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Electrochemical oxidation of toluene promoted by OH radicals

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Benzaldehyde can be produced from toluene by an electrochemical process involving OH radicals. In the cathodic compartment of the electrolytic cell the reduction of molecular O_2 and of a metal ion M^{OX}, are simultaneously carried out in the presence of a toluene suspension. M^{OX} is the oxidized form of a redox couple such as V(V)/V(IV), V(IV)/V(III), Cu(II)/Cu(I); the electrogenerated H_2O_2 and the reduced metal ion generates OH radicals and M^{OX}, which is converted back to the reduced form at the electrode. The reactivity of the redox couples examined were compared from the point of view of their effectiveness for the toluene oxidation process. In some cases, current yields very close to the theoretical ones could be obtained.

1. Introduction

The generation of an oxygen-containing functional group in benzene and its methyl substituted derivatives via electrochemically generated Fenton reagent have been reported in preceding papers [1–3]. The production of OH radicals from H_2O_2 and Fe(II), simultaneously generated by cathodic reduction of molecular oxygen and Fe(III), when carried out in the presence of aromatic hydrocarbons, starts an activation process (molecule → radical) of the organic substrate (usually OH addition and/or hydrogen abstraction).

The coupling of the substrate-derived radical with the molecular oxygen generates a peroxy radical which leads to the final products, for toluene mainly benzaldehyde and, in some cases, a smaller amount of benzyl alcohol.

The electrochemical and chemical processes occurring in the course of the electrolysis can be summarized as follows:

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \qquad (1)$$

$$M^{OX} + e \longrightarrow M^{red} \qquad (2)$$

$$M^{red} + H_2O_2 \xrightarrow{k_3} M^{OX} + OH + OH^- \qquad (3)$$

$$\text{OH + Toluene} \rightarrow \text{Benzaldehyde, benzyl alcohol} \qquad (4)$$

$$OH + M^{red} \xrightarrow{k_5} M^{OX} + OH^-. \qquad (5)$$

2. Experimental procedures

All chemicals used were reagent grade products; water and mercury were twice distilled. The electrochemical cell was equipped with a platinum counter electrode, and a saturated calomel reference electrode, while the cathode was either a 45 mesh Pt net (5% Ir) or a mercury pool (surface $\simeq$ 10 cm^2). The cathodic compartment (separated from the anode by a salt bridge) was filled with 20 cm^3 of toluene to which 25 cm^3 of aqueous acid solution, containing the redox couple, were added. This solution was stirred at a constant speed with a magnetic stirrer to obtain a fine suspension and was maintained O_2 saturated by a slow stream of high purity oxygen. After electrolysis the reaction mixture was neutralized by $NaHCO_3$ and the organic layer was analysed by gas phase chromatography. The chromatographic column (300 x 0.4 cm; 160°) was packed with diethyleneglycol succinate (LAC 728) and the carrier gas was

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N_2 (48 $cm^3 min^{-1}$). Benzonitrile was used as an internal standard.

3. Results

The range of electrode potentials at which Reactions 1 and 2 occur are reported in Fig. 1 for our experimental conditions; M^{OX}/M^{red} is one of the couples Cu(II)/Cu(I), V(V)/V(IV), V(IV)/V(III). From these data it appears that there is the possibility of running Reactions 1 and 2 simultaneously. The results obtained with different systems are reported below.

Table 1. Current yield of benzaldehyde in the system Cu^{++}–O_2–Toluene. 50°C Total charge passed 250 C

[Cu^{++}], M	*Electrode*	*Acid*	*% Yield*
5×10^{-3}	Hg	H_2SO_4*	9.7
10^{-2}	Hg	H_2SO_4	8.2
5×10^{-3}	Pt	H_2SO_4	11.8
10^{-2}	Pt	H_2SO_4	10.3
10^{-3}	Hg	HCl†	20.5
5×10^{-3}	Hg	HCl	20.6
10^{-2}	Pt	HCl	8.1
5×10^{-3}	Pt	HCl	7.2

* 0.5 mol dm^{-3}.
† 1 mol dm^{-3}.

3.1. *Cu^{++}–O_2–H_2SO_4–Toluene*

In H_2SO_4 solutions Cu^{++} ions are reduced to metallic copper at a potential of about 0.0 V vs SCE. In the presence of toluene and of the electrogenerated H_2O_2 the electrochemical and chemical processes result in the oxidation of toluene to benzaldehyde; benzyl alcohol and benzoic acid were not detected in the reaction mixture. The aldehyde yields are close to 10%, see Table 1, and depend on the nature of the electrode material. These low yields may be due to a particularly high reactivity of OH radicals with the copper redox system.

