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Oxidation of polymethylated benzenes promoted by $^{\bullet}$OH radicals

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$^{\bullet}$OH radicals, produced in aqueous acid media by the electrogenerated system Fe(II)/H_2O_2, promote the oxidation of polymethylated benzenes. Under our experimental conditions only one $-CH_3$ group was oxidized to $-CHO$. A reduction of aldehyde to alcohol by $^{\bullet}$OOH radicals was shown to occur when H_2O_2 was produced in excess over Fe(II). In hydrochloric acid or in perchloric acid with Cl^- ions added, a remarkable increase of the yields was observed. The results are discussed on the basis of the kinetic parameters of the reactions involved in the process.

1. Introduction

In aqueous acid solutions Fe(III) and O_2 are simultaneously reduced at $-0{\cdot}2$ V versus SCE by the electrode reactions

$$\mathrm{Fe(III)} + e \longrightarrow \mathrm{Fe(II)} \tag{1}$$

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2. \tag{2}$$

OH radicals are produced from the electrogenerated Fe(II) and H_2O_2 according to

$$\mathrm{Fe(II)} + H_2O_2 \longrightarrow \mathrm{Fe(III)} + {}^{\bullet}OH + OH^-. \tag{3}$$

We have shown recently that such $^{\bullet}$OH radicals can be utilized in the oxidation either of the aromatic nucleus [1] or of the methyl side group of toluene [2]. Pursuing these studies we have investigated the reaction between $^{\bullet}$OH radicals and polymethylated aromatic hydrocarbons.

2. Experimental

2.1. *Chemicals*

All the chemicals used were reagent grade products; high purity oxygen was employed to saturate the solutions. Twice distilled water and mercury were used.

2.2. *Apparatus and procedure*

The experimental apparatus and instrumentation have been described in a previous paper [2].

The experiments were carried out by electrolysing at $-0{\cdot}2$ V versus SCE, an aqueous acid solution (25 ml) O_2 saturated and containing variable amounts of Fe(III) and a large excess (20 ml) of aromatic hydrocarbon. The excess was to minimize the reactions between the primary products and $^{\bullet}$OH radicals. Preliminary runs have shown that, under these conditions, the products are quantitatively extracted in the organic phase. The current density was usually about 5 mA cm^{-2}.

At the end of the electrolysis, the organic phase was directly analysed by gl chromatography, employing benzyl alcohol as external standard.

Two columns (200 × 0·5 cm, temperature 180° C) were used: the first one was packed with LAC 728 (10% by weight) on Chromosorb W (80–100 mesh); the second one (to analyse the possible acid compounds), was packed with LAC 446 (10% by weight) and 85% phosphoric acid (2% by weight) on Chromosorb W (60–80 mesh).

3. Results

3.1. *Influence of Fe(III) concentration on the yields*

In the presence of 1,2- , 1,3- and 1,4-dimethyl-benzene only two reaction products have been detected, the corresponding methyl-benzaldehyde and methyl-benzyl alcohol. Likewise, when 1,2,4-trimethylbenzene was utilized as substrate, only dimethyl-benzaldehyde and dimethyl-benzyl alcohol were found.

The aldehyde and alcohol yields from 1,4-dimethyl-benzene are reported in Fig. 1 as a function of [Fe(III)] at different HCl concentrations. The aldehyde plots show a maximum yield at [Fe(III)] = $1{\cdot}65 \times 10^{-3}$ M, while the alcohol yields decrease steadily to zero with increasing [Fe(III)]. Furthermore a yield dependence on the HCl concentration was found with a maximum at 0·5 M HCl. At this HCl concentration the aldehyde was produced with a yield of about 100%.

The same yield patterns, but with lower values, were obtained when 1,2- , 1,3-dimethyl-benzene or 1,2,4-trimethyl-benzene were substituted for 1,4-dimethyl-benzene (see Figs. 2 and 3).

3.2. *Anions effect*

The influence of different anions on the electrochemical oxidation of 1,4-dimethyl-benzene was studied. The plots of yields versus [Fe(III)] for experiments carried out in H_2SO_4 and $HClO_4$ solutions (Fig. 4), were similar to those obtained in HCl solution (Fig. 1) but the yields were considerably lower. To understand this behaviour, experiments were done adding NaCl to the $HClO_4$ solutions. The substantial increase of the aldehyde yield, as reported in Fig. 5, indicates the existence of a 'Cl^- effect'.

