerium ammonium nitrate as mediator in an aqueous solution of 50% acetic acid.

The direct electrooxidation of the alkylaromatic in an electrochemical reactor was also proposed. A TBBZ yield of 35% was obtained for the electrooxidation of the TBT on Pb–5%Sb anode, in an aqueous solution of sulphuric acid [6]. Vaze et al. [7] obtained a similar yield in a filter press electrochemical reactor on a PbO_2 anode. BASF and Hoffman–La Roche [8] patented processes of direct oxidation of TBT on Ti/PbO_2 and Pb/PbO_2 anodes. The oxidation of TBT dissolved in an aqueous solution of acetic acid on a C/CrO_3 anode, with $NaBF_4$ as supporting electrolyte, was also proposed [9]. In this case, the TBBZ yield was 87%. These direct and indirect electrochemical techniques require the consumption of an electrical charge of 4 or 6 faradays per mole of alkylaromatic in order to obtain, respectively, the aldehyde or the acid. These processes often encounter operational difficulties due to the passivation of the anode in an aqueous medium [10–13].

On an industrial scale, the oxidation of alkylaromatics is often carried out by oxygen. This autoxidation reaction is performed in acetic acid as solvent. The reaction is catalysed by cobalt acetate [14]. The most significant example is *p*-xylene autoxidation into terephthalic acid [15]. Concerning TBT autoxidation, Chalk et al. [16] studied the influence of stirring rate and temperature. They obtained mixtures of TBBZ, TBBA and *p*-*t*-butylbenzylic acetate with the sum of aldehyde and acetate totalling about 50% of the products at 50% conversion.

In a first step, the autoxidation of the substituted toluene leads to the aldehyde and in a second step the autoxidation of aldehyde into acid is generally easy:

$$\mathrm{ArCH_3} \overset{\mathrm{O_2}}{\rightarrow} \mathrm{ArCHO} \overset{\mathrm{O_2}}{\rightarrow} \mathrm{ArCOOH} \tag{1}$$

The reaction scheme generally accepted for the formation of aldehyde [14] is the following:

$$\mathrm{ArCH_3} + \mathrm{Co^{III}} \rightarrow \mathrm{ArCH_3^{+\circ}} + \mathrm{Co^{II}} \tag{2}$$

$$\mathrm{ArCH_3^{+\circ}} \rightarrow \mathrm{ArCH_2^{\circ}} + \mathrm{H^+} \tag{3}$$

$$\mathrm{ArCH_2^{\circ}} + \mathrm{O_2} \rightarrow \mathrm{ArCH_2O_2^{\circ}} \tag{4}$$

$$\mathrm{ArCH_2O_2^{\circ}} + \mathrm{Co^{II}} \rightarrow \mathrm{ArCH_2O_2Co^{III}} \tag{5}$$

$$\mathrm{ArCH_2O_2Co^{III}} \rightarrow \mathrm{ArCHO} + \mathrm{HOCo^{III}} \tag{6}$$

$$\mathrm{HOCo^{III}} + \mathrm{H^+} \rightarrow \mathrm{Co^{III}} + \mathrm{H_2O} \tag{7}$$

Thus, the autoxidation leads straight to the aldehyde without passing through the alcohol. The initiation of the reaction is only possible in the presence of $\mathrm{Co^{III}}$ needed for the production of the cation radical $\mathrm{ArCH_3^{+\circ}}$ (Equation 2). $\mathrm{Co^{III}}$ is reduced to $\mathrm{Co^{II}}$ in this initial step, then $\mathrm{Co^{III}}$ is regenerated due to the peroxide radical $\mathrm{ArCH_2O_2^{\circ}}$ (Equation 5). In the absence of $\mathrm{Co^{III}}$ a latency period of several hours is observed. Partenheimer [17] showed that a reaction between $\mathrm{Co^{II}}$ acetate, dioxygen and acetic acid produces $\mathrm{Co^{III}}$ acetate. This reaction is initiated by traces of peroxide ROOH present in the acetic acid. Under industrial production conditions, sodium bromide NaBr is used as promoter for the formation of $\mathrm{Co^{III}}$ acetate. Titanium coating is used in the autoxidation reactors because of corrosion due to bromide [15].