With a platinum electrode the efficiency of benzaldehyde production is higher than with a mercury electrode. Furthermore the oxidation of toluene is only possible with the simultaneous generation at the electrode of H_2O_2 and M^{red}. No toluene oxidation product was detected during the electrolysis of the systems toluene–O_2 and toluene–M^{OX}.

3.2. *Cu^{++}–O_2–HCl–Toluene*

In supporting electrolytes containing HCl the reduction of the Cu^{++} occurs stepwise in two monoelectronic steps; the first one, which starts at about 0.0 V vs SCE, leads to a cuprous ion. This Cu(I) species reacts with the H_2O_2 produced simul-

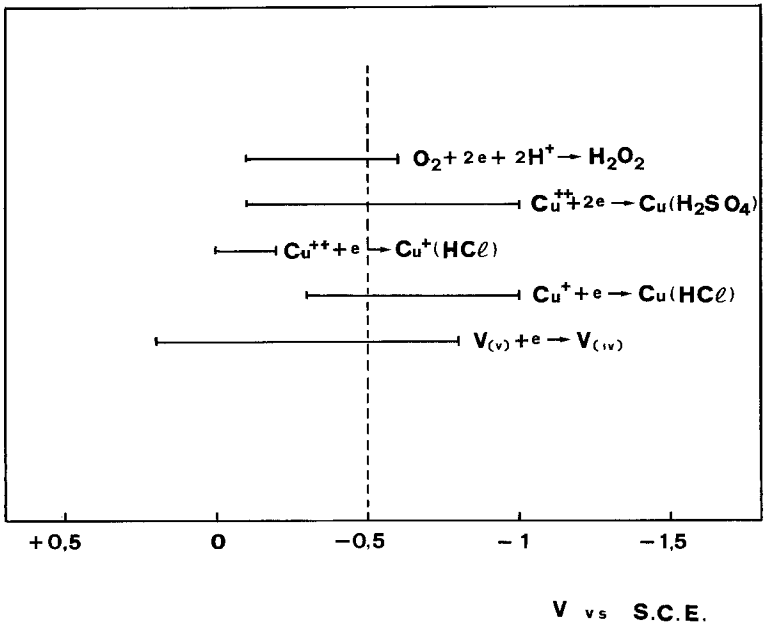

Fig. 1. Range of electrode potential available on a mercury cathode for the electrochemical processes utilized in this work (full lines). The dotted line indicates the limiting value of the cathodic potentials attainable with a Pt electrode.

taneously with a kinetic rate constant k_3 equal to 58 $dm^3 mol^{-1} s^{-1}$ [4], giving rise to a catalytic electrochemical process, because of the increase of the rate of Reaction 2. The benzaldehyde yields obtained in aqueous HCl media and on a mercury electrode are considerably higher than those obtained with the same system in H_2SO_4 solution, see Table 1.

3.3. VO_2^+–O_2–*Toluene*

As shown in Fig. 1 the reductions

$$V(V) \xrightarrow{e} V(IV)$$

and

$$O_2 \xrightarrow[H^+]{2e} H_2O_2$$

can be carried out in acid solution at the same electrode potential. Furthermore, the Reaction between V(IV) and H_2O_2 occurs with a high rate [5] and therefore this system appears to be a potential source of HO radicals (which can be utilized to oxidize toluene). The efficiency of this system in the oxidation of aromatic hydrocarbons is clearly shown by the data of Figs. 2 and 3.

In particular, for the experiments in 0.5 mol dm^{-3} H_2SO_4 and with a mercury cathode the plot of the yields vs $[VO_2^+]$ gives two maxima at concentrations of 2 mmol dm^{-3} (100% yield) and of 6 mmol dm^{-3} VO_2^+ (~90% yield).

The first maximum is obtained when $i_{O_2} = 2i_{VO_2^+}$ (i_{O_2} and $i_{VO_2^+}$ are the currents for the reduction of oxygen and pervanadyl ions, respectively) and a similar maximum is observed for the OH radical promoted oxidation of toluene in the system Fe(III)/H_2O_2/H_2SO_4 [2]. In fact, when this condition is attained, H_2O_2 and VO^{++} are produced at the electrode with a ratio 1:1 (see equation 3). The experimental yields above or below the maximum correspond to an excess in the production (and, as a consequence, in a current wastage) of one of two reactant namely H_2O_2 or VO^{++}.