4. Discussion

The main feature of this work is the remarkable increase of the aldehyde yield when the oxidation of methyl benzenes is carried out in aqueous solutions in the presence of Cl^- ions. Though in some cases an almost quantitative yield was obtained, some aspects of the electrolytic process should be interpreted. These include: (a) the maximum of Figs. 1–4; (b) the mechanism for alcohol formation; (c) the possible mechanism of the oxidation of the aromatic side chain to an aldehyde group; (d) the Cl^- ion effect.

The current yield maxima of Figs. 1–4 should be achieved when H_2O_2 and Fe(II) are produced at the same rate on the electrode surface. This condition is reached at [Fe(III)] $\simeq 2 \times 10^{-3}$ M on account of the O_2 solubility and of the diffusion coefficients of O_2 and Fe(III). A deviation from this ideal behaviour could arise from the wastage of $^{\bullet}OH$ radicals due to the reactions

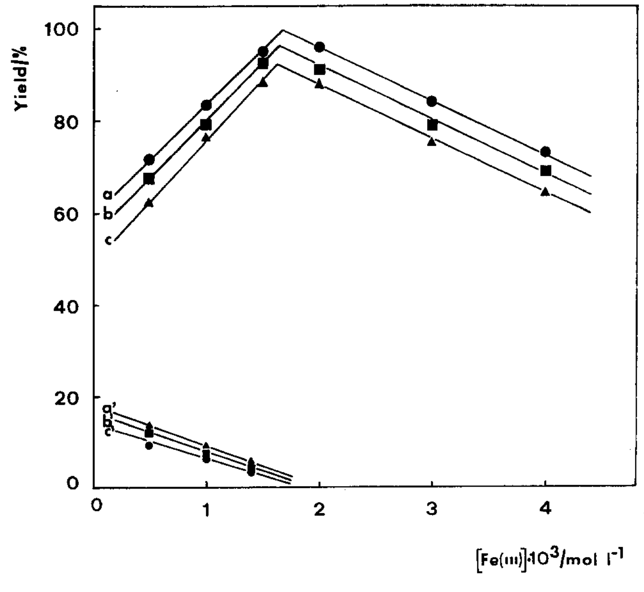


Fig. 1. Percentage current yields of 4-methyl-benzaldehyde and 4-methyl-benzyl alcohol production against Fe(III) bulk concentration at 50° C. Total amount of charge: 250 C. HCl: (■) 0·25 M; (●) 0·5 M; (▲): 0·75 M. Curves a, b, c: 4-methyl-benzaldehyde. Curves a′, b′, c′: 4-methyl-benzyl alcohol.

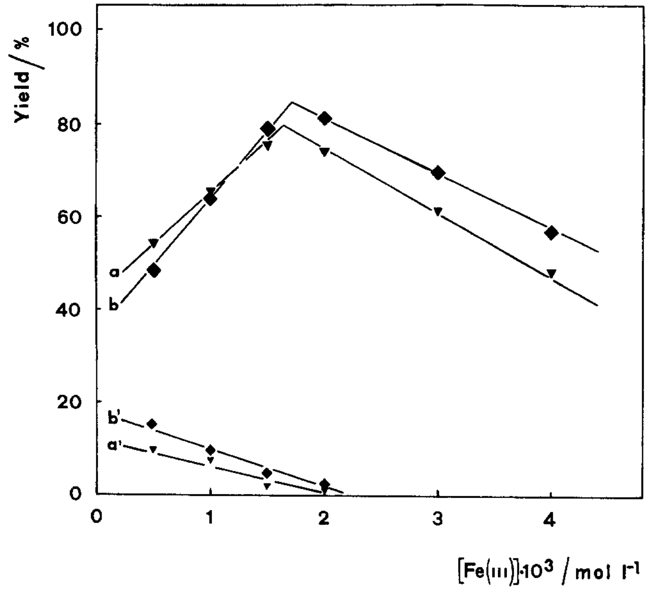


Fig. 2. Percentage current yields of 2- and 3-methyl-benzaldehyde and 2- and 3-methyl-benzyl alcohol production against Fe(III) bulk concentration at 50° C. 0·5 M HCl: total amount of charge 250 C. (◆): 2-methyl-benzaldehyde (Curve b) and 2-methyl-benzyl alcohol (Curve b′). (▼): 3-methyl-benzaldehyde (Curve a) and 3-methyl-benzyl alcohol (Curve a′).

$$^{\bullet}OH + Fe(II) \longrightarrow OH^- + Fe(III) \qquad (4)$$

$$^{\bullet}OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \qquad (5)$$

which are competitive with the reaction between $^{\bullet}$OH and the substrate.

