

The oxidation of *o*-nitrotoluene to *o*-nitrobenzaldehyde with electrogenerated cobaltic sulphate

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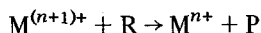
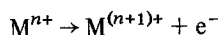
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Indirect electrochemical oxidation of *o*-nitrotoluene to *o*-nitrobenzaldehyde by Co(III) has been studied. The highest aldehyde yield (~ 80%) is obtained in dispersing a 70-fold excess of *o*-nitrotoluene in a solution of $\text{Co}_2(\text{SO}_4)_3$ in 60% H_2SO_4 at 12° C. The influence of acid concentration, excess of nitrotoluene and presence of catalyst are discussed and found to be compatible with a mechanism proposed by Bawn.

1. Introduction

The indirect electrochemical oxidation of organic compounds has been the subject of considerable study [1]. The reactions which are involved in this oxidation are



where the oxidizing agent $\text{M}^{(n+1)+}$ is produced in an electrochemical step and reacts chemically with the organic compound R to give the product P and the reduced species M^{n+} , which can be recycled. This method has been used for the oxidation of many methyl substituted aromatic compounds to the corresponding aldehydes in high yield using manganese (III) [2] and silver (II) ions [3].

The presence of a nitro-substituent in the ortho-position strongly decreases the reactivity of the methyl-substituent: Syper has found that *o*-nitrotoluene cannot be oxidized by silver (II) [4] but it is oxidized under vigorous conditions (80° C, 6 N HClO_4) by cerium (IV) [5] but with low yield.

In this work we have studied a two-stage process for the oxidation of *o*-nitrotoluene to *o*-nitro-

benzaldehyde using electrolytically generated $\text{Co}_2(\text{SO}_4)_3$.

2. Experimental

The electrolytic cell used for the preparation of cobaltic sulphate was described in a previous paper [6].

Electrolysis of a saturated solution of cobaltous sulphate in 40% H_2SO_4 solution gave dark blue-green crystals of cobaltic sulphate which were separated by filtration and dissolved in the appropriate H_2SO_4 concentration (at 12° C); *o*-nitrotoluene was introduced in excess into the cobaltic sulphate solution with stirring and the reaction was allowed to go to completion (indicated by the disappearance of the blue-green colour) or was stopped after 15 minutes by the introduction of hot water into the solution. In some experiments catalytic amounts of Ag_2SO_4 (0.01 M) were added.

The resulting solution was diluted with water and extracted with ether. The ethereal solution was analysed by thin layer chromatography (for *o*-nitrobenzoic acid) and gas chromatography (to determine *o*-nitrotoluene, *o*-nitrobenzaldehyde and *o*-nitrobenzylalcohol). The amount of cobaltic sulphate in the reaction medium was determined by iodometric titration.

3. Results

3.1. Electrolytic preparation of cobaltic sulphate

The electrolytic preparation of cobaltic sulphate has been studied in an earlier paper [6]. The optimum conditions were: PbO_2 anode, presence of Ag_2SO_4 as catalyst, low current density ($20\text{--}50 \text{ mA cm}^{-2}$), low H_2SO_4 concentration ($\sim 40\%$ H_2SO_4) and low conversion.

3.2. Chemical oxidation of *o*-nitrotoluene with cobaltic sulphate

The reaction must be conducted with vigorous stirring to minimize the amount of *o*-nitrobenzoic acid formed and at relatively low temperature ($5\text{--}15^\circ\text{C}$) to minimize the decomposition of cobalt (III) sulphate by reaction with water.

The H_2SO_4 concentration influences strongly the selectivity and the rate of the reaction. A series of experiments was conducted at 12°C with a high excess of *o*-nitrotoluene (70 times the theoretical) at different H_2SO_4 concentrations and we have found that:

(a) At H_2SO_4 concentrations below 25% the reaction does not occur.

(b) At H_2SO_4 concentrations between 30–50% the reaction occurs slowly (time of reaction, 3–4 hours) with low yield (5–15%), the main reaction being the decomposition of Co(III) sulphate by water which was accelerated by the presence of *o*-nitrotoluene and/or the product of its oxidation.

(c) At H_2SO_4 concentration of $60 \pm 1\%$ the reaction occurs more rapidly (time of reaction 25–35 min) and with high yield (78%).

(d) At very high H_2SO_4 concentration (above 70%) the reaction is very rapid (few minutes) but the main product formed was the *o*-nitrobenzyl-alcohol.

Fig. 1 shows the influence of excess of nitrotoluene (expressed in multiples of the amount needed by the stoichiometry) upon the yield of *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid (the reaction was stopped after 15 minutes and at this stage 56–58% of cobalt (III) sulphate had reacted).

The total yield from the reaction is not 100%. This is due to the two side-reactions, benzyl alcohol formation and reaction of Co(III) with water, especially at low excess of nitrotoluene.