The second maximum may indicate the occurrence of an equilibrium between free pervanadyl ions and its polymers [6], characterized by a dif-

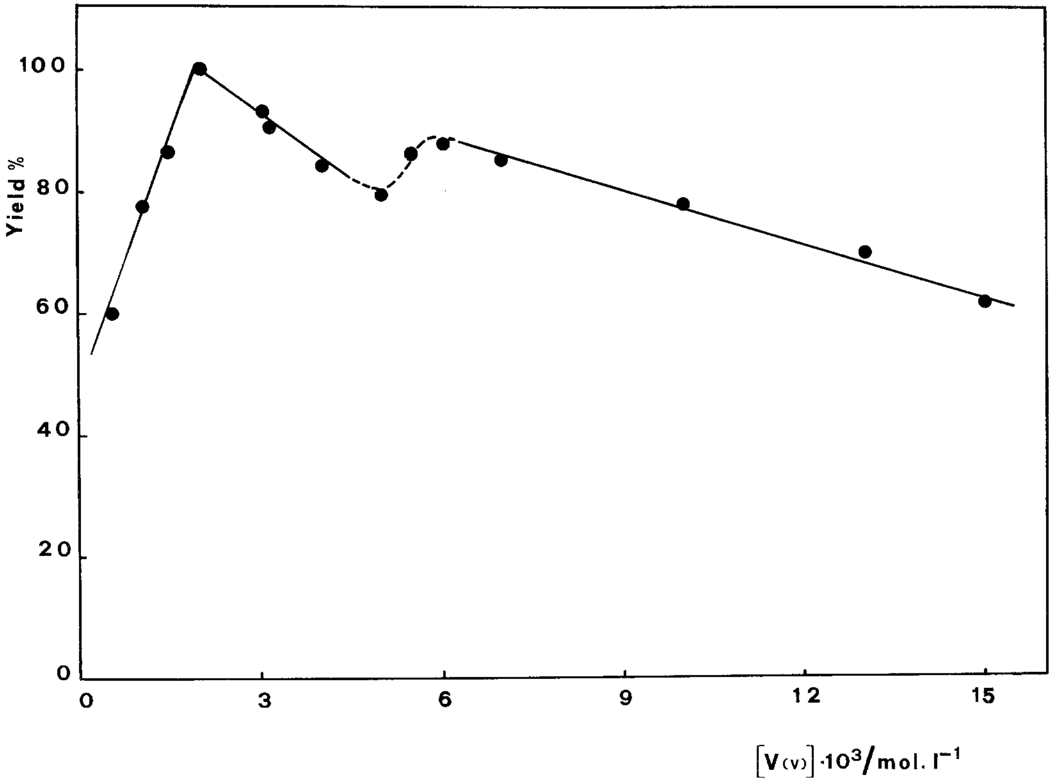

Fig. 2. Current yield of benzaldehyde vs [V(V)] in 0.5 mol dm^{-3} H_2SO_4; 50° C; $E = -0.5$ V vs SCE; Hg electrode. Total amount of charge 250 C.