In this context, we began to study the alkylaromatic autoxidation processes activated by electrochemical means [18]. The reaction was produced using an electrochemical technique to regenerate $\mathrm{Co^{III}}$ acetate on a graphite anode. This technique allowed the latency period to be suppressed in the autoxidation of methoxytoluene [18, 19] and toluene [19–21]. The principal consequence of electrolysis was to enhance the catalytic activity of $\mathrm{Co^{III}}$ by increasing its concentration in the reactor. The reaction kinetics were significantly accelerated.

This work reports the results of the electrochemically assisted autoxidation of TBT at 80 °C. To avoid the electrooxidation of the substrate, the electrolysis current was limited to a level such that only $\mathrm{Co^{II}}$ is oxidized on the anode. In the first place, a voltammetric study of $\mathrm{Co^{II}}$ acetate oxidation on a graphite anode was carried out to evaluate this optimum electrolysis current. Secondly, the influence of the total cobalt acetate concentration on the kinetics and selectivity of the electrochemically assisted autoxidation of the TBT was studied.

2. Experimental details

2.1. *Autoxidation reactor*

The chemicals supplied by Aldrich were used without further purification. The autoxidation experiments were carried out in a Metrohm cell 150 $\mathrm{cm^3}$ in capacity. This cell was maintained at constant temperature by a double envelope through which thermostatted water was pumped. The volume of solution used for each experiment was 100 $\mathrm{cm^3}$. The reactor was topped by two condensers in series so as to condense the solvent and the vapours of organic substances. The temperature of the first condenser was 0 °C, that of the second was −30 °C. The solution was agitated by a magnetic stirrer at 750 rpm. Dioxygen was sparged into liquid phase through a Teflon tube ending with a sintered glass disc, 1 cm in diameter. The gas flow rate (150 $\mathrm{cm^3\ min^{-1}}$) was regulated by a valve incorporated into a flowmeter. The oxygen quantity introduced was much higher than that needed for the complete oxidation of the substrate. Sodium acetate (1 $\mathrm{mol\ dm^{-3}}$) was present in the solution to increase its conductivity. An electrical current was applied throughout the experiment via two cylindrical graphite electrodes immersed in the solution. The diameters of the electrodes were 0.5 cm for the cathode and 1.2 cm for the anode. A current of 0.1 A allowed the electrochemical oxidation of $\mathrm{Co^{II}}$ to $\mathrm{Co^{III}}$. The surface of the anode (16 $\mathrm{cm^2}$), appreciably larger than that of the cathode (7 $\mathrm{cm^2}$), increases the $\mathrm{Co^{II}}$ oxidation and conversely decreases the $\mathrm{Co^{III}}$ reduction by favouring hydrogen evolution. Electrolysis in the galvanostatic mode was performed using a stabilized power source (potentiostat/galvanostat EGG model 362). To evaluate the optimum value of the electrolysis current, voltammetric curves for oxidation of $\mathrm{Co^{II}}$ acetate were plotted with the same reactor, with concentrations ranging from 0.01 to 0.20 $\mathrm{mol\ dm^{-3}}$ and with a potential sweep rate of 0.5 $\mathrm{mV\ s^{-1}}$. The flow rate of oxygen bubbling into the solution was 150 $\mathrm{cm^3\ min^{-1}}$ so the hydrodynamic conditions were identical to those of an autoxidation experiment. The above-described anode was used as the working electrode and the cathode served as the counter electrode. The potentials were referred to a saturated calomel electrode (SCE), placed in a tube ending with a Luggin capillary containing a solution of the same composition as the solution studied.

