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ONE-STEP OXIDATION OF BENZENE TO 1,4-DIHYDROXYBENZENE IN THE PRESENCE OF COPPER(I)CHLORIDE

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Aerial oxidation of benzene in a mixture of copper(I)chloride, sulfuric acid and acetonitril-water yields phenol and through a direct route 1,4-dihydroxybenzene under ambient conditions. The maximum hydroxylation efficiency is 42% at pH = 5.

Recently Sasaki et al.[1] reported the CuCl mediated oxidation of benzene to phenol. At 298 K and the reported optimum concentration of 0.05 M H_2SO_4 these authors obtained a yield of 17% phenol based on copper according to the equation

$$C_6H_6 + 2\ Cu^+ + 2\ H_3O^+ + O_2 \longrightarrow C_6H_5OH + 2\ Cu^{2+} + 3\ H_2O \qquad (1)$$

which accompanies the Cu(I) oxidation (eq. 2).

$$4\ Cu^+ + 4\ H_3O^+ + O_2 \longrightarrow 4\ Cu^{2+} + 6\ H_2O \qquad (2)$$

On investigating this interesting system, we found besides phenol a significant amount of 1,4-dihydroxybenzene. This prompted us to examine these reactions further.

CuCl was purified by precipitation from concentrated HCl by diluting the solution with water. When contact with oxygen was prevented the product contained at least 99.5% CuCl. The reactions were performed in a thermostatted stirred vessel (200 ml) which was, in order to maintain a constant oxygen pressure, equipped with a thermostatted buffer volume of 1.5 l in a way that prevented depletion of oxygen in the reactant vessel. The entire set-up was connected to a pH-control device and an apparatus that automatically recorded the oxygen consumption[2]. The reaction products were determined by extracting the mixture four times with diethyl ether and analysing the samples against an internal standard by gas chromatography over a CP-WAX 57-CB as well as a TENAX-GC column.

In a preliminary experiment the conditions where the diffusion of oxygen into the solution was not rate limiting, were determined by studying the effect of the stirrer speed on the rate of the autoxidation of CuCl (Fig. 1). Since diffusion limitation is evident below a stirrer speed of 1000 rpm, all reactions were performed at 1200 rpm. It is noteworthy that the product distribution is dependent on the stirrer speed (Fig. 2). As Sasaki et al.[1] probably worked under conditions of diffusion limitation this might explain the fact that our observations are, in part, at variance with their results.

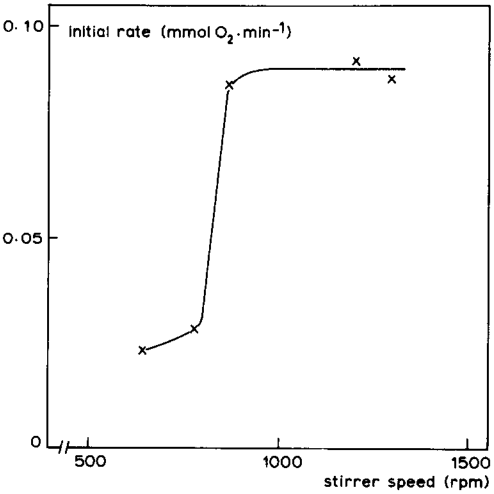

Fig. 1. Effect of the stirrer speed on the rate of autoxidation of CuCl.
pH = 1.3; 298 K; 4.0 mmol CuCl/100 ml.

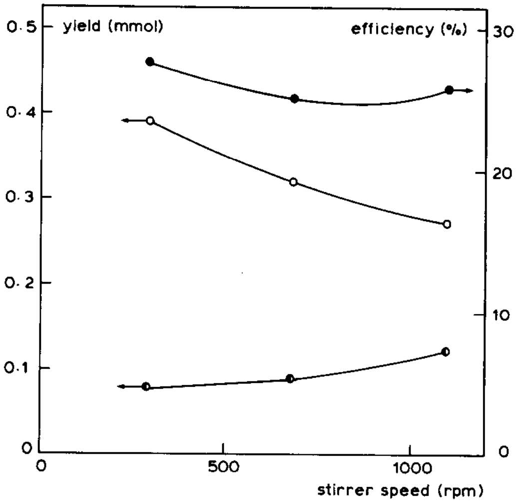

Fig. 2. Effect of the stirrer speed on the product distribution of the hydroxylation of benzene. Phenol (○); 1,4-dihydroxybenzene plus 1,4-benzoquinone (◐); total hydroxylation efficiency (●).
pH = 4.0; 298 K; 4.0 mmol CuCl/100 ml.

In an attempt to suppress reaction (2) and to solubilize Cu^+ we added CH_3CN as a ligand to the reaction mixture (Fig. 3). Apart from the not well understood effects at low CH_3CN content, the rate of oxygen uptake decreased and indeed an increase in the amount of phenol produced was found, but the relatively large increase in the yield of 1,4-dihydroxybenzene was most promising. Furthermore the presence of a highly polar polymeric species was noted together with an additional oxygen uptake (Fig. 3). Biphenyl was never detected.

Experiments at various pH-values revealed an optimum in the yield of phenol at a pH between 3 and 4, while a distinct maximum in the yield of 1,4-dihydroxybenzene together with 1,4-benzoquinone was observed at pH = 5 (Fig. 4). The ratio 1,4-dihydroxybenzene/1,4-benzoquinone was found to decrease with increasing reaction times, indicating the role of Cu^{2+} in the oxidation of 1,4-dihydroxybenzene. The maximum in the hydroxylation efficiency is probably due to retardation of the autoxidation of Cu^+ on the one hand[3] and the formation of the scarcely soluble Cu_2O at pH > 4, which results in a very slow oxygen uptake and therefore in a relatively large amount of polymeric products by the action of Cu^{2+}, on the other hand.

