Electrocatalytic production of OH radicals and their oxidative addition to benzene

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The feasibility of the electrochemical generation of Fenton's reagent is demonstrated and the subsequent reaction of produced OH radical with benzene studied. Under the proposed working conditions, phenol is obtained as the main product, with current yield as high as 60% (on the basis of 3 F/mole of phenol) and with only traces of other higher oxidized compounds. At fixed H_2SO_4 concentration and with suitable $[Fe^{3+}]/[O_2]$ ratio, a maximum in current yield is obtained; this yield may presumably be increased if continuous removal of phenol is employed during the electrolysis.

Introduction

There is ample evidence that in the reaction between Fe^{2+} and H_2O_2 (Fenton's reagent), in aqueous acid solution, the rate-determining step is the reaction 1 [1–7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (1)$$
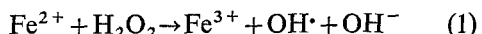
which is followed by

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^-. \quad (2)$$
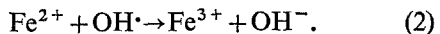
Other H_2O_2 decomposing reactions may occur if hydrogen peroxide is present in large excess over ferrous iron [3–4].

The occurrence of reaction 2 inevitably leads to a lower than theoretical oxidation yield when Fenton's reagent is employed in the oxidation of organic compounds.

Much is known on the oxidation of aromatic compounds by Fenton's reagent [8–11]; in this field Lindsay Smith and Norman [12] investigated the benzene (and toluene) oxidation in detail and concluded that the first step must be the addition of OH· radical to the aromatic nucleus, with formation of the resonance stabilized adduct (I) [13]:
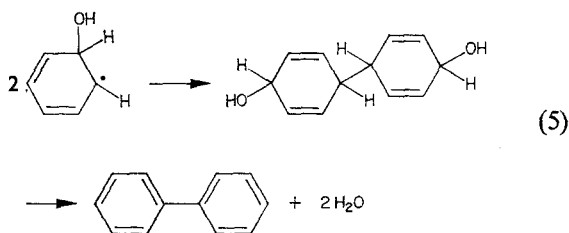

(3)

(I)
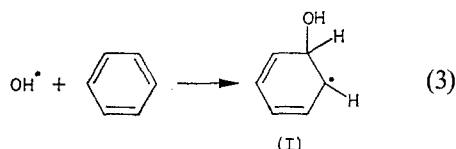
The adduct is then oxidized to phenol by ferric ions:

(4)
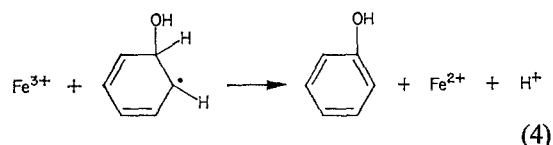
and, if oxygen is present, also by oxygen [14].

Another fate of radical (I) could be the formation of biphenyl [12] according to:

(5)

The conclusions of the cited authors are as follows. (a) Total yield (phenol + biphenyl)

depends on the initial ratio Fe^{2+}/H_2O_2; a maximum value is obtained if the ratio is 1. (b) Increasing the concentration of Fe^{3+} increases the phenol yield, but the total yield remains unaltered.

In our work, we have investigated the oxidative addition of $OH^{\bullet}$ to benzene, in the case in which the Fenton's reagent is electrochemically produced by simultaneous reduction of Fe^{3+} and O_2 in aqueous acid solution, so as to realize a controlled formation of $OH^{\bullet}$ radicals.

Experimental

Materials

H_2SO_4, Na_2SO_4, ether, benzene: 'RP' Erba Products. $FeNH_4(SO_4)_2.12$ H_2O: 'pro analysis' Merck product. O_2: compressed gas UPP SIO (99, 99%). Water and mercury: twice distilled.

Apparatus and procedure

Voltammetric data obtained with the DME and a conventional polarizing unit were recorded on a Sefram Graphispot. Controlled potential electrolysis and coulometric measurements were carried out with an Electronic Multipurpose Unit Mod. 563 (Amel, Milan).