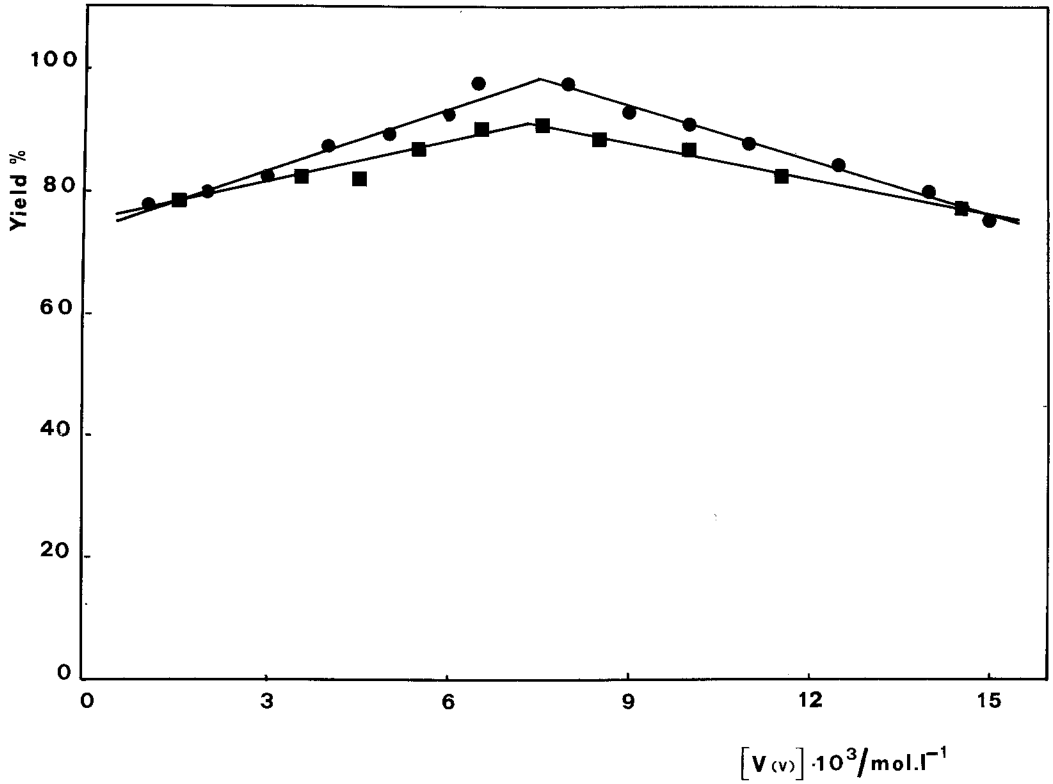

Fig. 3 Current yield of benzaldehyde vs [V(V)] in 1 mol dm^{-3} HCl. $t = 50°$ C • Pt electrode; $E = -0.1$ V vs SCE. ▪ Hg electrode; $E = -0.4$ V vs SCE. Total amount of charge 250 C.

fusion coefficient much lower than that of the free ion.

The curves of the yields obtained in 1 mol dm^{-3} HCl as a function of VO_2^+ concentration reported in Fig. 3 are characterized by a maximum at $[VO_2^+]$ about 7.5 mol dm^{-3}, independent of the nature of the electrode material. Knowledge of the nature and the properties of the complexes formed between VO_2^+ ions and chloride ions in acid solution is inadequate to explain this effect. Moreover the initial formation of polymeric vanadium ions in hydrochloric acid may give a qualitative explanation of the shift of the maximum yield toward higher VO_2^+ concentrations, see Figs. 2 and 3.

3.4. *VO^{++}-Cu^{++}-O_2-Toluene*

This system has also been used for the production of OH radicals because of the good results obtained in the study of toluene amination by NH_2 radicals [7] and of the oxidizing properties of Cu^{++} ions towards organic radicals [8]. According to Fig. 1, carrying out the electrolysis of this system at −0.1 V and at −0.35 V vs SCE the primary reaction products are Cu^+, H_2O_2 and Cu, H_2O_2.

However, in the presence of sufficiently high concentrations of VO^{++}, which at the above electrode potentials is not electroactive, the following reactions may occur:

$$Cu^+ + VO^{++} \xrightarrow[H^+]{k_6} Cu^{++} + V^{3+} + H_2O \quad (6)$$

$$Cu + 2VO^{++} \xrightarrow[H^+]{k_7} Cu^{++} + 2V^{3+} + 2H_2O. \quad (7)$$

In this way V^{3+} is produced chemically instead of reduced copper species. To obtain a better insight into these systems, the kinetic rate constants of Reactions 6 and 7 have been measured using the electrochemical method of catalytic currents.

3.4.1. Kinetic rate constant of Cu^+ oxidation by VO^{2+}.

In Fig. 4 the $\bar{i}_l/\bar{i}_d$ ratio is reported for different values of $[VO^{2+}]^{1/2}$, where $\bar{i}_l$ and $\bar{i}_d$ are