2.2. *Preparation of the solutions used for the autoxidation reaction*

An earlier study [19] showed that the autoxidation reaction starts immediately, when toluene is introduced into the acetic acid solution saturated with dioxygen, only if the cobalt is in its higher degree of oxidation, that is, Co^{III}. Consequently, a cobalt acetate mother solution was prepared by electrolysis of a solution of Co^{II} acetate in acetic acid (0.2 mol dm^{-3}) with sodium acetate as supporting electrolyte (1.1 mol dm^{-3}). The electrolysis of the Co^{II} acetate solution (500 cm^3) was carried out at a current intensity of 0.14 A in a filter-press type flow reactor (Microflow Cell, Electrocell AB, Sweden) fitted with two flat graphite electrodes (16.5 cm^2) and two compartments separated by a Nafion® membrane. The Co^{III} acetate concentration after about 45 h of electrolysis was 0.13 mol dm^{-3}. The ratio of Co^{III} to total cobalt acetate ($[Co^{III}] : [Co]$) was thus approximately 65% ($[Co] = [Co^{II}] + [Co^{III}]$). The different solutions used in the experiments were prepared by diluting this mother solution with a solution of sodium acetate in acetic acid (1.1 mol dm^{-3}).

2.3. *Reaction and analyses*

The Co^{III} acetate solution containing 1.1 M sodium acetate (90 cm^3) was saturated with oxygen and the temperature was brought up to 80 °C. Next, the reaction was started by simultaneously beginning electrolysis and adding TBT (10 cm^3) to the Co^{III} acetate solution (90 cm^3) saturated with oxygen. Under these conditions the actual sodium acetate concentration was 1 mol dm^{-3}. The solution reached thermal equilibrium after about 5 min and the first sample of solution was then taken. The solutions were analysed at regular intervals by liquid chromatography (HP 1050). The reaction products were separated on an ODS2 C18 column. The eluent was a mixture of phosphate buffer (pH 7) and methanol of variable composition flowing at 1 cm^3 min^{-1}. Separation of products was ensured by linearly varying the methanol volume fraction in the eluent from 10% to 93% in 20 min. The values of the TBT, TBBZ and TTBA concentrations were obtained using *p*-chlorobenzoic acid as the internal standard. The Co^{III} acetate concentrations were measured by spectrophotometry at 650 nm, taking into account a correction for the residual absorption of Co^{III}.

3. Results

Figure 1 shows the voltammetric curve of a Co^{II} acetate solution (curve 1). The voltammogram of a solution without Co^{II} (ground current, curve 2), shows a significant oxidation current beyond the potential of 1.00 V vs SCE. The intensity of this residual current reaches 63 mA at 1.80 V vs SCE. The residual current corresponds to the electrolysis of the acetic acid [22], that is, the oxidation of the acetate ion on the anode:

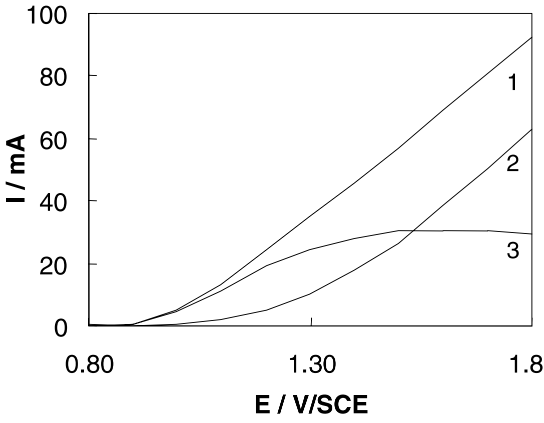

Fig. 1. Oxidation current on the graphite anode. Key : (1) total oxidation current, (2) residual current, (3) oxidation current for cobalt(II) acetate. $T = 80$ °C. (sweep rate 0.5 mV s^{-1}). Oxygen flow rate 150 cm^3 min^{-1}. $[NaCH_3COO] = 1$ mol dm^{-3}; $[Co(CH_3COO)_2] = 0.05$ mol dm^{-3}.

