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Electrochemical assistance of catalytic oxidation in liquid phase using molecular oxygen: oxidation of toluenes

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Abstract

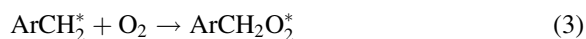
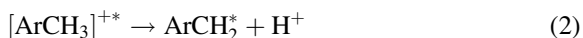
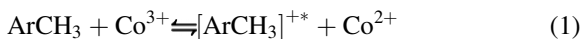
Liquid phase autoxidation of toluene and *p*-methoxytoluene in acetic acid has been studied under electrolysis in the presence of cobalt acetate. The latency period disappears when Co^{3+} is electrogenerated in the medium either before or during autoxidation experiments. The kinetics of the oxidation process is accelerated under electrolysis condition. The effects of temperature, current intensity, Co concentration, oxygen flow rate are investigated. The transition between the kinetic and the mass transfer limitations is determined in the case of *p*-methoxytoluene. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Autoxidation; Gas-liquid reaction; Catalyst electrochemical activation; Electrochemical oxidation; Toluene; *p*-Methoxytoluene; Cobalt acetate

1. Introduction

The oxidation of alkylated aromatic hydrocarbons by molecular oxygen (autoxidation) is the source of many products of commercial interest. Oxidation conducted in the liquid phase provides good yield and selectivity due to the mild conditions afforded by the use of transition metals as catalysts.

As a general rule autoxidation of alkylaromatics by oxygen is realized in acetic acid in the presence of a catalytic redox couple such as $\text{Co}^{3+}/\text{Co}^{2+}$. The process is conducted at relatively low temperature (90–110°C) in a gas–liquid reactor. The generally accepted mechanism is [1]:



The Co^{III} regenerated by reaction (4) pursues the catalytic cycle of reactions (1)–(4). In the next step, also catalysed by the $\text{Co}^{3+}/\text{Co}^{2+}$ couple, the aldehyde is oxidized in the corresponding benzoic acid:



The mechanism of reaction (5) is more complex and less known than that of the aldehyde formation from the initial alkylaromatic [2].

The autoxidation process is characterized by a latency period of several hours if only Co^{2+} and oxygen are present in the solution of alkylaromatic. The initiation period is generally reduced by the action of a cocatalyst such as methyl ethyl ketone or sodium bromide which can initiate the Co^{3+} formation from the catalyst [1,3].

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Our interest in the field of autoxidation is to improve the catalytic performance of the gas–liquid reaction by using the electrochemical technique. In preliminary work the electrochemical behaviour of 4-methoxytoluene, toluene and Co(II) in acetic acid was investigated [4,5]. Then it was shown that the oxidation process of toluene or 4-methoxytoluene can be triggered off by the in situ electrochemical generation of Co^{3+} by anodic oxidation of Co^{2+} [6]. In this way, the Co^{3+} concentration can also be maintained at an appropriate value for a faster kinetics than that which exists in the autoxidation without electrochemical assistance [7,8]. In a two-phase oxidation process involving oxygen, the main parameters which control the kinetics are temperature, composition of the medium (concentration of cobalt, ratio of $\text{Co}^{3+}/\text{Co}^{2+}$, ratio of water/acetic acid) and hydrodynamic conditions related to the oxygen flow injected into the liquid phase.

Here we report the results of kinetic studies of the liquid phase oxidation of 4-methoxytoluene and toluene in acetic acid in the presence of the $\text{Co}^{3+}/\text{Co}^{2+}$ redox couple and under electrochemical assistance. The effects of current intensity, temperature, cobalt concentration, and oxygen flow rate were investigated.

2. Experimental

The reagents used, toluene, 4-methoxytoluene, cobalt(II) acetate tetrahydrate, acetic acid and sodium acetate, were supplied by Aldrich. The isothermal cylindrical reactor (Metrohm cell) had a capacity of 150 ml and two reflux devices placed in series on top of it: the first was thermostated to 0°C and the second to -30°C in order to avoid the loss of solvent and products. The oxygen was bubbled into the liquid phase by means of a fritted glass tube at different flow rates. The stirring was performed with a magnetic bar at constant rotation rate.