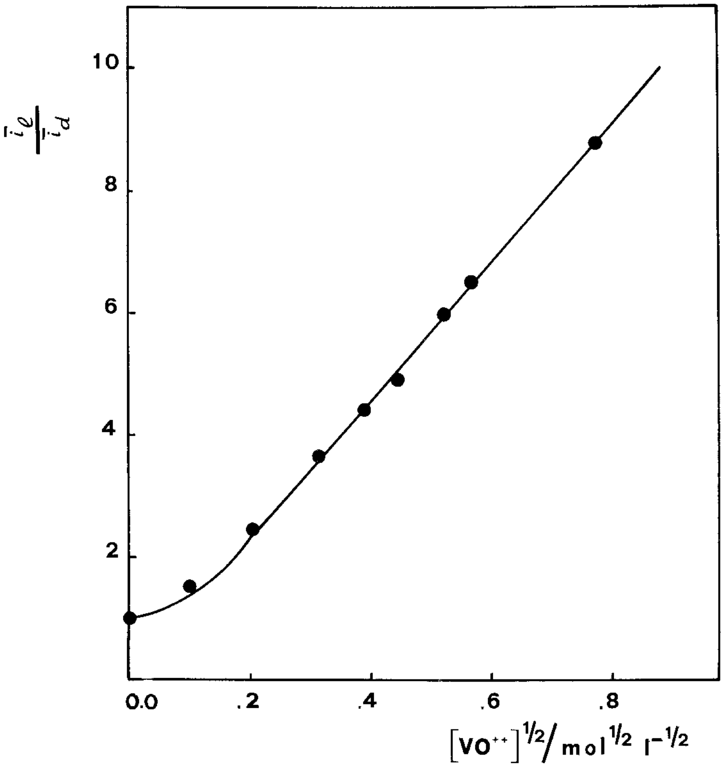

Fig. 4. Dependence of the ratio $\bar{i}_l/\bar{i}_d$ on $[VO^{++}]$ for the electrode reaction $Cu^{++} + e \rightarrow Cu^{+}$ in 1 mol dm^{-3} HCl; 50° C; $[Cu^{++}] = 5 \times 10^{-4}$ mol dm^{-3}; drop time of the mercury electrode: 2.95 s.

the mean limiting currents for the process $Cu^{++} + e \rightarrow Cu^{+}$ measured in the presence and in the absence of VO^{++}, respectively. According to Koutecky [9], in the presence of an excess of VO^{++} (pseudo first order conditions) we may write:

$$\frac{\bar{i}_l}{\bar{i}_d} = 081\,\{\alpha k_6[VO^{++}]t\}^{1/2} \qquad (8)$$

where α is the stoichiometric coefficient for the oxidation of Cu^{+} by VO^{++} species in HCl media. In this case, $\alpha = 1$, and t is the drop time of the mercury electrode. By this procedure, from the slope of the linear part of the plot of Fig. 4 a k_6 value of 67.5 dm^3 mol^{-1} s^{-1} has been calculated.

3.4.2. Kinetic rate constant of copper oxidation by VO^{++}. The dependence of the $\bar{i}_l/\bar{i}_d$ ratio for the electroactive couple Cu^{++}/Cu on the VO^{++} concentration is reported in Fig. 5 for the parallel processes described by equation $Cu^{2+} + 2e \rightarrow Cu$ and by Equation 7, occurring at −0.35 V vs SCE in HCl media.

On the basis of Equation 8 (which holds still but with $\alpha = 0.5$) and from the data of Fig. 5 a k_7 value of 357 dm^3 mol^{-1} s^{-1} has been calculated.

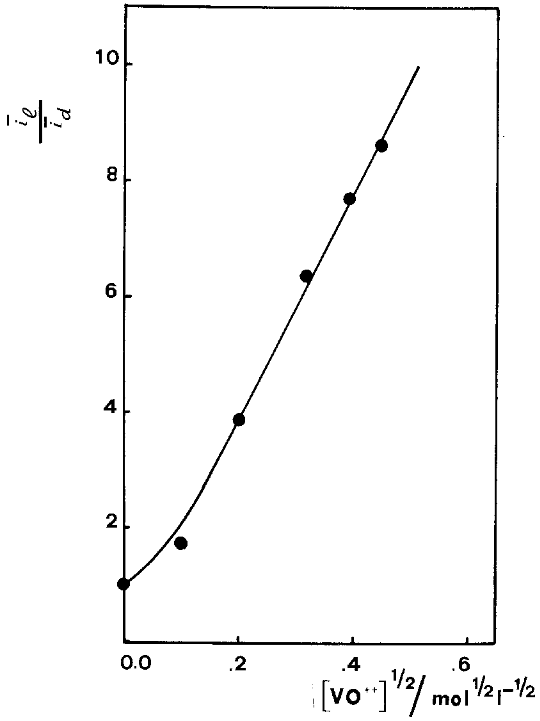

Fig. 5. Dependence of the ratio $\bar{i}_l/\bar{i}_d$ on $[VO^{++}]$ for the electrode reaction $Cu^{++} + 2e \rightarrow Cu$ in 1 mol dm^{-3} HCl; 50° C; $[Cu^{++}] = 5 \times 10^{-4}$ mol dm^{-3}; drop time of the mercury electrode: 3.25 s.