The cathode compartment of the electrolysis cell was separated from the anode by means of a salt bridge; the working and reference electrodes were a Hg pool (stirred) and a S.C.E., respectively.

The electrolyses were carried out in a suspension of benzene (0·5 ml) in water (30 ml), with various concentrations of H_2SO_4 and Fe^{3+} and with continuous flow of oxygen (presaturated with benzene), so as to maintain constant oxygen concentration in every run (order of magnitude 10^{-3} M).

The working potential was always fixed at -0.35 V (versus S.C.E.): at this potential the reduction processes 6 and 7 were simultaneously realized:

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (6)$$

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \qquad (7)$$
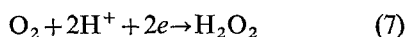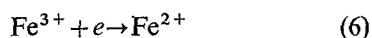
After electrolysis the reaction mixture was

extracted with ether (4 × 30 ml) and the ethereal solution was dried (Na_2SO_4), evaporated to 4–5 ml and analysed by gas chromatography, employing n-amyl alcohol as the internal standard. A 'Fractovap GV' gas chromatograph (Erba) was employed. The column (200 cm × 5 mm) was packed with diethylene-glycolsuccinate (LAC 728, 25% w/w) on Chromosorb W (60–80 mesh) and was operated at 170°C. The carrier gas was nitrogen (55 ml/min) at an inlet pressure of 45·5 cm Hg above atmospheric and with atmospheric pressure at the outlet. A H_2 flame ionization detector was employed in all measurements. The results quoted are mean values from three analyses each of two or more reaction mixtures obtained in each set of conditions. The analytical technique was shown to be accurate to $\pm 4\%$.

Preliminary runs showed that oxidation yields are higher the lower the temperature: the temperature of the electrolysis was therefore fixed at 8·5 (± 0.2) °C.

Results and Discussion

The only extractable product, phenol, was identified by comparison of retention time with authentic sample. Only traces of other products were present in the ethereal extract, but the small amount precludes their positive identification.

The reported current yields are calculated on the basis of 3 F/mole of phenol formed. Strictly speaking, the value of 3 F/mole is correct only if electrolysis conditions give rise to Fe^{2+} and H_2O_2 in 1/1 ratio on the electrode, otherwise there is a loss of charge for the formation of excess of one of the reagents.

The effect of initial [Fe^{3+}] on current yield (amount of charge, 550 coulombs) is shown in Fig. 1 for two different H_2SO_4 concentrations (0·1 and 0·6 M, respectively).

In Fig. 2 the current yields versus [H_2SO_4] are plotted for two different amounts of charge (550 and 750 coulombs respectively), while [Fe^{3+}] was maintained constant at 5×10^{-4} M.

Finally, Fig. 3 shows current yields versus amount of charge passed, for a solution 5×10^{-4} M in Fe^{3+} and 0·1 M in H_2SO_4.

In all experiments, the current yields for phenol production are definitely smaller than the

theoretical ones; this is undoubtedly due to the participation of OH· in various competitive reactions.

In no case was biphenyl found in appreciable amounts in the reaction products. In our conditions, therefore, reaction 5 does not appreciably contribute to the fate of radical (I), which disappears essentially by reaction 4, the oxidizing reaction partner being preferentially O_2 instead of Fe^{3+} [11].

The curves, phenol yield versus $[Fe^{3+}]$ of Fig. 1, show a clear maximum, as does the curve

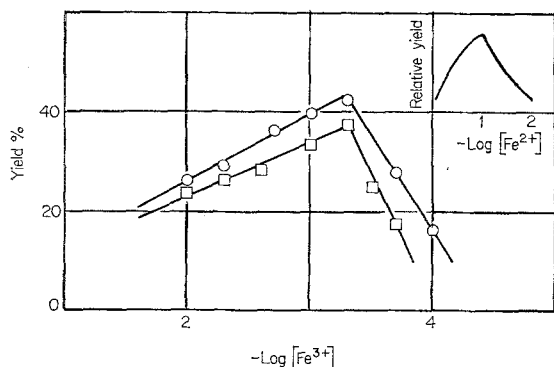Fig. 1. % current yield in phenol production against $[Fe^{3+}]$.
Total amount of charge, 550 coulombs. $[H_2SO_4]$, 0·1 (O) and 0·6 (□) M. The insert is plotted from data of [12].

