Electrochemical production of OH· radicals and their reaction with toluene

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The reaction between electrochemically generated Fenton's reagent and toluene was studied. The products arising from this reaction system were consistent with a primary hydrogen atom abstraction from the methyl group of toluene to give benzyl radicals.

Benzaldehyde was obtained with a current yield higher than 60%; benzyl alcohol was also produced in smaller quantities in some experiments. The dependence of the yields on reagent concentrations, temperature and coulombs passed was examined. On the basis of the experimental results a mechanism is proposed involving peroxy and alkoxy radicals as intermediates.

1. Introduction

The interaction between benzene and OH· radicals produced as intermediates in the reaction between Fe^{2+} and H_2O_2 has been investigated by many authors [1–3]. It was shown that the formation of phenol and biphenyl involves the direct addition of the radicals to the aromatic ring, followed by oxidation of the adduct, or by its dimerization and dehydration. In a previous work [4], OH· radicals were produced by the simultaneous electrolysis of Fe(III) and oxygen at a mercury cathode. In this way phenol was produced with high selectivity. Moreover from the literature data it appears that the reaction between OH· radicals and toluene has been not extensively investigated. It was reported that when hydrogen peroxide is added to a stirred suspension of toluene in dilute sulphuric acid containing ferrous sulphate [3], the toluene undergoes both nuclear OH· addition and hydrogen abstraction on the side chain.

The aim of this work was to investigate the oxidation of toluene by OH· radicals in view of a preparative application of the electrochemically generated Fenton's reagent. The production of this reagent, by simultaneous electrolysis of Fe(III)

and O_2 in aqueous acid solutions, is proposed bearing in mind that, under these conditions, a controlled rate of radical production is obtained.

2. Experimental

2.1. Chemicals

Sulphuric and perchloric acid, ferric and sodium sulphates, toluene and other chemicals used were reagent grade products. 99·99% oxygen was employed to saturate the solutions. Water and mercury were twice distilled.

2.2. Apparatus and procedure

Voltammetric data were obtained by a multi-function unit (model 563 (Amel)) in a thermostated polarographic cell equipped with a dropping mercury electrode, a platinum counter electrode and a saturated calomel electrode as reference.

Controlled potential electrolyses were performed with a model 557 potentiostat–galvanostat (Amel); the transferred charge was determined by means of a model 558 integrator (Amel).

In the course of the electrolysis the cathodic

compartment (thermostated) was separated from the anode by a salt bridge. The mercury pool electrode was stirred at a high enough speed to realize a fine suspension of toluene in the aqueous phase. The speed of the stirrer (magnetic) was maintained constant in all the experiments.

The electrolysis were performed at a potential corresponding to the polarographic limiting current for Fe(III) and O_2 reduction, at -0.2 V versus S.C.E.

To limit the wastage of the primary products by consecutive reactions with the continuously generated radicals, a large excess (20 ml) of toluene was added to 25 ml of the aqueous solution. To the reaction mixture, after electrolysis, 3 g of sodium sulphate were added to reduce the solubility of the organic products in the aqueous phase. It was previously checked that, under these conditions, no loss of products occurred. Aliquots of the toluene phases, to which benzonitrile was added as an external standard, were analysed by G.L. chromatography. A 'Fractovap' GV gas-chromatograph (C. Erba) was employed, equipped with a hydrogen-inject flame ionization detector. The column (100 x 0.5 cm) was packed with Carbowax 20 M (10% by weight) on Chromosorb W (80–100 mesh) and was operated at 180°C. The carrier-gas was nitrogen (50 ml min^{-1}). Retention times were (in s): benzaldehyde 270, benzonitril 362, benzyl alcohol 815.

In the course of the experiments the reaction mixtures were analysed also on a second column (200 x 0.5 cm) packed with LAC 446 (10% by weight) and 85% phosphoric acid (2% by weight) on Chromosorb W (60–80 mesh) at 180°C. This column, which is not suitable to resolve the peaks of benzaldehyde and benzyl alcohol, was used to investigate if benzoic acid or other products arising both from nuclear hydroxylation and dimerisation of the intermediate [3], were formed. Relative amounts of materials were determined measuring the peak areas generated by the chromatograph detector by means of a Hewlett–Packard 3373 B automatic electronic integrator. Unless otherwise stated the reported experimental results were obtained by carrying out the electrolysis at 50°C.