A theoretical calculation of the yields dependence on the [Fe(III)]/[O_2] ratio cannot be done since in our experiments the steady-state conditions are not achieved. However since $k_4 \gg k_5$ [3, 4] the maximum should be shifted towards [Fe(III)] values below 2×10^{-3} M as experimentally observed.

As regards the alcohol production it appears that the alcohol is formed on the left-hand side of the maximum, that means in the region where Reaction 5 should occur. Since the $^{\bullet}$OOH radical

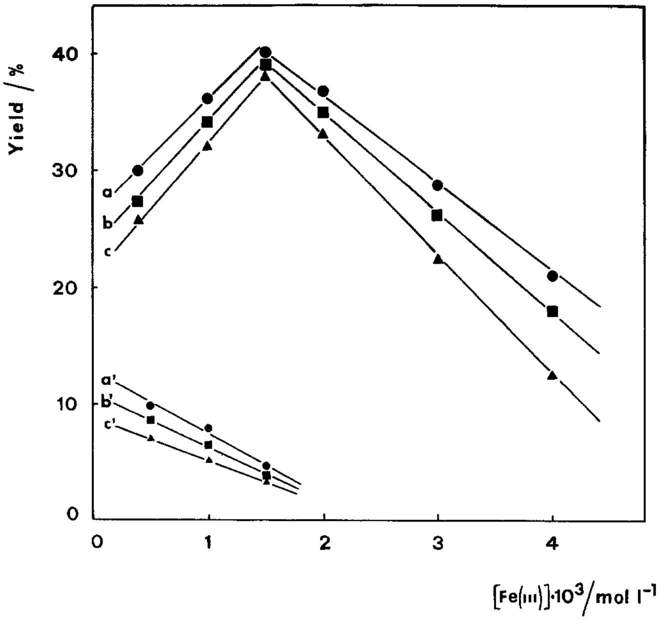


Fig. 3. Percentage current yields of dimethyl-benzaldehyde and dimethyl-benzyl alcohol production against Fe(III) bulk concentration at 50° C. Total amount of charge 250 C. HCl: (■) 0·2 M; (●) 0·5 M; (▲) 0·75 M. Curves a, b, c: dimethyl-benzaldehyde. Curves a′, b′, c′: dimethyl-benzyl alcohol.

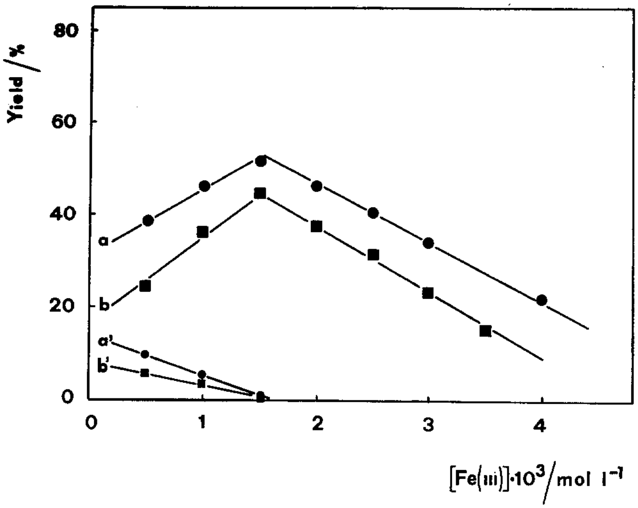
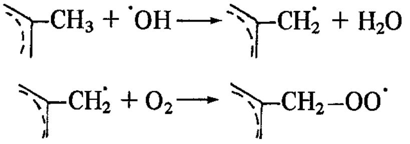


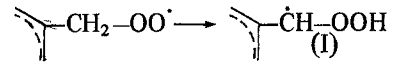
Fig. 4. Percentage current yields of 4-methyl-benzaldehyde and 4-methyl-benzyl alcohol production against Fe(III) bulk concentration. Total amount of charge 250 C. (●): 0·5 M $HClO_4$, $t = 50°$ C; (■): 0·5 M H_2SO_4, $t = 30°$ C. Curves a, b: 4-methyl-benzaldehyde. Curves a', b': 4-methyl-benzyl alcohol.

is a mild reducing agent, $E^0_{\cdot OOH/O_2} = -0{\cdot}32$ V [5], the alcohol could be formed from aldehyde reduction by $HO_2^{\cdot}$. This hypothesis was supported by the fact that benzyl alcohol was the only reaction product when an aqueous alkaline solution of O_2^- [6] was slowly added to a C_6H_5CHO solution in about 0·1 M H_2SO_4, pH = 1, in presence of Fe^{2+} ions. When the same experiment was carried out using toluene instead of benzaldehyde no reaction product was detected. These experiments suggest that the aldehyde is the first oxidation product in the radical-promoted oxidation of the aromatic methyl group.