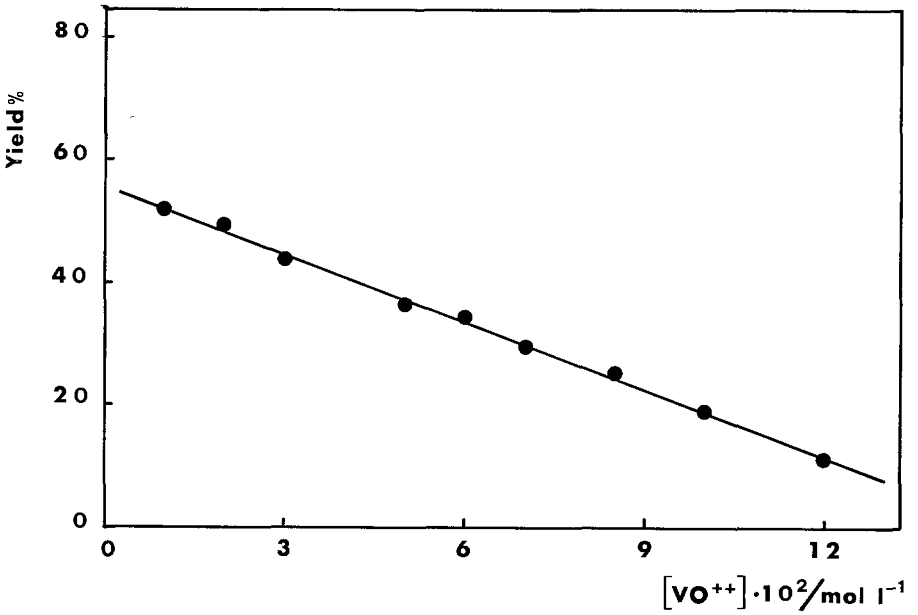

Fig. 6. Current yield of benzaldehyde vs [VO^{++}] for the system $Cu^{++}/VO^{++}/O_2$ on Pt electrode in 1 mol dm^{-3} HCl. [Cu^{++}] = 10^{-3} mol dm^{-3}. $E = -0.1$ V vs SCE. 50° C.

3.5. *Oxidation of toluene by OH radicals generated via Cu^{++}–O_2–VO^{++} system*

In this system, OH radicals can be generated from H_2O_2 reduction by Cu^+, Cu or V^{3+}. In fact in HCl medium, k_6 is equal to or higher than k_3, and since [VO^{++}] $\gg$ 10[H_2O_2] under our experimental conditions, OH radicals should be produced mainly by the reaction:

$$V(III) + H_2O_2 \longrightarrow V(IV) + OH + OH^- \quad (9)$$

when the Reactions 2 and 6 are carried out in the

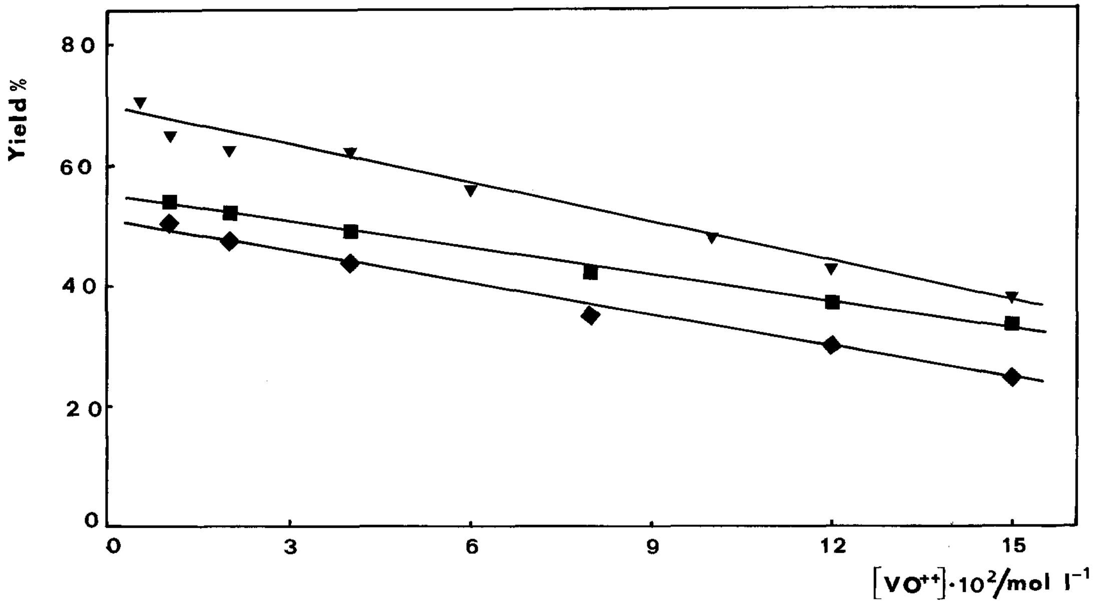

Fig. 7. Current yield of benzaldehyde vs [VO^{++}] for the system $Cu^{++}/VO^{++}/O_2$ on Pt electrode in 1 mol dm^{-3} HCl. [Cu^{++}] = 10^{-3} mol dm^{-3}. $E = -0.33$ V vs SCE. t: ◆ 20; ■ 35; 50° C.

