

Manganese(II) naphthenate as effective catalyst for the clean oxidation of 2-methylnaphthalene by hydrogen peroxide

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Abstract Oxidation of 2-methylnaphthalene (2-MN) with aqueous hydrogen peroxide was conducted in acetic acid. The epoxidation pathway was investigated by increasing the $\text{CH}_3\text{CO}_3\text{H}$ content and adding manganese(II) naphthenate (MnPc) as catalyst. 2-Methyl-1,4-naphthoquinone was obtained in 75.6% conversion and with 80.0% selectivity under the latter conditions. A probable mechanism in which MnPc catalyzes the oxidation of 2-MN by hydrogen peroxide in acetic acid is proposed.

Keywords 2-Methylnaphthalene · 2-Methyl-1,4-naphthoquinone · Hydrogen peroxide · Manganese(II) naphthenate · Oxidation · Vitamin K_3

Introduction

Vitamins are fine chemicals produced in amounts ranging between 1,000 and 10,000 tons per annum [1]. It is well known that quinones have pronounced bio-activity and are important in medicinal applications. Since 2-MNQ (vitamin K_3), used therapeutically under the name menadione, was found to have more antibleeding activity than the natural vitamins K_1 or K_2 [2], many methods have been described for controlled oxidation of 2-MN (Scheme 1) using a variety of oxidizing agents in the presence of catalyst [3–9]. Traditionally, menadione is produced on an industrial scale by stoichiometric oxidation of 2-MN by CrO_3 in sulfuric acid. Yield and selectivity are moderate (typically approx. 50%) [10]. The drawbacks of this method are obvious: production of inorganic salts as by-product (18 kg salt per kg product) and necessary treatment of chromium-containing waste water [11, 12]. Adam and co-workers [13] described the use of acetic acid, hydrogen peroxide, and methyl trioxorhenium

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(conversion of 2-MN was 81%, affording 47% 2-MNQ; Pd(II)-polystyrene sulfonic acid resin [14] was used as catalyst). The rhenium catalyzed oxidation of 2-MN, using 85% H_2O_2 solution gave conversion of 93% at 40 °C after 4 h. However, this reaction is rather hazardous, because concentrated hydrogen peroxide is potentially explosive [15]. In another method, metalloporphyrin-catalyzed oxidation of 2-MN by potassium monopersulfate was reported [16], with selectivity up to 53% for 2-MNQ. Phthalocyanine-like compounds (PCS) are similar to metalloporphyrins in many chemical properties, so their use as catalysts could enable effective oxidation of organics with similar steric configuration and electron configuration as for use of the metalloporphyrins [17, 18], especially mild oxidation of organics at room temperature by hydrogen peroxide or other organic peroxides [19]. In this work we studied the oxidation of 2-MN in detail using two kinds of oxidant (30% H_2O_2 and a mixture of H_2O_2 and $\text{CH}_3\text{CO}_3\text{H}$) in the presence of acetic acid. Manganese(II) naphthenate (MnPc), as catalyst, was also added to investigate the epoxidation pathway. A possible mechanism of the catalysis by MnPc is proposed in this paper. The highest yield was 60.5%, with conversion and selectivity of 75.6 and 80.0%, respectively.

Experimental

Materials and methods

Reagents A and B, which were mixed together in the ratio 1:1 (v/v) then left at room temperature for several days to form a mixture of the oxidants $\text{CH}_3\text{CO}_3\text{H}$ and H_2O_2 , were bought from Aladdin corporation. KMnO_4 solution (0.01 M) and $\text{Na}_2\text{S}_2\text{O}_3$ solution (0.01 M) were used to detect the amounts of H_2O_2 and $\text{CH}_3\text{CO}_3\text{H}$ separately; the results are listed in Table 1.

2-MN and 30% H_2O_2 were purchased from National Reagents Corporation. MnPc was purchased from TCL Corporation.