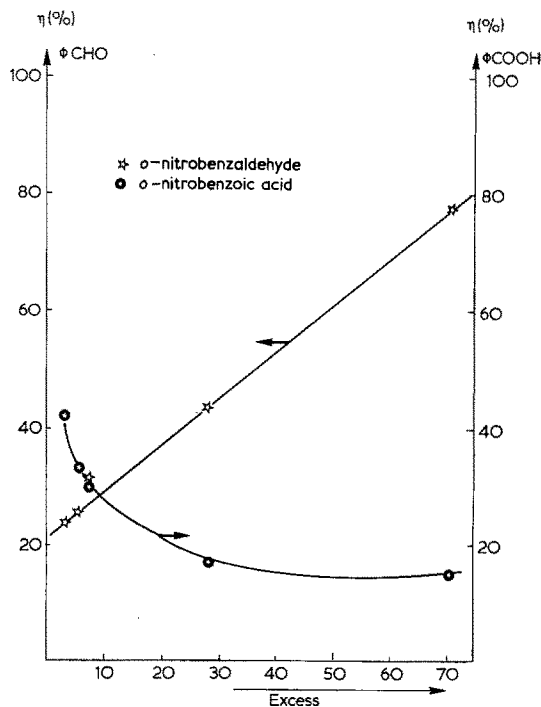


Fig. 1. Influence of the excess of nitrotoluene (expressed in multiples of the amount required by stoichiometry) on the yield of *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid. Concentration H_2SO_4 , 60%; $T = 12^\circ\text{C}$.

The presence of catalytic amounts of Ag_2SO_4 (0.01 M) in the reaction medium at 60% H_2SO_4 decreased the yield of the reaction to 30%.

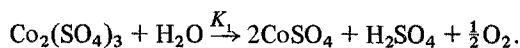
4. Discussion

During the oxidation of *o*-nitrotoluene to *o*-nitrobenzaldehyde with $\text{Co}_2(\text{SO}_4)_3$ in concentrated H_2SO_4 three side reactions occur; the oxidation of *o*-nitrotoluene to *o*-nitrobenzyl alcohol, further oxidation of *o*-nitrobenzaldehyde to *o*-nitrobenzoic acid, and the reaction of cobaltic sulphate with water.

The operating conditions influence the extent of these side reactions.

4.1. H_2SO_4 concentration

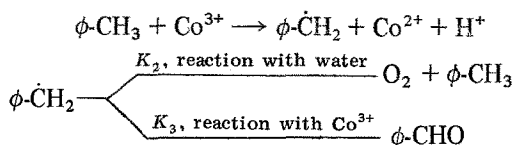
In the range of H_2SO_4 concentration between 0–50% the main reaction which occurs is the decomposition of $\text{Co}_2(\text{SO}_4)_3$ by water



The rate of this reaction K_1 is increased by the presence of *o*-nitrotoluene and/or the products of its oxidation as has been noted by Swann and Xanthakos [7].

At high H_2SO_4 concentration (above 60%) the main reaction is the oxidation of *o*-nitrotoluene.

Bawn [8] has studied the mechanism of oxidation of organic compounds by $Co(III)$ and has concluded that the primary step in the oxidation is an electron transfer between the cobaltic ion and the organic compound with the generation of a free radical. The radical thus produced may then react with the solvent or with another cobaltic ion. Applying this mechanism to the oxidation of *o*-nitrotoluene ($\phi-CH_3$) we have:



The yield of oxidation product from the organic compound depends on the ratio of the two rate constants K_2 and K_3 . This ratio is influenced by the H_2SO_4 concentration, thus for concentrations below 60% H_2SO_4 $K_2 > K_3$ and above 60% $K_3 > K_2$.

In the electrochemical preparation of $Co_2(SO_4)_3$ [6] we have found that its yield decreases sharply for high H_2SO_4 concentrations. This has been attributed to an increase in the oxidation potential of the $Co^{2+}-Co^{3+}$ couple. This shift may be produced by the formation of a complex with sulphate ions in concentrated H_2SO_4 . This complex has a higher reactivity than the less associated Co^{3+} ion present at lower H_2SO_4 concentrations.

The formation of *o*-nitrobenzyl alcohol at very high H_2SO_4 concentration (above 70%) may be due to the formation of *o*-nitrobenzyl hydrogen sulphate which is not further oxidized.

4.2. Excess of nitrotoluene

The fact that *o*-nitrobenzaldehyde can be prepared with high yield by oxidation with $Co(III)$ is due to

two properties of the mixture: firstly, the small but significant solubility of *o*-nitrotoluene in aqueous H_2SO_4 solution and, secondly, the extraction of *o*-nitrobenzaldehyde with *o*-nitrotoluene from the H_2SO_4 solution which prevents further oxidation of the aldehyde. Increasing the excess of *o*-nitrotoluene decreases the amount of *o*-nitrobenzaldehyde present in the H_2SO_4 solution and leads to an increase in the yield of the reaction.

4.3. Presence of silver as catalyst

Silver ion is a stronger oxidizing agent than Co^{3+} . This may be the reason for the decrease in yield of the reaction in the presence of a catalytic amount of Ag^+ . An increase in the acid formation has been observed in the presence of a silver salt.

4.4. Regeneration of Co^{3+}

The main problem in this indirect electrochemical oxidation is to handle the opposing requirement of the electrochemical and chemical reactions with respect to the concentration of H_2SO_4 . High chemical conversions to the aldehyde and high yield are obtained at high concentration and in the absence of catalyst (silver), whereas high current efficiency of $Co(III)$ is obtained at low H_2SO_4 concentration and in the presence of silver as catalyst.

References

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