of chemical yield versus $[Fe^{2+}]$ [12]. In the latter case, the maximum was explained bearing in mind the wastage of reagents in reaction 1, minimum wastage (maximum oxidation yield) corresponding to a 1/1 ratio of $[Fe^{2+}]/[H_2O_2]$ in the solution.

In our case the same explanation is also applicable, the only difference being that the maximum must correspond to a 1/1 ratio of Fe^{2+}/H_2O_2 on the electrode and not in the bulk of the solution. Obviously, the two values must be related, but the catalytic nature of the limiting current at -0.35 V [15] hinders simple correlations between bulk and surface concentrations, particularly in the present case, owing to the simultaneous presence of OH· scavengers.

With increasing concentration of H_2SO_4 (Fig. 2) the phenol yield is diminished: this is not due to the kinetic salt effect or to the changes in pH, [16] or to the lower oxygen concentration in more concentrated acid solutions, as experimen-
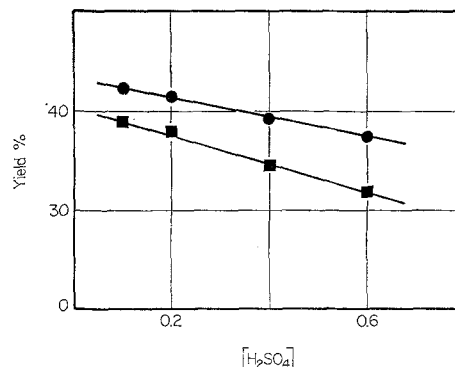

Fig. 2. % current yield in phenol production against $[H_2SO_4]$. $[Fe^{3+}]$, 5×10^{-4} M. Total amount of charge, 550 (■) and 750 (●) coulombs.

tally verified. It is more probably due to the increased contribution of competitive reaction between OH· radical and sulphate ions [17, 18].

The lower oxygen concentration, however, explains qualitatively the slight drift, on the concentration axis, of the maximum in the most concentrated acid solutions.

The last thing to justify is the diminished phenol yield with increasing amount of charge (Fig. 3): the chemical oxidation of phenol by
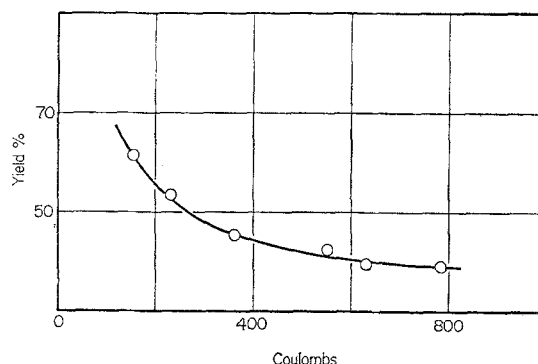

Fig. 3. % current yield in phenol production against total amount of charge. $[H_2SO_4]$, 0·1 M; $[Fe^{3+}]$, 5×10^{-4} M.

oxygen present in solution is ruled out by blank experiments, because without electrolysis the decrease in the amount of phenol is not of the required order of magnitude.

A more probable explanation may be found in subsequent reactions of OH· with already formed phenol, with simultaneous formation of unidentified (see experimental section) higher oxidized products [14].

The results so far obtained confirm the feasi-

bility of electrochemical generation of Fenton's reagent: the values of current yield in phenol production, although smaller than theoretical ones, are nevertheless interesting from a preparative point of view; better results may perhaps be obtained with electrolysis involving continuous extraction of phenol as soon as it is produced.

Acknowledgments

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