Preparation of 2-methyl-1,4-naphthoquinone

2-MN (2.5 g, 17.6 mmol) and MnPc (0.65 g, 0.92 mmol) were dissolved in 35 ml glacial acetic acid in a 100-ml four-necked flask equipped with a stirring bar, a reflux condenser, a thermometer, and a 50-ml dropping funnel. The mixture was heated to 60 °C, at which temperature the oxidant 30% H_2O_2 or mixture of oxidants was added to the raw material solution over a period of 1.5 h. The mixture was kept

Scheme 1 Oxidation of 2-MN to 2-MNQ

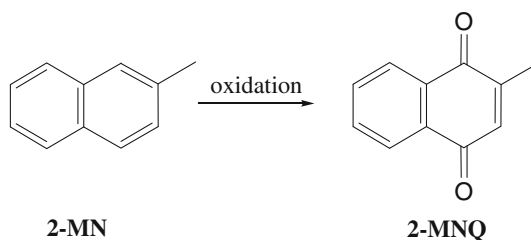


Table 1 Amounts of $\text{CH}_3\text{CO}_3\text{H}$ and H_2O_2

| Time/day | | 3 | 5 | 6 | 7 | 12 |
|------------|----------------------------------|------|------|------|------|------|
| Amounts/w% | $\text{CH}_3\text{CO}_3\text{H}$ | 13.5 | 16.8 | 22.5 | 23.7 | 26.2 |
| | H_2O_2 | 15.4 | 13.1 | 9.9 | 8.4 | 6.3 |

At room temperature (approx. 20 °C); reagent A:reagent B = 1:1 (v/v)

warm for 1.5 h. At the beginning of the reaction the solution was light green but the color gradually deepened as time passed. There was a color-change from green to orange after a specific time. Finally the solution turned bright orange. It should be noted that at different temperatures the reaction mixture has different colors for different periods. At low temperatures (40 and 60 °C) the green color should stay for a long time, even for several minutes after the oxidant was added; the reaction mixture then turns orange. At higher temperatures (100 and 80 °C), the color changed quickly from green to black, and ended as orange.

Analysis

The crude product solution was analyzed by HPLC under the following operating conditions:

ODS C_{18} , 250 mm \times 4.6 mm (inner diameter) particle size 5 μm

Mobile phase: $\text{CH}_3\text{OH}-\text{H}_2\text{O}-\text{CH}_3\text{CN}$ 1:1:1 (v/v/v)

Flow rate: 1.0 mL/min

Detection wavelength: 254 nm

Sample volume: 20 μl

Figure 1 shows the result from HPLC analysis of the solution of the crude product. The compounds at retention times 4.080 and 9.168 min are 2-MNQ and 2-MN, respectively

Results and discussion

In the presence of acetic acid, 2-MN is oxidized by hydrogen peroxide to, mainly, 2-MNQ. Anne Bohle [20] supplied us with an epoxidation pathway (Scheme 2). Because $\text{CH}_3\text{CO}_3\text{H}$ was the effective oxidant in the reaction, two types of oxidant were investigated in detail for oxidation of the raw material, 30% H_2O_2 and mixtures of H_2O_2 and $\text{CH}_3\text{CO}_3\text{H}$ containing the amounts of H_2O_2 and $\text{CH}_3\text{CO}_3\text{H}$ listed in Table 1. The table shows that after 7 days the amount of $\text{CH}_3\text{CO}_3\text{H}$ had increased slowly to approximately 24%, so the oxidant mixture we used later in the work was always the solution which had been left for 7 days.

Effect of two types of oxidant without any catalyst in the reaction

The effect of two types of oxidant on the selectivity, conversion, and yield of oxidation reaction were studied in detail (Table 2).