$$2\ CH_3COO^- \rightarrow 2\ CO_2 + C_2H_6 + 2\ e^- \quad (8)$$

and the reduction of the proton on the cathode:

$$2\ H^+ + 2\ e^- \rightarrow H_2 \quad (9)$$

In the presence of Co^{II}, the increase in oxidation current is due to the electrochemical production of Co^{III}

$$Co^{II} \rightarrow Co^{III} + e^- \quad (10)$$

The oxidation current for Co^{II} (curve 3) is obtained by subtracting the residual current from the total current. Beyond 1.40 V vs SCE, the plateau observed corresponds to the maximum transfer rate of Co^{II} from the bulk solution to the electrode. The limiting current is roughly proportional to the concentration of Co^{II}. Figure 2 shows the variation of the total current

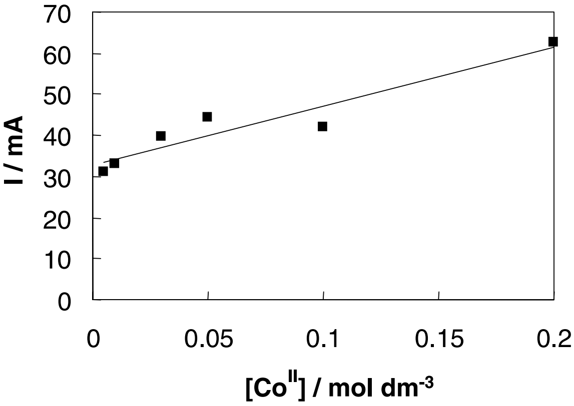

Fig. 2. Total oxidation current as a function of cobalt(II) acetate concentration at 1.4 V vs SCE. $T = 80$ °C. Oxygen flow rate 150 cm^3 min^{-1}. $[NaCH_3COO] = 1$ mol dm^{-3}. Continuous line is the linear regression for the data: $I/mA = 144\ [Co^{II}] + 33$.

intensity (curve 1) as a function of the concentration of Co^{II} at a potential value of 1.40 V vs SCE. These data constitute an estimate of the maximum value of the current beyond which the electrochemical regeneration rate of Co^{III} could not be increased. Indeed, they correspond to the extreme case where the whole of the cobalt would be in the Co^{II} form in an experiment of electrochemically assisted autoxidation. For a Co^{II} acetate concentration of 0.2 mol dm^{-3}, the value of this limiting current is 63 mA. Taking into account this result, the current intensity for electrolysis in an autoxidation reaction was fixed at 100 mA, a value that ensures a maximum rate of electrochemical regeneration of Co^{III} acetate.

The operating conditions for the autoxidation runs are summarized in Table 1. Six experiments of TBT autoxidation under electrolysis were performed for a total cobalt acetate concentration [Co] varying from 0.0188 to 0.169 mol dm^{-3}. The TBT concentration and the initial Co^{III} ratio ($[Co^{III}] : [Co] = 65 \pm 2\%$) were almost identical at the beginning of each experiment. During the oxidation reaction, the quantity of TBT decreases regularly then TBBZ and TBBA appear successively. Unlike the toluene and methoxytoluene autoxidations [18–20], there is no electrochemical oxidation of the TBT on the anode in the presence of sodium acetate as supporting electrolyte; this was proved in a preliminary experiment by carrying out a TBT electrolysis in an anaerobic solution without cobalt acetate [23]. On the other hand, the TBT is oxidized into *p-t*-butylbenzylic acetate in the presence of Et_4NBF_4 as supporting electrolyte [8], but not in the presence of sodium acetate [23].