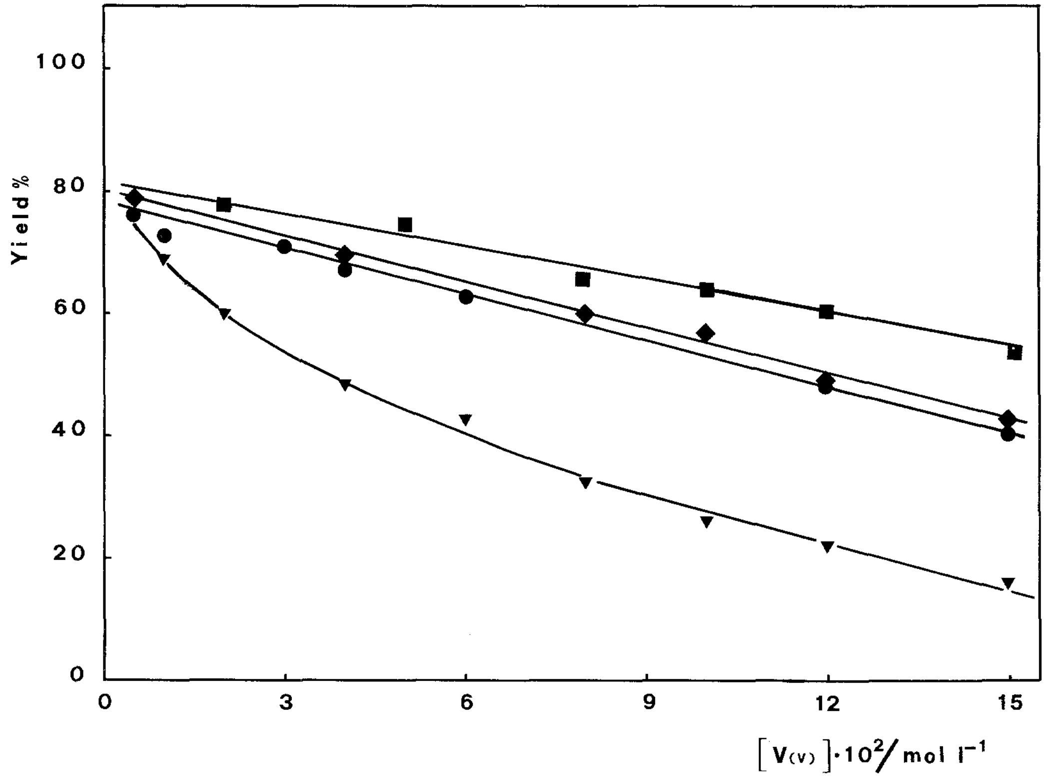

Fig. 8. Current yield of benzaldehyde vs [VO^{++}] for the system Cu^{++}/VO^{++}O$_2$ on Hg electrode. [Cu^{++}] = 10^{-3} mol dm^{-3}; $t = 50$°C $E = -0.5$ V vs SCE [HCl]: ■ 0.25; ● 0.5; ♦ 1; ▼ 2 mol dm^{-3}.

presence of molecular oxygen. The addition of toluene to these systems leads to benzaldehyde formation, as expected. Plotting vs the VO^{++} concentration the yields of the aldehyde produced at an electrolysis potential corresponding to the e and 2e reduction of the cupric species, the curves reported in Figs. 6 to 9 were obtained for different experimental conditions.

From these figures it appears that the highest yields, in the range 50–80%, are obtained with 5 mmol dm^{-3} VO^{++} and are slightly dependent on the experimental conditions.

In particular in HCl media, increasing the electrolysis temperature from 20 to 50° C increases the yields from 50 to 70% (at [VO^{++}] = 10^{-2} mol dm^{-3}) while other experimental parameters such as [HCl], nature of the electrode materials and the primary reduction process barely influence the toluene oxidation yield.