Samples of the solution were taken and analysed quantitatively with respect to time by HPLC (Hewlett-Packard 1050 series) using a Brownlee Spherisorb ODS2 column and a mixture of buffer solution ($\text{pH}=7$) and methanol as eluent circulating at a rate of $1\text{ cm}^3/\text{min}$. The separation was accomplished by creating a methanol gradient from 10% to 77% in

volume in 16 min for toluene and from 10% to 78% in 25 min for 4-methoxytoluene. The cobalt(III) acetate was analysed quantitatively with respect to time by UV–Vis spectrophotometry (Hewlett-Packard 8452A) at $\lambda=700\text{ nm}$, a wavelength at which only the cobalt (III) absorbs.

The electrolyses were performed under galvanostatic conditions with two graphite electrodes with a surface area of 16 and 7 cm^2 for the anode and cathode, respectively.

The faradaic contribution C_f is defined as the ratio between the amount of effective charge supplied to the system, $Q_{\text{exp}}(Q_{\text{exp}}=It)$ and the charge required to form the various products obtained by electrolysis, Q_{th} (calculated with Faraday's law). The value of C_f only gives an indication of the electrochemical contribution in toluene oxidation; indeed, the charge supplied can serve for direct or indirect oxidation reactions of the toluene as well as for secondary reactions such as the solvent oxidation.

The conversion of a starting component is defined as the quotient of the amount reacted and its initial quantity.

The yield of a reaction product is defined as the quotient of the amount of reaction product and initial quantity of starting component.

3. Results and discussion

3.1. Initiation and assistance of toluene autoxidation by electrochemistry

3.1.1. Initiation

Oxygen bubbled through a solution containing only toluene and Co^{2+} acetate in acetic acid at 90°C cannot cause any reaction before 6 h; this latency period is generally observed in the absence of either a promoter or the Co^{3+} species [1,3,7,8]. Fig. 1 (curves 1(a) and (c)) shows that, in the presence of Co^{3+} acetate, electrochemically generated before bubbling oxygen in the medium, the oxidation of toluene starts immediately; however, after 6 h of reaction only 12.5% of benzoic acid is obtained.

3.1.2. Assistance

Curves 2 in Fig. 1 show that under continuous electrolysis ($I=0.9\text{ A}$) the kinetics of the toluene

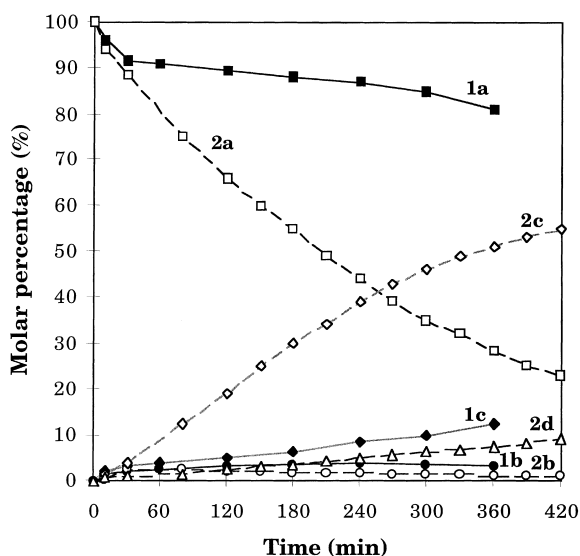


Fig. 1. Autoxidation of toluene. Acetic acid solution of toluene (1 M) containing NaOAc (0.87 M); initial catalyst concentration: $\text{Co}(\text{OAc})_2$ (0.13 M)+ $\text{Co}(\text{OAc})_3$ (0.07 M). $T=100^\circ\text{C}$; oxygen flow rate=150 ml/min. Curves 1 – purely chemical; curves 2 – assisted by electrochemistry, $I=0.9$ A. (a) toluene; (b) benzaldehyde; (c) benzoic acid; (d) benzyl acetate.