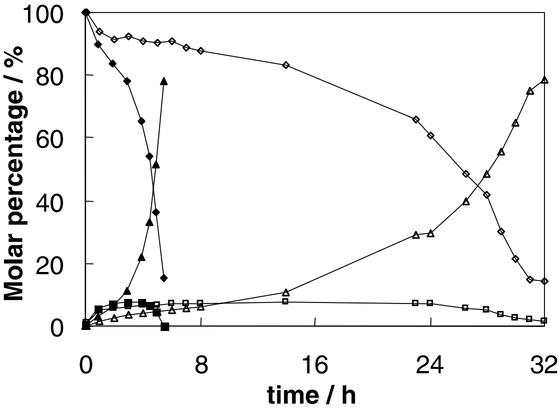

Fig. 3. TBT, TBBZ and TTBA mole percentages as a function of time. $[Co] = 0.113$ mol dm^{-3}; $[Co^{III}] : [Co]$ (initial) = 63%. Experiment 5 ($I = 0.1$ A): (♦) *p*-tert-butyltoluene, (■) *p*-tert-butylbenzaldehyde, (▲) *p*-tert-butylbenzoic acid. Experiment 7 ($I = 0$ A) : (◇) *p*-tert-butyltoluene, (□) *p*-tert-butylbenzaldehyde, (△) *p*-tert-butylbenzoic acid.

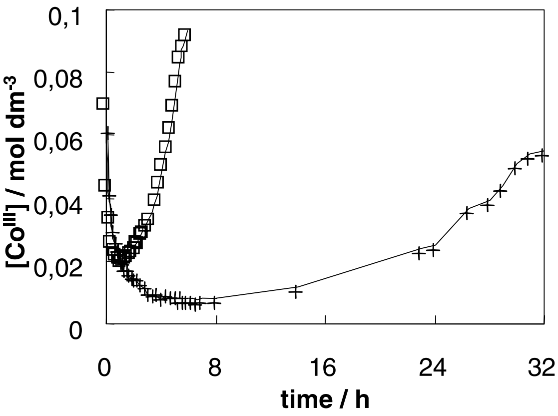

Fig. 4. Cobalt(III) acetate concentration as function of time. Experiment 5 (□); Experiment 7 (+). Same conditions as Figure 3.

Figure 3 shows the variation of the TBT, TBBZ and TBBA mole percentages in two experiments carried out with and without current, under otherwise identical operating conditions. Under electrolysis, the reaction is complete after 6 h, instead of 32 h without electrolysis. The oxidation kinetics are parallel to the variation in the Co^{III} concentration in each experiment (Figure 4). During the first hour, the drop in Co^{III} concentration is almost identical in the two cases. This drop in catalyst concentration can be attributed to the chemical reduction of Co^{III} to Co^{II} by the acetate ion [24, 25]: a suggestion concerning the stoichiometry of this reaction was previously proposed [15, 24]. Under electrolysis, the drop in Co^{III} concentration is gradually compensated by the rise in the rate of electrochemical regeneration of Co^{III}, which increases with the Co^{II} concentration. The minimum in Co^{III} concentration is reached when the global rate of reduction of Co^{III} and the Co^{III} electrochemical regeneration rate are equal. The minimum in Co^{III} concentration is approximately three times higher than in the absence of electrolysis, under otherwise identical operating conditions. The higher Co^{III} concentration results in a very appreciable increase in the TBT oxidation rate. The acceleration of the reaction rate occurs in parallel with the increase in catalyst concentration. The beginning of the continuous rise in Co^{III} concentration, that continues until the end of the reaction, coincides with the appearance of significant

Table 1. Operating conditions for PBT autoxidation
Volume of solution: 100 cm^3. Oxygen flow rate: 150 cm^3 min^{-1}. $T = 80$ °C. $[NaCH_3COO] = 1$ mol dm^{-3}.