A possible reaction mechanism is:



followed by a 1–3 hydrogen shift [7]



and disappearance of the radical (I) by one of the following reactions

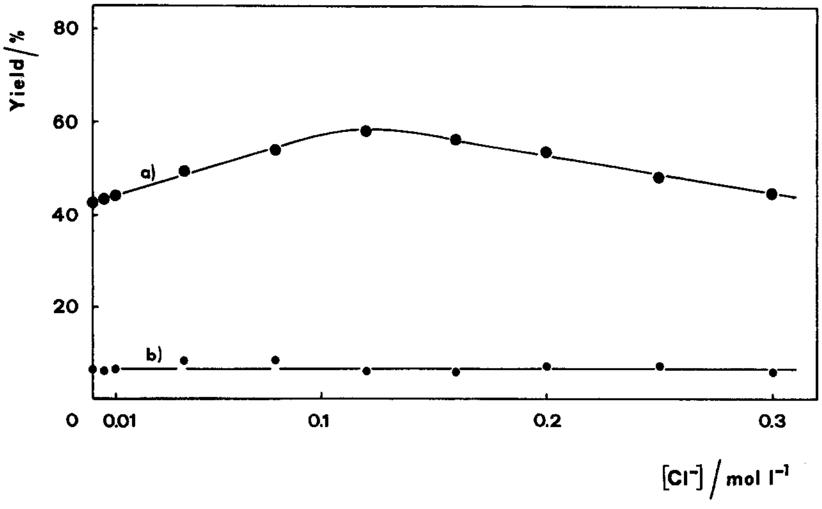
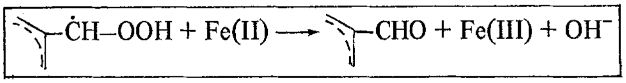
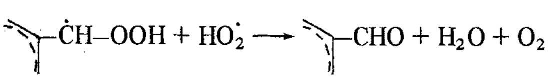


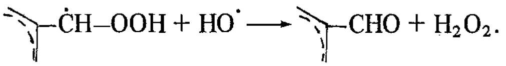
Fig. 5. Percentage current yields of 4-methyl-benzaldehyde (Curve a) and 4-methyl-benzyl alcohol (Curve b) against Cl^- concentration at 50° C. 0·5 M $HClO_4$; $1{\cdot}11 \times 10^{-3}$ M $Fe(ClO_4)_3$. Total amount of charge, 250 C.

Table 1. Kinetic data

Reaction	$k(\times 10^{-9})$ ($M^{-1}s^{-1}$)	*Reference*
$C_6H_5CH_3 + {}^{\bullet}OH$	3·0	[8]
1,2-dimethylbenzene + $^{\bullet}OH$	14·3	[8]
1,3-dimethylbenzene + $^{\bullet}OH$	24·0	[8]
1,4-dimethylbenzene + $^{\bullet}OH$	15·3	[8]
$Cl^- + {}^{\bullet}OH \longrightarrow Cl^{\bullet} + {}^-OH (pH = 0)$	4·0	[9]
$Cl^- + {}^{\bullet}OH \longrightarrow Cl^{\bullet} + {}^-OH (pH = 1)$	0·4	[9]
$Cl^- + Cl^{\bullet} \longrightarrow Cl_2^-$	2·1	[10]
$Fe^{2+} + Cl^{\bullet} \longrightarrow Fe^{3+} + Cl^-$	5·9	[10]
$Fe^{2+} + Cl_2^- \longrightarrow Fe^{3+} + 2Cl^-$	0·014	[10]







Regarding the 'Cl^- effect', the strong increase in the yields when the electrolyses were carried out in presence of high Cl^- concentrations call for a direct involvement of Cl^- in the mechanism of the methyl oxidation. In fact from the kinetic data of Table 1 it appears that in the presence of about 1 M Cl^- the primary reaction product of the $^{\bullet}OH$ radicals is the radical species, $Cl^{\bullet}$, whose reactivity towards the aromatic methyl group is of the same order of magnitude as that of $^{\bullet}OH$. However, the yield dependence on Cl^- is not straightforward since the species Cl^- and $Cl^{\bullet}$ are involved in different steps of the reaction process, as it appears in Table 1. In addition it must be recalled that Cl^- ions, under our experimental conditions, form chloro-complexes with both Fe^{2+} or with Fe^{3+} ions,with an obvious change of the redox potentials and of the kinetic rate constants.

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