3. Results and discussion

The following reduction processes take place simultaneously in aqueous acid solution at a working potential of -0.2 V versus SCE:

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2.$$
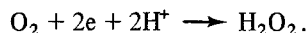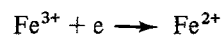
The ferrous iron and the hydrogen peroxide react along the pathway:

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + OH^{\cdot} + OH^-. \quad (1)$$
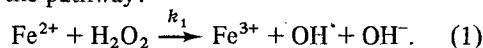
The generated OH$^{\cdot}$ radicals can be reduced by Fe^{2+}:

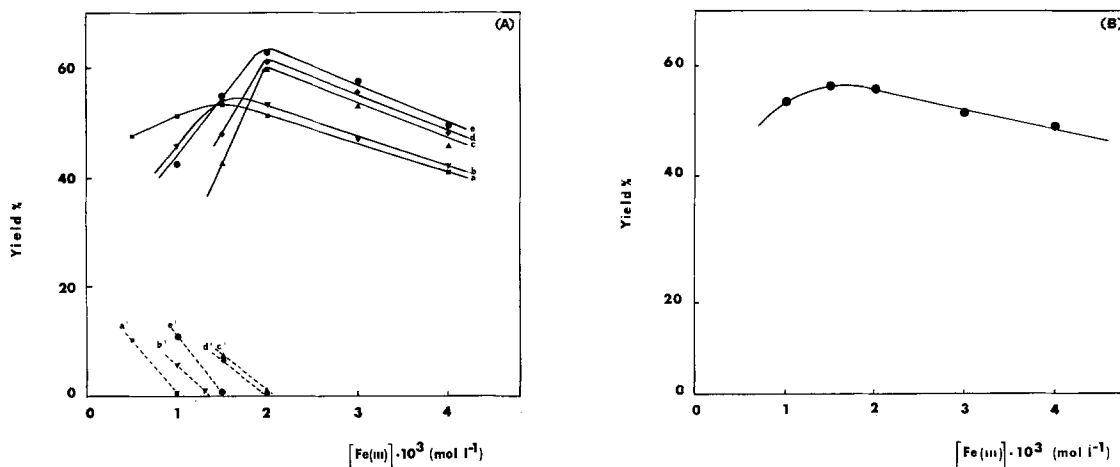$$OH^{\cdot} + Fe^{2+} \xrightarrow{k_2} OH^- + Fe^{3+} \quad (2)$$

Fig. 1. % current yields in benzaldehyde and benzyl alcohol production against Fe(III) bulk concentration at 50°C. Total amount of charge 150 coulombs. (a) H_2SO_4; (■) 0.1 M; (▼) 0.3 M; (●) 0.5 M; (♦) 0.7 M; (▲) 1 M; Curves a, b, c, d, e: benzaldehyde; Curves a', b', c', d', e': benzyl alcohol. (b) Benzaldehyde produced in $HClO_4$ 0.5 M.

(with $k_2 > k_1$) or react with other components of the solution. Moreover, when the Fenton's reagent is used, for instance, to oxidize some organic compounds, the competitive Reaction 2 always limits the yields to a lower value than the theoretical one.

In our experimental conditions the gas chromatographic analysis revealed the production in detectable amounts only of benzaldehyde and benzyl alcohol. Neither products arising from the hydroxylation of the aromatic ring, such as cresol or hydroxybenzaldehyde, nor more oxidized species such as benzoic acid were detected.

Species arising from dimerization processes such as bitolyl or bibenzyl were also absent in the reaction mixtures.

In Fig. 1a the current yields of benzaldehyde and benzyl alcohol as a function of initial Fe(III) bulk concentration are reported for different H_2SO_4 concentrations. As previously reported [4], these yields are expressed on the basis of a consumption of 3 F mol^{-1} of products, since three electrons are engaged in the simultaneous reduction of O_2 and Fe(III).

From Fig. 1a one can conclude that the maximum yields were obtained for an O_2 concentration of about 10^{-3} M, at a Fe(III) concentration of 2×10^{-3} M in the experiments carried out with $[H_2SO_4] \geqslant 0.5$ M. This indicates, on account of the diffusion coefficients of O_2 (2.6×10^{-5} cm^{2}s^{-1}) and Fe^{3+} (0.6×10^{-5} cm^{2}s^{-1}), that the minimum OH˙radical loss occurs when the molar ratio between Fe(II) and H_2O_2 produced at the electrode is 1:1.

In fact for $[H_2O_2] < [Fe(II)]$ and for $[H_2O_2] > [Fe(II)]$, OH˙radicals are lost both [5, 6] in the Reactions 2 and in:

$$OH˙ + H_2O_2 \longrightarrow H_2O + HO_2˙. \qquad (3)$$
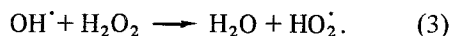
One can also conclude from the curves of Fig. 1a that the yields increase when the H_2SO_4 concentration is increased from 0.1 to 0.5 M while for more concentrated solutions (0.7–1 M) the yields decrease.

In their studies of the effect of sulphuric acid and sulphate ions on the oxydation of Fe(II) by H_2O_2, Wells and Salam [7, 8] showed that, at pH values below 3, the bimolecular rate constant k_1 of this reaction increases with the concentration of the sulphate ions until a limiting value is reached.
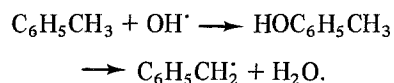
Using these data, the decrease of the yields observed with increasing H_2SO_4 concentrations at a $[H_2SO_4]$ higher than 0.5 M can be explained on the basis of a decreased toluene solubility and consequently in a larger wastage of OH˙radicals by Reaction 2 or by reaction with sulphate ions [9, 10]. In Fig. 1b, the yields of benzaldehyde, obtained in diluted solutions of perchloric acid are plotted. This curve is quite similar to those obtained for $[H_2SO_4] \leqslant 0.3$ M, see Fig. 1a. As a consequence the difference between the curves a, b and c, d, e of Fig. 1a could be ascribed to a different reactivity between Fe^{2+} and FeSO$_4$ at high SO$_4^{2-}$ concentrations [7, 8].