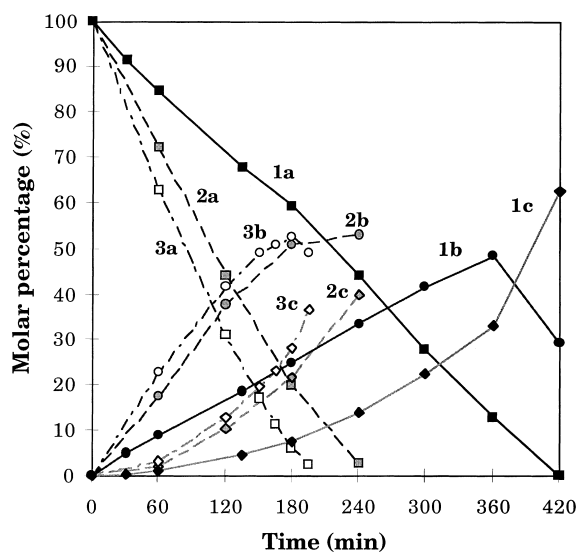


Fig. 2. Autoxidation of 4-methoxytoluene. Influence of the current intensity on the reaction kinetics. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M). $T=90^\circ\text{C}$; oxygen flow rate=50 ml/min. Curves 1 – $I=0$ A; initial catalyst concentration: $\text{Co}(\text{OAc})_2$ (0.138 M)+ $\text{Co}(\text{OAc})_3$ (0.062 M). Curves 2 and 3 – initial catalyst concentration: $\text{Co}(\text{OAc})_2$ (0.2 M); electrochemical assistance: 2 – (0.1 A); 3 – (0.6 A). Curves (a) 4-methoxytoluene; curves (b) *p*-anisaldehyde; curves (c) *p*-anisic acid.

oxidation process increases with respect to the purely chemical reaction. Benzoic acid is the main product formed; after 6 h the chemical yield of benzoic acid reaches 51% (value to be compared with 12.5% for curve 1(c)). The Co^{3+} analyses show that for the operating conditions of Fig. 1 the Co^{3+} /total Co ratio equal to 35% at the beginning, decreases in 30 min, then remains practically constant along the reaction. However, the average value of this concentration ratio is higher in the case of the electrochemically assisted autoxidation (10% for curves 1 and 22% for curves 2; Fig. 1) [7]. The strong increase in the rate of the oxidation process can be related to the electrochemical regeneration of Co^{3+} . The faradaic contribution is 40% after 6 h that proves the Co^{3+} regeneration is in majority due to molecular oxygen action.

3.2. Assistance of 4-methoxytoluene autoxidation by electrochemistry

3.2.1. Effect of current intensity

The 4-methoxytoluene shows the same behaviour than toluene (see Fig. 2 and [6]). However, there are

some differences in the kinetics of the processes. The autoxidation of 4-methoxytoluene is immediately initiated if Co^{3+} is generated by electrolysis before chemical reaction (Fig. 2; curve 1(a), $I=0$ A). 4-Methoxytoluene is faster oxidized at 90°C than toluene at 100°C (compare with curve 1(a) in Fig. 1). The oxidation of 4-methoxytoluene is easier to achieve compared to that of toluene because of the electron donating effect of the methoxy group.

For the same experiment with 4-methoxytoluene, starting with only Co^{2+} , but under electrolysis conditions ($I=0.1$ A), the oxidation rate is faster than without electrolysis (Fig. 2; curves 2(a) and 1(a)). However, increasing the current intensity from 0.1 to 0.6 A does not cause further large increase of the process rate.

One can notice that electrochemically assisted autoxidation leads to an aldehyde/acid ratio which depends on conversion and is always higher than that obtained by non-assisted autoxidation (compare in Fig. 2 curves 1(b) and (c), and 2(b) and (c) for example).

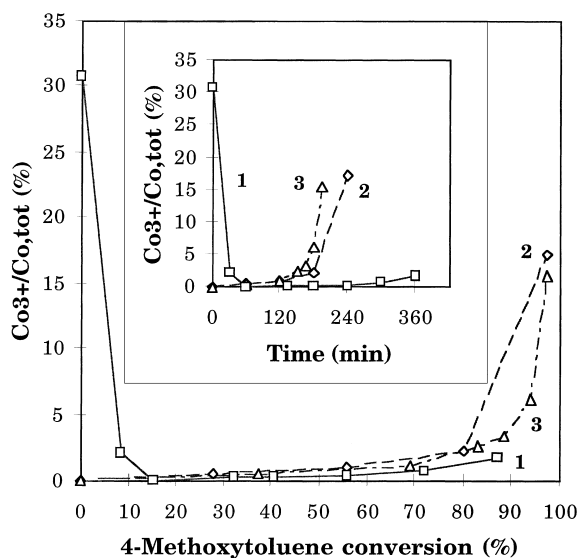


Fig. 3. Variation of $[\text{Co}^{3+}]/[\text{total Co}]$ ratio during the autoxidation of 4-methoxytoluene. Same conditions as in Fig. 2.

