# Three Reagents in One: Ammonium Permanganate in the Oxidation of Benzyl Alcohol

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The oxidation or consecutive ammoxidation reaction of benzyl alcohol with solid ammonium permanganate was studied. The first oxidation step leads to the formation of benzaldehyde, ammonia, and  $MnO_2$ . The  $MnO_2$  is present in the system in a colloidal form which facilitates the reaction between aldehyde and ammonia, and this latter reaction then yields benzonitrile. All these products are formed in a heterogeneous system under relatively mild conditions. The yield of benzaldehyde has an optimum at room temperature and increases with increasing reaction time. At higher temperature (e.g. 80 °C) benzonitrile is formed together with minor amounts of benzyl benzoate.

### Introduction

Benzyl alcohol and its ring-substituted derivaives can be easily oxidized by various permangalates [1-14]. Reaction conditions, such as the naure of the oxidant and the medium, temperature, tc. have significant influences on the yield, selecivity, and formation of by-products. Previous inestigations [1-14] have indicated that benzaldeyde and/or benzoic acid are the main products. f, however, ammonia is also present beside the xidant the alcohols or aldehydes are converted to itriles [15–19]. For this reason, ammonium perhanganate may behave as a multiple reagent leadng to nitrile formation. At the same time, ammoium permanganate is a more stable oxidant than he previously applied permanganates [20], it is asily available [21,22], and inexpensive. Thus, its application may provide an advantageous new hethod to produce aromatic nitriles.

Accordingly, we studied the benzyl alcohol oxilation with ammonium permanganate with repect to reaction products, and the effect of the ammonium ion.

## Results and Discussion

In chlorinated solvents, only benzaldehyde and ienzonitrile could be identified as the products of the reaction of **1** and solid  $NH_4MnO_4$  beside the inorganic residue. After one hour at 22 °C, only the formation of benzaldehyde (2) could be observed, and its yield increased with increasing temperature. Benzonitrile (3), however, appeared only at 60-80 °C after 3 h. Eq.(1) illustrates the formation of **2**.

$$3 \text{ Ph-CH}_{2}\text{OH} + 2 \text{ NH}_{4}\text{MnO}_{4} \rightarrow 1$$

$$3 \text{ Ph-CHO} + 2 \text{ NH}_{3} + 2 \text{ MnO}_{2} + 4 \text{ H}_{2}\text{O} \qquad (1)$$

$$2$$

Increasing production of 2 was incident to the formation of increasing amounts of  $NH_3$  and  $MnO_2$ . The formation of 3 would be attributed to the reaction between 2 and ammonia produced as illustrated by eq.(2).

$$\begin{array}{c} \text{Ph-CHO+NH}_3 \xrightarrow{\text{MnO}_2, -2H} \text{Ph-CN+H}_2\text{O} & (2) \\ \mathbf{2} & \mathbf{3} \end{array}$$

This mechanism is supported by the observation that the amount of benzaldehyde decreases with increasing nitrile production. Changes in the benzyl alcohol/ammonium permanganate molar ratio did not result in higher nitrile yields. This means that neither 1 nor  $NH_4MnO_4$  participated in the consecutive reactions of benzaldehyde. (Colloidal  $MnO_2$  acts as oxidant in this process.) The process

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(1) determines the ratio of the final products. Since the formation of three equivalents of 2 is incident to the liberation of only two equivalents of ammonia, the whole amount of the aldehyde could only be consumed (see eq.(2)), if additional ammonia was introduced into the system.

Other reactions [23] may also lead to the formation of benzonitrile. However, benzoic acid, benzamide and/or benzyl amine could not be detected among the reaction products or intermediates. The formation of 3 via the oxidation of benzyl amine [23,24] could also be excluded.