Experiment	$I = 0.1$ A						$I = 0$ A
	1	*2*	*3*	*4*	*5*	*6*	*7*
$[Co] = [Co^{II}] + [Co^{III}]$/mol dm^{-3}	0.0188	0.0377	0.0754	0.0845	0.113	0.169	0.113
$[Co^{III}]_0$/mol dm^{-3}	0.0122	0.024	0.050	0.058	0.072	0.094	0.071
$[TBT]_0$/mol dm^{-3}	0.557	0.554	0.546	0.561	0.566	0.533	0.543

quantities of aldehyde. Now, aldehydes effectively activate the alkylaromatic autoxidation [26]. Hendriks et al. [27] showed that the autoxidation of benzaldehyde is an autocatalytic reaction. The final increase in Co^{III} concentration during TBT autoxidation suggests the same type of reaction. Under these conditions, the reaction equation for the TBBZ autoxidation would be similar to that proposed for benzaldehyde [27]: namely,

$$\begin{aligned}&(CH_3)_3C\text{-}C_6H_4-CHO + 2\,Co^{II}(CH_3COO)_2\\&\quad + O_2 + 2\,CH_3COOH \rightarrow (CH_3)_3C\text{-}C_6H_4-COOH\\&\quad + 2\,Co^{III}(CH_3COO)_3 + H_2O \qquad (11)\end{aligned}$$

The TBBZ selectivities of the two reactions, given by the ratio [TBBZ] : [TBBZ] + [TBBA], are represented in Figure 5 as a function of the TBT conversion. They are identical at the beginning of the reaction. From 10% to 50% of TBT conversion, the selectivity under electrolysis becomes higher. For a conversion of 17%, the difference in selectivities is maximum, i.e. 53% and 42%, respectively. This maximum difference coincides with the acceleration of the reaction under electrolysis induced by the final increase in the Co^{III} concentration after 2 h of reaction (cf. Figures 3 and 4). Without electrolysis, at the same TBT conversion, the reaction is in an inhibition phase related to the very low level of Co^{III}.

The variation of TBBA mole percentage under electrolysis (Figure 6) shows that the reaction rate increases with the quantity of cobalt acetate. The mean value of the $[Co^{III}] : [Co]$ ratio varies in the same way as the TBBA formation rate (Figure 7). After an initial drop, the value of the $[Co^{III}] : [Co]$ ratio passes through a minimum before increasing continuously. The larger the quantity of cobalt acetate, the more quickly the minimum in the $[Co^{III}] : [Co]$ ratio is reached 8 h for experiment 2, 1 h for experiment 6. These observations suggest that the limiting factor in the TBT autoxidation kinetics is the $[Co^{III}] : [Co]$ ratio. The parallel increase in the $[Co^{III}] : [Co]$ ratio with the total cobalt acetate concentration (Figure 7) can be ascribed to the increasing efficiency of the electrochemical production of Co^{III}, as the catalyst regeneration kinetics are proportional to the Co^{II} acetate concentration.

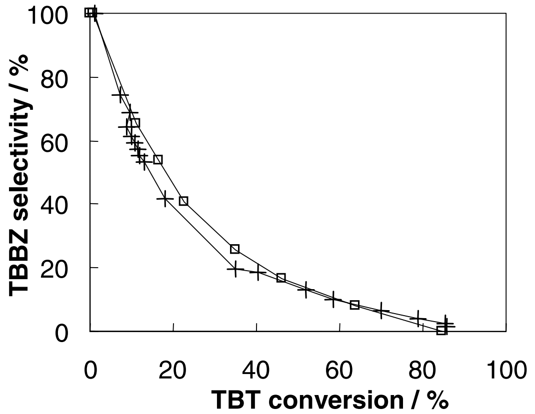

Fig. 5. TBBZ selectivity as a function of TBT conversion rate. Experiment 5 (□); Experiment 7 (+). Same conditions as Figure 3.