Fig. 3 shows the variation of $\text{Co}^{3+}/\text{total cobalt}$ concentration ratio in terms of time and 4-methoxytoluene conversion. In the case of a purely chemical process (curves 1), the initial 0.062 M Co^{3+} concentration falls down after 1 h and keeps a value less than 1% of the total cobalt concentration. On the contrary, in the case of reactions conducted under electrolysis ($I=0.1$ and 0.6 A), the Co^{3+} concentration slowly rises from zero to about 2–3% of the total cobalt during the time required for the 4-methoxytoluene conversion to reach 85%; the Co^{3+} concentration rises quickly as soon as aldehyde concentration reaches its maximum.

Fig. 4 shows the influence of current intensity on the faradaic contribution. The values found mean that the charges used contribute for direct and indirect oxidation of 4-methoxytoluene for less than 4–27% of the total compounds formed by oxidation (say, alcohol, aldehyde, acetate, acid assayed by HPLC). We can consider that the faradaic contribution augmentation with the current is essentially due to anodic oxidation of acetic acid; in fact, the amount of acetic acid oxidized was not determined in these experiments.

Hence, like in the case of toluene the main contribution in the oxidation process is due to molecular oxygen action.

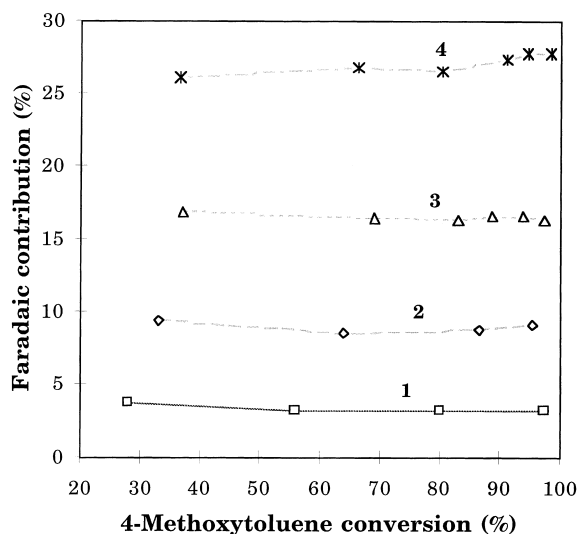
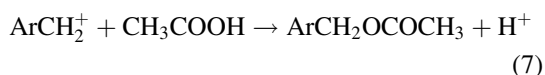


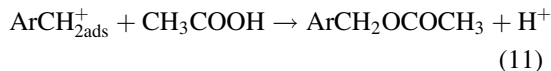
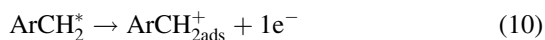
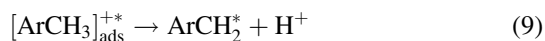
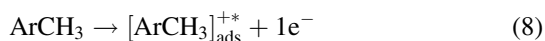
Fig. 4. Variation of faradaic contribution during the autoxidation of 4-methoxytoluene assisted by electrochemistry. Influence of the current intensity. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M) and $\text{Co}(\text{OAc})_2$ (0.2 M); $T=90^\circ\text{C}$; oxygen flow rate=50 ml/min. 1 – 0.1 A; 2 – 0.3 A; 3 – 0.6 A; 4 – 0.9 A.