A remarkable feature of the reaction of toluene with the electrochemically generated Fenton's reagent is the very high selectivity in the methyl group oxidation, since under our experimental conditions no product of aromatic ring hydroxylation was detected. It is interesting to look into the distribution of the three possible products of methyl group oxidation: benzyl alcohol, benzaldehyde and benzoic acid. The experimental data show the absence of the latter compound and a molar ratio of benzyl alcohol/benzaldehyde decreasing from 0.2 to 0 with increasing concentration of electrogenerated Fe(II). Moreover the disappearance of benzyl alcohol occurs at a Fe(II) concentration corresponding to the maximum yield of benzaldehyde (see Fig. 1a). This product distribution, considering the very high ratio of [toluene]/[products], calls for a mechanism in which benzaldehyde is not formed through benzyl alcohol oxidation.
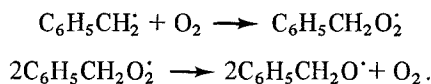
The probable reaction pathway involves a benzyl radical which can be formed by the direct hydrogen abstraction from a CH$_3$ group [11, 12]:

$$C_6H_5CH_3 + OH˙ \longrightarrow C_6H_5CH_2˙ + H_2O$$
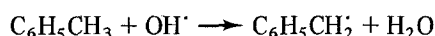
or by water elimination from an OH˙addition complex [13]:

$$C_6H_5CH_3 + OH˙ \longrightarrow HOC_6H_5CH_3$$
$$\longrightarrow C_6H_5CH_2˙ + H_2O.$$

Subsequent reactions are [14–22]:

$$C_6H_5CH_2˙ + O_2 \longrightarrow C_6H_5CH_2O_2˙$$
$$2C_6H_5CH_2O_2˙ \longrightarrow 2C_6H_5CH_2O˙ + O_2.$$

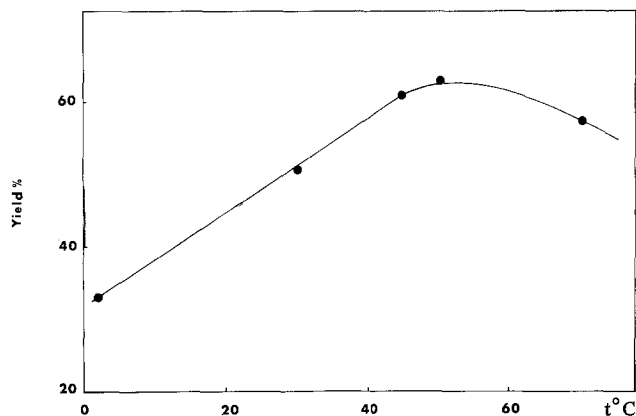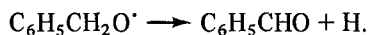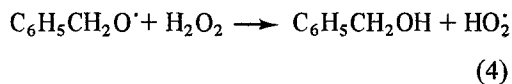It was suggested that disproportionation of the

Fig. 2. % current yield in benzaldehyde production at different temperatures. Total amount of charge 150 coulombs. $2 \cdot 10^{-3}$ M Fe(III), 0·5 M H_2SO_4.

alkoxy radicals gives benzyl alcohol and benzaldehyde [23]. However this step is not significantly operative under our experimental conditions since the molar ratio benzyl alcohol/benzaldehyde ranges from 0·2–0. Under these conditions benzyl alcohol and benzaldehyde should be formed in parallel reactions from the alkoxy radicals [23–24]:

$$C_6H_5CH_2O^{\cdot} + H_2O_2 \longrightarrow C_6H_5CH_2OH + HO_2^{\cdot}$$

$$(4)$$

$$C_6H_5CH_2O^{\cdot} \longrightarrow C_6H_5CHO + H.$$

Reaction 4 explains the detection of benzyl alcohol only for the case where H_2O_2 is electro-generated in excess over Fe(II) (i.e. conditions corresponding to the left hand sides of the curves of Fig. 1a). The experimental data showed a very small decrease of the benzaldehyde yield with increasing total amount of charge transferred. This means that the reaction between the primary products of toluene oxidation and the Fenton's reagent only occurs to a very limited extent. The identification of these secondary products was not possible because of their small quantities. In Fig. 2 the yields of benzaldehyde obtained in the electrolysis of solutions containing constant Fe(III) and H_2SO_4 concentrations at different temperatures are reported. It emerges that in the electrochemical generation of the Fenton's reagent the highest yield of benzaldehyde from toluene is obtained at a temperature of about 50°C.

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