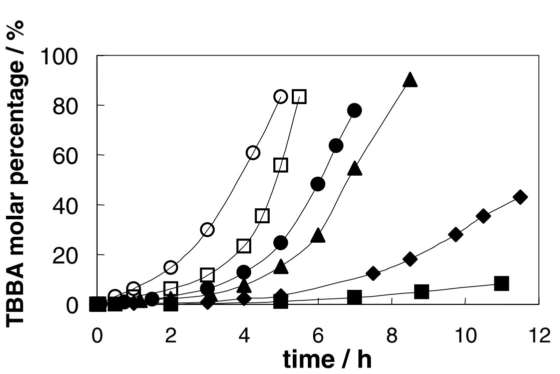

Fig. 6. TBBA mole percentage as a function of time. $I = 0.1$ A. $T = 80$ °C. Experiments 1 (■), 2 (♦), 3 (▲), 4 (●), 5 (□), 6 (○).

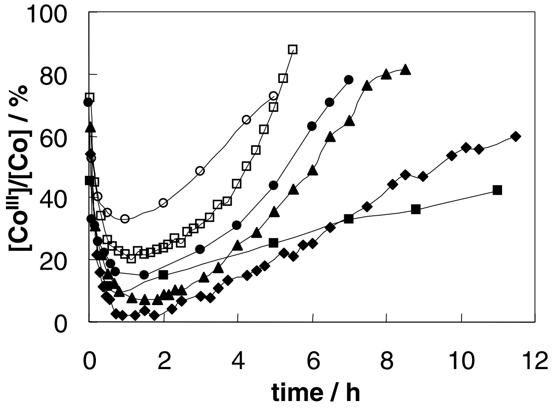

Fig. 7. Variation of $[Co^{III}] : [Co]$ ratio as a function of time. Experiments 1 (■), 2 (♦), 3 (▲), 4 (●), 5 (□), 6 (○). Same conditions as Figure 6.

The maximum TBBZ yield rises from 5.2% to 8.4% from experiment 1 to experiment 6 (Table 2). This significant result indicates that the TBT autoxidation becomes increasingly faster than TBBZ autoxidation as the $[Co^{III}] : [Co]$ ratio increases.

It is interesting to compare the quantity of electricity involved in the electrolysis with the electric charge needed for electrochemical formation of the reaction products. The calculation from Faraday's law is on the basis of 4 faradays per mole of aldehyde and 6 faradays per mole of acid. For an 80% PBT conversion, the

Table 2. Maximum yield of TBBZ

Experiment	Time /h	TBBZ maximum yield/%	TBT conversion rate/%
1	11	5.2	22.0
2	7.5	6.8	24.7
3	5	8.1	26.2
4	4	7.7	21.6
5	3	7.7	22.5
6	2	8.4	25.9

quantity of electricity used lies between 7% and 12% of the theoretical quantity in Experiments 3–6. This result shows that the PBT oxidation products are not produced by an electrochemical oxidation. So the oxidant in the reaction is indeed oxygen. In addition to the electrochemical regeneration of Co^{III}, a part of the electrical current is consumed in the oxidation of the acetic acid and free water (Figure 1).

4. Conclusion

This work shows that the catalytic action of cobalt in the *p*-*t*-butyltoluene autoxidation can be electrochemically activated. The technique implemented is relatively simple: the electrolysis cell is fitted with two graphite electrodes, without a separating diaphragm, directly immersed in the autoxidation reactor. The electrochemical regeneration of Co^{III} using a weak current, allows the duration of the reaction to be reduced by a factor of 5. The *p*-*t*-butylbenzaldehyde selectivity of the autoxidation process is not basically improved. It is, however, higher under electrolysis for substrate conversions below 50%. The faradaic contribution to the formation of the products is negligible: the oxidant of *p*-*t*-butyltoluene is thus the oxygen. Thus, the electrochemical assistance of the autoxidation reaction of *p*-*t*-butyltoluene (whose principal benefit is an acceleration of process kinetics under the operating conditions studied) consumes a very small quantity of electricity compared with the final quantity of acid formed.

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