In the same time as aldehyde and acid are formed there is an anisyl acetate production with a yield which reaches about 5% in the case of purely chemical autoxidation and for experiments conducted at low current intensity (Fig. 5, curves 1, 2 and 3); the acetate is formed in higher yield under the high values of current intensity (Fig. 5, curves 4 and 5). The acetate formation competes with the aldehyde formation and can be explained by two mechanisms:

- the indirect reaction: the Co^{3+} action on the benzylic radical formed in reaction (2) [1]:



- the direct anodic reaction according to an electrochemical–chemical–electrochemical mechanism:



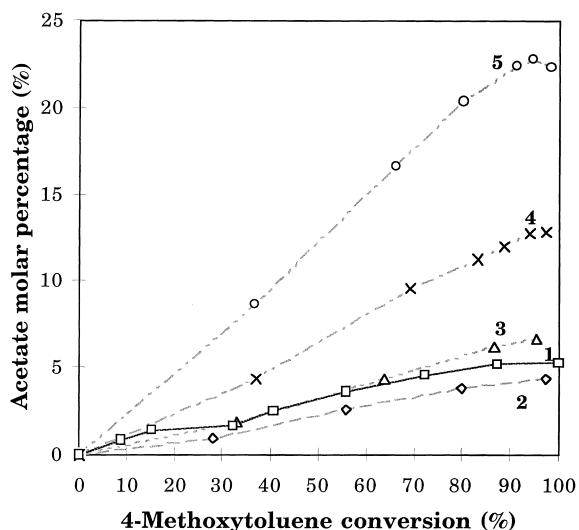


Fig. 5. Variation of *p*-anisyl acetate molar percentage during the autoxidation of 4-methoxytoluene. Influence of the current intensity. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M); $T=90^{\circ}\text{C}$; oxygen flow rate=50 ml/min. Curves 1 – purely chemical ($I=0$ A); initial catalyst concentration: $\text{Co}(\text{OAc})_2$ (0.138 M)+ $\text{Co}(\text{OAc})_3$ (0.062 M); Curves 2–5 – initial catalyst concentration: $\text{Co}(\text{OAc})_2$ (0.2 M); electrochemical assistance: 2 – (0.1 A), 3 – (0.3 A), 4 – (0.6 A), 5 – (0.9 A).

The two mechanisms probably take place in the case of 4-methoxytoluene which is oxidizable on an anode [9].

The acetate could be converted into corresponding alcohol due to water formation during the reaction. This is one of the sources of alcohol formed in small amounts (about 4%).

3.2.2. Temperature effect

In the case of 4-methoxytoluene, in acetic acid containing 0.2 M of total cobalt, under constant oxygen flow rate and constant current (0.1 A), the temperature effect on the conversion rate is important between 50°C and 90°C (curves 1–3 in Fig. 6). A rough estimation shows that the activation energy is of the order of 70 kJ/mol. It may be assumed that the increase in the rate observed in the gap 50 – 90°C results from the increase of the kinetic constant of the limiting step which should be under thermal activation. This is confirmed by the fact that there is no effect of oxygen flow rate between 50 and 300 ml/min for all the experiments displayed in Figs. 2 and 6 (total cobalt concentration 0.2 M).

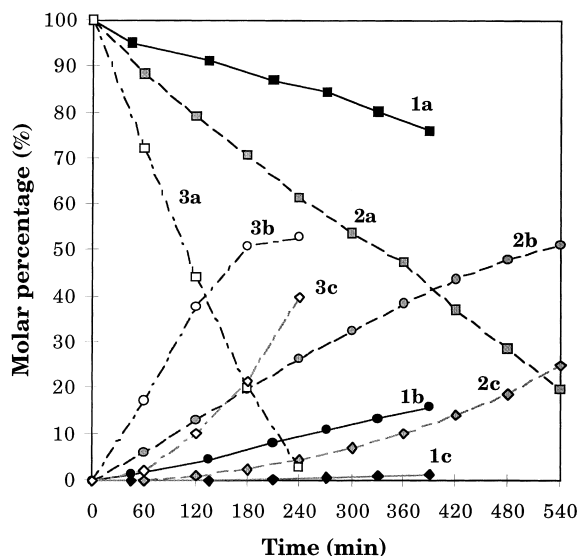


Fig. 6. Autoxidation of 4-methoxytoluene assisted by electrochemistry. Influence of the temperature on the reaction kinetics. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M) and $\text{Co}(\text{OAc})_2$ (0.2 M). $I=0.1$ A; Oxygen flow rate=300 ml/min. Curves 1 – 50°C ; curves 2 – 70°C ; curves 3 – 90°C . (a) 4-methoxytoluene; (b) *p*-anisaldehyde; (c) *p*-anisic acid.