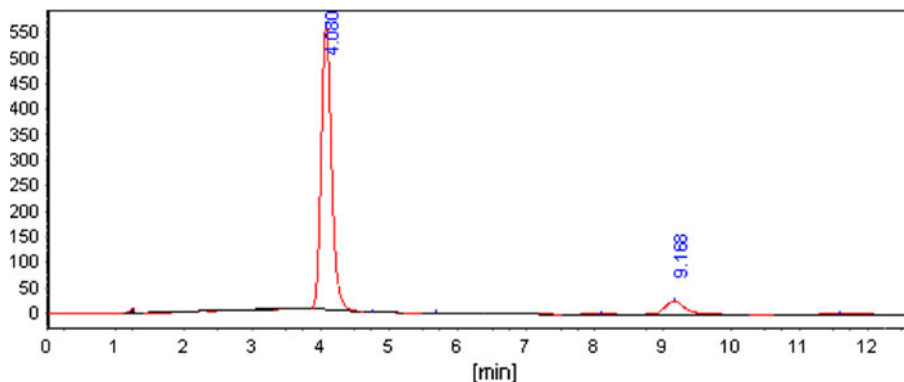
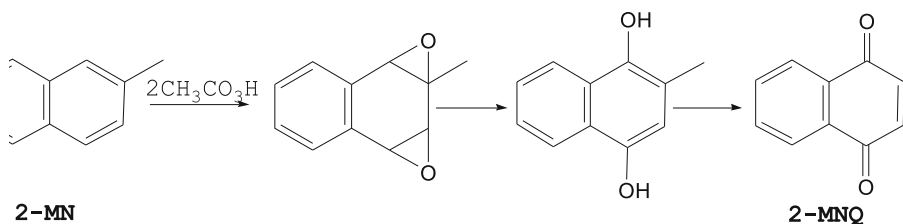


Fig. 1 HPLC of the solution of the crude product



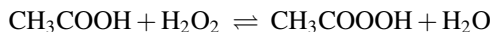
Scheme 2 Epoxidation pathway from 2-MN to 2-MNQ

Table 2 Oxidation of 2-methylnaphthalene by two types of oxidant

| Oxidant | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) |
|--------------------------------------|------------------|----------------|-----------------|-----------|
| 1. 30% H ₂ O ₂ | 40 | 44.5 | 22.7 | 10.1 |
| | 50 | 50.7 | 28.2 | 14.3 |
| | 60 | 74.3 | 38.1 | 28.3 |
| | 80 | 86.2 | 31.9 | 27.5 |
| | 100 | 90.0 | 19.0 | 17.1 |
| 2. mixture | 40 | 51.3 | 71.3 | 36.6 |
| | 50 | 51.7 | 63.3 | 32.7 |
| | 60 | 53.4 | 61.8 | 33.0 |
| | 80 | 45.2 | 43.8 | 19.8 |
| | 100 | 52.8 | 34.3 | 18.1 |

2-MN = 2.5 g, acetic acid = 35 ml, reaction = 3 h, 30% H₂O₂ = 15 ml or mixed solution = 15 ml

There was an equilibrium in our reaction system using hydrogen peroxide as sole oxidant in acetic acid, as follows [21]:



Because CH₃CO₃H was the effective oxidant in the reaction [20], the mixture which contained CH₃CO₃H prepared in advanced is always more selective than

30% H₂O₂. However, conversion by the mixture decreased obviously compared with 30% H₂O₂, mainly because CH₃CO₃H is less stable than H₂O₂.

With increasing temperature, the oxidizing strength of 30% H₂O₂ increased, leading to distinctly improved conversion. For the mixed oxidant, however, decomposition of CH₃CO₃H countered the effect of increasing the temperature. So there was an evident minimum in the conversion tendency of 2-MN at 80 °C.

The combined effect of this behavior was that the respective highest yields of 2-MNQ as a result of oxidation by 30% H₂O₂ and by the mixture were 28.3% at 60 °C and 36.6% at 40 °C.

MnPc as catalyst in the presence of CH₃CO₂H

Decomposition of CH₃CO₃H sharply reduces the amount in the reaction liquid, which leads to lack of enough oxidant for our target reaction. To solve this problem, MnPc was added as catalyst because of its sensitivity to superoxides; a specific metal oxy-compound formed was assumed to be an effective oxidant. We hoped to improve the experimental results by fixing oxygen in the form of a manganic oxy-compound. All related experimental results are listed in Table 3.