The reduction product of ammonium permanganate was MnO<sub>2</sub> present in the system in a colloidal form. This was confirmed by the UV spectra of the final solution according to ref. [25]. Other Mncontaining species could not be detected. In comparison to microcrystalline MnO<sub>2</sub> obtained by sonification [26] or electrolytically [27], the colloidal  $MnO_2$  is a more active oxidant and therefore can behave as an oxidizing agent in the process described by equation (2). Increased reaction time and/or temperature improved the yield of nitrile. Colloidal MnO<sub>2</sub> can also form by the intramolecular redox reaction of the ions of NH<sub>4</sub>MnO<sub>4</sub> [5], and the  $MnO_2/2$  (or benzaldimine) ratio therefore may increase from the original 2/3 to a higher value (>1).

At higher temperatures (80 °C) and/or longer reaction times (e.g., 24-48 h) a small amount (<1%) of benzyl benzoate (6) was obtained beside the main products. Since 1 cannot be oxidized to 4 by solid NH<sub>4</sub>MnO<sub>4</sub> or colloidal MnO<sub>2</sub>, esterification of 4 with 1 does not have to be taken into account. Benzoate 6 may be derived from other reactions, e.g.: (i) from the oxidation of hemiacetal ( $\alpha$ -hydroxy-ether) intermediates [16]; (ii) from oxidation of 1 by activated  $MnO_2$  [28]; (iii) from a Cannizaro reaction of 2 (catalyzed by manganese centers, similar to ester formation catalyzed by metal centers of enzymes [29]). The molar ratio of the reactants has no effects either on the selectivity or the amount of the ester found. Therefore, formation and oxidation of a hemiacetal type intermediate as well as oxidation of 1 (by MnO<sub>2</sub>) could be excluded. The catalytic Cannizaro-type reaction or a modified Corey-type reaction [28], however, are likely pathways.

#### Experimental

The preparation of ammonium permanganate has been described previously [21,22]. Benzyl alcohol (1) was used after distillation, while the solvents were applied without further purification.

The reactions were carried out in a doublenecked flask equipped with a condenser and a magnetic stirrer. Alcohol 1 was oxidized with different amounts of ammonium permanganate (molar ratio alcohol:NH<sub>4</sub>MnO<sub>4</sub> = 0.4-4): (i) in refluxing solvents under atmospheric pressure; (ii) in a stirred mixture at room temperature. The reaction time was varied between 1 and 48 h. The conversion was followed by GC, and the products were identified via their mass and IR spectra. The GC measurements were performed with a Finnigan MAT GCQ instrument including a medium polar CP WAX 52CB (ChromPack) column (length: 30 m; i.d.: 0.25 mm; film thickness: 0.25  $\mu$ m). The linear flow rate of the helium carrier gas and the injection temperature were set to 35 cm s<sup>-1</sup> and 230 °C, respectively. The column temperature was increased from 65 °C to 160 °C with a rate of 5 °C min<sup>-1</sup>, then, after 1 min, to 200 °C with a rate of 10 °C min<sup>-1</sup>. Detection was performed in the 10-650 amu mass range using the electron impact (EI+) technique at 70 eV energy.

Samples for infrared spectroscopy were prepared as KBr pellets and the spectra were recorded in the 400-4000 cm<sup>-1</sup> range with a Nicolet 205 FT-IR spectrometer. UV-Vis spectra were recorded in the range of 200-600 nm with a Unicam UV-4 spectrometer. X-ray powder diffraction data were obtained by means of a Phillips PW 3710 diffractometer equipped with a Cu monochromator.

### Conclusion

Oxidation of 1 by solid ammonium permanganate leads to the formation of benzaldehyde, ammonia, and  $MnO_2$ . The  $MnO_2$  present in the system in a colloidal form then oxidizes the benzaldimine formed from the aldehyde and ammonia. This latter reaction yields benzonitrile. Different molar ratios of the reactants have no influence on the product selectivity. The yield of **2** has an optimum at room temperature and increases with increasing reaction time. The formation of **3** is favoured at higher temperature (*e.g.* 80 °C).

At higher temperatures (80 °C) and longer reaction times (24 h) **6** appears as a by-product formed *via* metal-center catalyzed Cannizaro or a catalysed modified Corey-type reaction of **2**.

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