3.2.3. The initial Co^{2+} concentration effect

Fig. 7 shows that under the same conditions of temperature, current intensity and oxygen flow rate, the increase of the initial Co^{2+} concentration provides a faster kinetics of the process. Thus, in the experiment using 0.44 M cobalt initial concentration (curves 1(a)–(d)), the aldehyde reaches its maximum (52%) after 105 min compared with 47% after 165 min in the experiment using 0.2 M cobalt initial concentration (curves 2(a)–(d)). The faster kinetics could be explained by the higher Co^{3+} concentration in the first case (Fig. 8, curves 1 and 3).

3.2.4. The oxygen flow rate effect

In the case of toluene autoxidation assisted by electrochemistry the oxygen flow rate has no effect on oxidation rate [6].

In the case of 4-methoxytoluene, at the higher initial concentration of $\text{Co}(\text{OAc})_2$ studied (0.44 M) the decrease of oxygen flow rate from 300 to 50 ml/min gives a slower kinetics (Fig. 9). Thus, the maximum of aldehyde is obtained after 105 min (52%) at 300 ml/min compared with 150 min (47%) at 50 ml/min. In

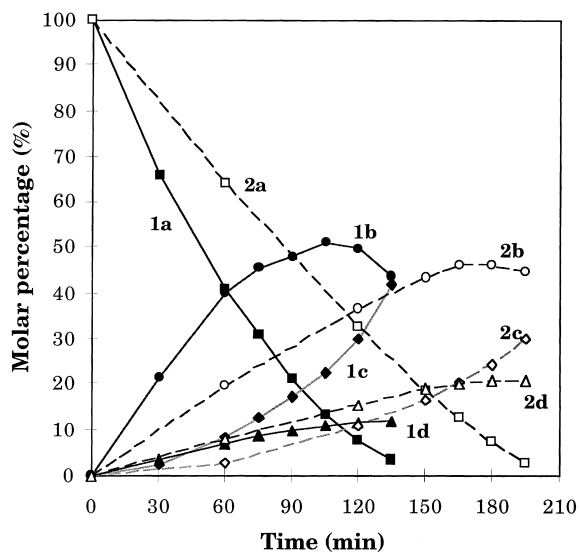


Fig. 7. Autoxidation of 4-methoxytoluene assisted by electrochemistry. Influence of the initial catalyst concentration. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M); $T=90^{\circ}\text{C}$; $I=0.9\text{ A}$; oxygen flow rate=300 ml/min. Curves 1 – $[\text{Co}(\text{OAc})_2]=0.44\text{ M}$; curves 2 – $[\text{Co}(\text{OAc})_2]=0.2\text{ M}$. (a) 4-methoxytoluene; (b) *p*-anisaldehyde; (c) *p*-anisic acid; (d) *p*-anisyl acetate.

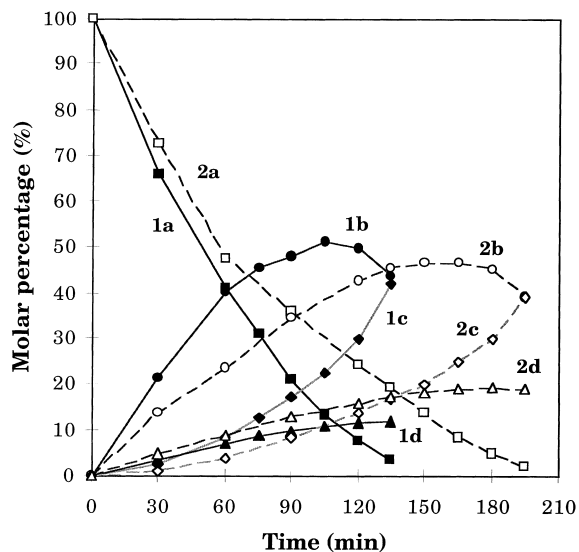


Fig. 9. Autoxidation of 4-methoxytoluene assisted by electrochemistry. Influence of the oxygen flow rate on the reaction kinetics. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M) and $\text{Co}(\text{OAc})_2$ (0.44 M); $T=90^{\circ}\text{C}$; $I=0.9\text{ A}$. Curves 1 – 300 ml/min; curves 2 – 50 ml/min. (a) 4-methoxytoluene; (b) *p*-anisaldehyde; (c) *p*-anisic acid; (d) *p*-anisyl acetate.