Effect of MnPc as catalyst

There was a distinct point at 60 °C in the conversion of 2-MN when MnPc as catalyst of the oxidation reaction, compared with nothing added, resulted in greater conversion than the latter. It was supposed that temperature has a substantial effect on oxidation. The results at low temperature show the positive effect of the formation of the manganic oxy-compound, which is effective as an oxidant in our

Table 3 MnPc as catalyst in the oxidation of 2-MN

| System | Temperature (°C) | Conversion (%) | Selectivity (%) | Yield (%) |
|--|------------------|----------------|-----------------|-----------|
| 1. 30%H ₂ O ₂ + MnPc + CH ₃ CO ₂ H | 40 | 62.2 | 11.4 | 7.1 |
| | 50 | 65.3 | 25.1 | 16.4 |
| | 60 | 75.6 | 80 | 60.5 |
| | 80 | 57.7 | 40.9 | 23.6 |
| | 100 | 34.2 | 28.4 | 9.7 |
| 2. Mixture + MnPc + H ₃ CO ₂ H | 40 | 27.4 | 46 | 12.6 |
| | 50 | 29.7 | 43.4 | 12.9 |
| | 60 | 35.0 | 41.3 | 14.5 |
| | 80 | 52.6 | 35.4 | 18.6 |
| | 100 | 64.8 | 17.7 | 11.5 |
| 3. Mixture + MnPc + DMF | 40 | 40.0 | 16.3 | 6.5 |
| | 50 | 41.1 | 18.8 | 7.8 |
| | 60 | 43.5 | 21 | 9.1 |
| | 80 | 49.9 | 19.8 | 9.9 |
| | 100 | 53.6 | 17.2 | 9.2 |

2-MN = 2.5 g, acetic acid = 35 ml or DMF = 35 ml, reaction = 3 h, MnPc solution = 0.6 ml, 30% H₂O₂ = 15 ml or mixture = 15 ml

reaction, however it seems that this manganic oxy-compound tended to be more abundant at 60 °C than 40 °C. In contrast, higher temperatures than 60 °C led to faster decomposition of the manganic oxy-compound with lower conversion of 2-MN.

In a similar tendency to the influence of MnPc as catalyst on the conversion, there was also a distinct point at 60 °C for selectivity. Except for 40 °C, all other selectivities for 2-MNQ with MnPc as catalyst were better than with nothing added; this was especially true for 60 °C.

The combined effect of this behavior was that the highest yield of 2-MNQ by oxidation with 30% H₂O₂ and MnPc as catalyst was 60.5% with conversion 75.6% and selectivity 80%.

Effect of oxidant type in the reaction with MnPc as catalyst

When the mixture referred to above was used in place of 30% H₂O₂ to oxidize 2-MN to 2-MNQ with MnPc as catalyst, the results showed a mainly negative effect on our target product. There was a sharp decrease both in the conversion of 2-MN and selectivity for 2-MNQ at 60 °C, which implied the supposed manganic oxy-compound cannot be formed by MnPc reacting with CH₃CO₃H generated in advance. Use of CH₃CO₃H resulted in better selectivity for 2-MNQ than 30% H₂O₂; however, this gradually decreased with increasing temperature because of the increasing decomposition of CH₃CO₃H. It can also be inferred that CH₃CO₂H could not be combined with MnPc directly to take part in the reaction. However molecular H₂O₂ seems to be effective when it combines with MnPc before participating in the oxidation.

Effect of solvent type on selectivity and conversion with MnPc as catalyst

N,N-Dimethylformamide (DMF) is a classic nonprotonic solvent different from CH₃CO₂H, which is a strong proton-donating solvent in reactions to form a new compound with much more stability via a reactive intermediate. To confirm that CH₃CO₂H participated in the oxidation, we replaced it with DMF as solvent. As a result, selectivity for 2-MNQ with DMF as solvent was very low—approximately 20%, which was much different from when CH₃CO₂H was used as solvent. There was a similar contrast in the conversion of 2-MN under these two conditions. The different proton-donor capacity of DMF and CH₃CO₂H to form reactive intermediates explains this discrepancy.

From all the analysis above, a probable reaction process with MnPc as catalyst in the presence of acetic acid in the oxidation of 2-MN by 30% H₂O₂ was proposed (Process 1). The molecule of H₂O₂ seems to be effective, and this combines with MnPc, in contrast with CH₃CO₃H. A five-membered ring could then be formed from the solvent-CH₃CO₂H close to the H₂O₂. Subsequent loss of H₂O improves the electrophilicity of the oxygen–oxygen bond. With regard to steric configuration in the oxidation of 2-MN, simultaneous cyclo-oxidation has also been proposed by Svetlana V. Barkanova and others [22]. Further experiments on this reaction should be carried out in the near future.

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