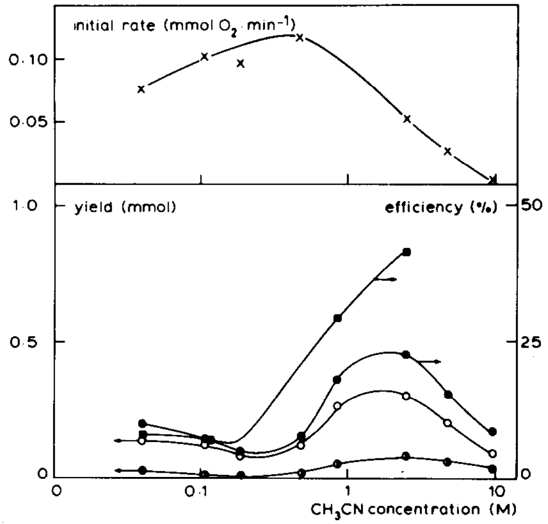

Fig. 3. Hydroxylation of benzene in the presence of CH_3CN. Phenol (○); 1,4-dihydroxybenzene (◐); total hydroxylation efficiency (●); hydroxylation efficiency calculated from oxygen uptake (■); rate of oxygen uptake (X).
pH = 1.3; 298 K; 4.0 mmol CuCl/100 ml.

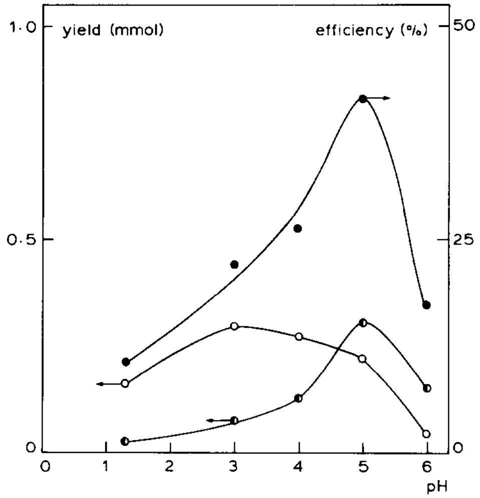

Fig. 4. pH Dependence of the hydroxylation of benzene. Phenol (○); 1,4-dihydroxybenzene plus 1,4-benzoquinone (◐); total hydroxylation efficiency (●).
298 K; 4.0 mmol CuCl/100 ml.

Repeating the experiments in the presence of 0.61 M CH_3CN resulted in a similar course as depicted in Fig. 2. From these experiments and a series of experiments at pH = 4 with varying amounts of CH_3CN it was concluded that the maximum yields of phenol and 1,4-dihydroxybenzene plus 1,4-benzoquinone were 18% at pH = 4, 0.16 M CH_3CN and 33% at pH = 4, 0.61 M CH_3CN, respectively. The maximum hydroxylation efficiency was 42% at pH = 5 in the absence of CH_3CN.
The oxidation of phenol to 1,4-benzoquinone in CH_3CN in the presence of copper salts has recently been claimed[4]. Under our conditions a different product distribution was found: the oxidation of 4.0 mmol CuCl in a solution of phenol in 100 ml 0.05 M H_2SO_4 proceeded slowly and was accompanied by the production of 1,2-dihydroxybenzene, only minor amounts of 1,4-dihydroxybenzene and a trace of 1,3-dihydroxybenzene (Fig. 5). Thus, apart from the formation of 1,2- and 1,3-dihydroxybenzene, the amount of 1,4-dihydroxybenzene was not only significantly less than obtained by the oxidation of benzene but also considerably slower formed. It therefore must be concluded, that the 1,4-dihydroxybenzene obtained from benzene is not the product of a consecutive reaction of phenol, but rather of a one-step oxidation of benzene. A further indication for this came from an experiment where phenol was removed from the aqueous phase during the reaction by continuous extraction by the reactant benzene in order to suppress side reactions to polymeric compounds. As expected these latter products were not observed but besides phenol 1,4-dihydroxybenzene and 1,4-benzoquinone were also found.

Attempts to determine the mechanism by performing the experiments with $^{18}O_2$ or $H_2{}^{18}O$ were hampered by isotopic exchange reactions possibly during the formation of the oxygenates. The conclusions that the oxygen atoms in 1,4-dihydroxybenzene originate from two different oxygen molecules and that water is not directly involved in the reaction seem justified however.

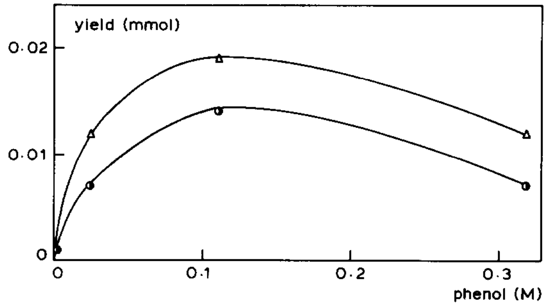

Fig. 5. Hydroxylation of phenol. 1,4-dihydroxybenzene (◑); 1,2-dihydroxybenzene (△).
pH = 1.3; 298 K; 4.0 mmol CuCl/100 ml.

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