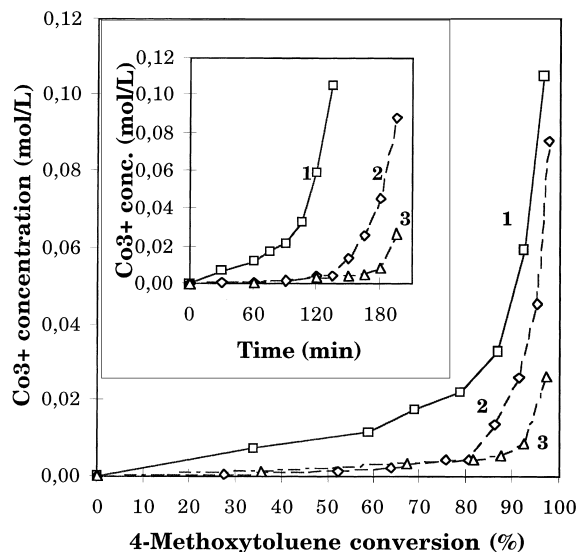


Fig. 8. Variation of Co^{3+} concentration during the autoxidation of 4-methoxytoluene. Acetic acid solution of 4-methoxytoluene (1 M) containing NaOAc (1 M); $T=90^{\circ}\text{C}$; $I=0.9\text{ A}$. 1 – $[\text{Co}(\text{OAc})_2]=0.44\text{ M}$; oxygen flow rate=300 ml/min. 2 – $[\text{Co}(\text{OAc})_2]=0.44\text{ M}$; oxygen flow rate=50 ml/min. 3 – $[\text{Co}(\text{OAc})_2]=0.2\text{ M}$; oxygen flow rate=300 ml/min.

this case (0.44 M cobalt initial concentration, 90°C , 0.9 A) the chemical reaction rate in the solution is high enough so that the transfer rate of molecular oxygen into the liquid phase given by

$$\text{NO}_2 = K_L(C_{\text{O}_2}^* - C_{\text{O}_2}^{\text{bulk}}) \quad (12)$$

($C_{\text{O}_2}^*$: equilibrium molar concentration of O_2 in the liquid phase; $C_{\text{O}_2}^{\text{bulk}}$: oxygen molar concentration in the bulk of the liquid phase; K_L : overall liquid phase transfer coefficient) becomes the limiting step of the process.

One can say that in experiments corresponding to curves 1 and 2 in Figs. 8 and 9 the production rate of Co^{3+} by electrolysis is practically the same; indeed, the values of the current are the same and the Co^{2+} concentrations are of the same order: $0.44-0.01=0.43\text{ M}$ in experiment 1 and $0.44-0.005=0.435\text{ M}$ in experiment 2 (Fig. 8). In these conditions it is assumed that a decrease in the oxygen flow rate favours the parallel reaction (6) with respect to reaction (3). Thus, step (7) is favoured, that increases the acetate yield (Fig. 9, curves 1(d) and 2(d)).

Fig. 8 shows that the Co^{3+} concentration increases as the flow rate of oxygen increases (curves 1 and 2, Fig. 8). This higher value of Co^{3+} concentration allows to explain the higher rate of the aldehyde formation (curves 1(b) and 2(b), Fig. 9) via steps (3) and (4).

4. Conclusion

This work shows that electrochemical initiation and assistance of toluenes autoxidation is an alternative with reference to classical process providing a faster kinetics and avoiding the use of bromide and formation of halogenated by-products.

The role of electrolysis is to avoid the long latency period in producing the active form of the catalyst and to maintain the Co^{3+} /total Co ratio to a suitable level during the reaction. However, in the case of 4-methoxytoluene the increase of the current produces a double activation which results in a higher yield in acetate production. For the lower values of the current intensity the acetate formation is of the same order than the purely chemical oxidation.

The main part in products formation is due to the chemical reaction by molecular oxygen. The oxidation rate of 4-methoxytoluene depends both on oxygen transfer rate and on Co^{3+} concentration. In the case of toluene the limiting step is purely kinetic.

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