4. Conclusions

A common feature of the electrochemical systems we have studied is the simultaneous cathodic reduction of molecular oxygen and of M$^{\text{OX}}$ to H_2O_2 and M$^{\text{red}}$, respectively, which is followed by a Fenton-type reaction, see Equation 3, resulting in OH radical production. Since the M$^{\text{red}}$ and H_2O_2 concentrations are in the range 10^{-3} to 10^{-2} mol dm^{-3} and the k_3 values are of the order of 50 dm^3 mol^{-1} s^{-1}, the generation of OH radicals should occur in the bulk of the solution. Therefore these electrochemical systems can be compared with homogeneous chemical systems generating OH radicals as, for instance, Fenton reagent.

In the presence of toluene the OH radicals oxidize the $-CH_3$ group to $-CHO$ with 100% selectivity. In fact for the electrochemical systems studied in this paper no product other than benzaldehyde could be detected either with gas chromatographic or with mass spectrometry techniques.

A comparison of the results shows that vanadium salts are the most efficient catalysts for the oxidation of toluene to benzaldehyde via electrochemically generated hydrogen peroxide.

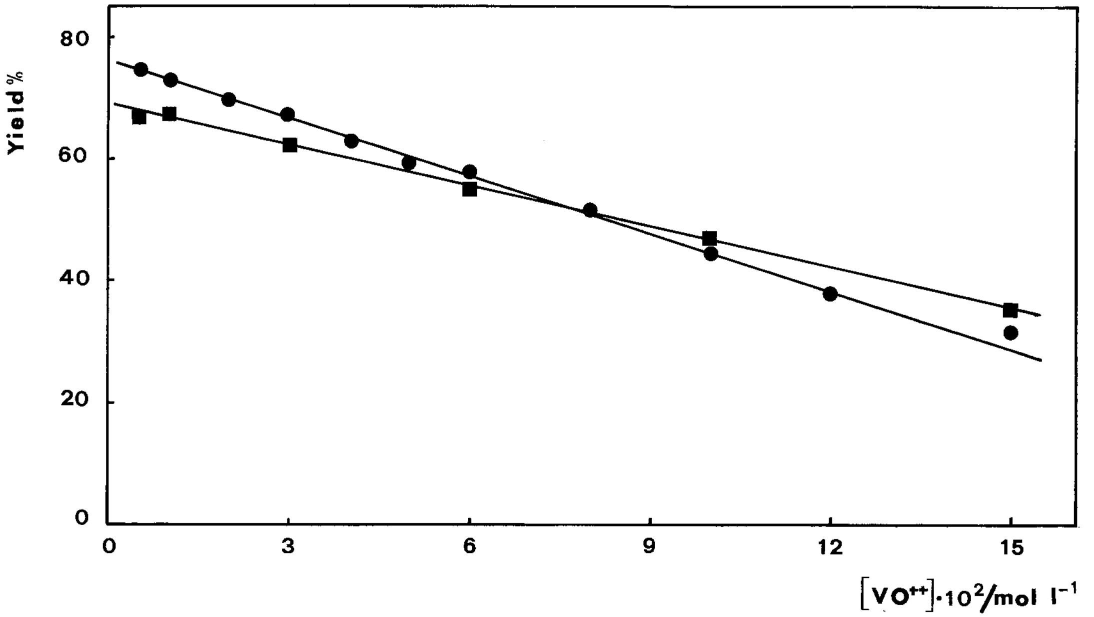

Fig. 9. Current yield of benzaldehyde vs [VO^{++}] for the system $Cu^{++}/VO^{++}/O_2$ in 0.5 mol dm^{-3} H_2SO_4. [Cu^{++}] = 10^{-3} mol dm^{-3}; 50° C; ● Hg electrode $E = -0.5$ V vs SCE. ■ Pt electrode $E = -0.33$ V vs SCE.

In fact the maximum yields range from about 50% for the couple V(IV)/(V(III) to about 100% for the couple V(V)/V(IV). A higher current yield is obtained with these systems than with those based on indirect toluene oxidation using such inorganic redox couple as Mn(III)/Mn(II) [10], Ce(IV)/Ce(III) [11] or Ag(II)/Ag(I) [12].

In spite of the very high yield and selectivity of benzaldehyde production using V(IV) ions, however, the low oxygen solubility in the reaction media (about 10^{-3} mol dm^{-3}) leads to a low volume yield in the electrochemical cell. A possible way to overcome this limiting characteristic would be to add the hydrogen peroxide from outside into the electrolysis cell.

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