Sulfric acid as Effective Catalyst for the Oxidation of 2-Methyl Naphthalene by hydrogen peroxide

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Abstract: The oxidation of 2-Methylnaphthalene (2-MN) was carried out in actic acid with 30%H$_2$O$_2$. 2-Methyl-1,4-Naphthoquinone (2-MNQ) was obtained in a yield of 81.3% when sulfric acid used as catalyst. The aromatic substituted pathway is speculated as the dominated oxidation pathway with a higher conversion than the epoxidation one due to the activity of CH$_3$CO$_3$H$^+$ formed by actic acid and H$^+$ supplied from sulfric acid. The reaction has been studied by varying different parameters like dosages of 30% H$_2$O$_2$ and actic acid, reaction time. Compared to the conventional preparation of Vitamin K$_3$, this method could be economical and ecofriendly as the traditional yield only 30-50% and chromium pollution.

Key Words: 2-Methylnaphthalene; 2-Methyl-1,4-Naphthoquinone; Acetic acid; Oxidation; Hydrogen peroxide; Vitamin K$_3$

INTRODUCTION

The clean synthesis of organic products with reduced or eliminated use of hazardous substances is still a challenging task in our current organic chemistry, especially for the oxidation area. It is well known that quinones possess pronounced bioactivity and find important medicinal applications[1]. Ever since 2-MNQ (vitamin K$_3$), used therapeutically under Menadione, was found to have more antibleeding activity than the natural vitamins K$_1$ or K$_2$. Many methods have been described to bring about the controlled oxidation of 2-MN (Scheme 1) using various oxidizing agents in the presence of catalyst[2]. Traditionally, menadione is produced on an industrial scale via stoichiometric oxidation of 2-MN by CrO$_3$ in sulfuric acid. Yield and selectivity are moderate (typically around 50%)[3]. The drawbacks of this method are obvious: production of inorganic salts as by-product (18kg of salt per kg of product) and a necessary treatment of chromium-containing waste water[4]. Adam and co-workers[5] described the use of acetic acid, hydrogen peroxide and methyl trioxorhenium (conversion of 2-MN was 81%, affording 47% of 2-MNQ, Pd(II)-polystyrene sulphonic acid resin[6] as catalyst. The rhenium catalyzed oxidation of 2-MN, using 85%H$_2$O$_2$ solution gave a conversion 93% at 40 °C after 4h. But this high concentration of H$_2$O$_2$ is critical dangerous for operation.

We have now studied the oxidation of 2-MN in detail using just 30% H$_2$O$_2$ in the presence of acetic acid with sulfric acid as catalyst in a higher yield of 81.3% than other reported. The aromatic substituted pathway is speculated as the dominated oxidation pathway with a higher conversion than the epoxidation one due to the activity of CH$_3$CO$_3$H$^+$ formed by actic acid and H$^+$ supplied from sulfric acid compared to nothing as catalyst and only CH$_3$CO$_2$H as oxidant in reaction.

Scheme 1: Oxidation of 2-MN to 2-MNQ

EXPERIMENTAL

The Preparation and Detection of Mixture Oxidants (H$_2$O$_2$ and CH$_3$CO$_2$H)

The reagent A and B we bought from Aladdin corporation were mixed together by 1:1(V/V), and
then the mixture formed was stayed aside at the room temperature for several days. During this period, we took the traditional titration-iodometry, KMnO₄ solution (0.01M) to titrate H₂O₂ and Na₂S₂O₃ solution (0.01M) to detect CH₃CO₂H of the mixture we obtained, to get the contents of H₂O₂ and CH₃CO₂H respectively.

**Synthesis of 2-Methyl-1,4-Naphthoquinone**

2-MN (2.5g, 17.6mmol) were dissolved in 55mL of glacial acetic acid with 0.55mL of sulfuric acid in a 250mL four-necked flask equipped with a stirring bar, a reflux condenser, a thermometer and a 50mL dropping funnel. The mixture was heated to 60°C, at which temperature 30%H₂O₂ was added to the raw material solution over a period of 1.5h. Then it was kept warm for 1.0h. At the beginning of this reaction, solution showed shallow orange, but the color gradually deepen as time lapse. At a higher temperature (100°C and 80°C), the color could change quickly to black, and ended in orange. The product solution was analysed by HPLC, which chromatograph condition were listed as followed:

ODS C₁₈, 250mm×4.6mm (inner diameter) particle size 5µm

Mobile phase:
- Methanol: H₂O:CH₃CN=1:1:1 (V/V/V)
- Flow rate: 1.0mL/min
- Detection wavelength: 250nm
- Sample volume: 20µL

**Results and Discussion**

In the presence of acetic acid, 2-MN is oxidized by hydrogen peroxide preferentially to the 2-MNQ. Anne Bohle[7] supplied us with two oxidation pathways. Since the CH₃CO₂H was necessary in reaction, two types of oxidants were explored to oxidize the raw material in detail, 30%H₂O₂ and the mixture of H₂O₂ and CH₃CO₂H, in which the contents of H₂O₂ and CH₃CO₂H were listed in Table 1. And it shows after seven days, the content of CH₃CO₂H increased slowly in about 24%, so all of the mixture oxidant we applied later was that solution stayed aside for 7 days.

**The Effect of Different Oxidants**

Initially, we kept other conditions same except the types of oxidant, one is 30%H₂O₂ but the other one is the mixture we prepared above. We found higher content of CH₃CO₂H brings out well selectivity of 2-MNQ than 30% H₂O₂ while a lower conversion of 2-MN. As a result it gave a yield of 2-MNQ in 40.7% when 30%H₂O₂ as oxidant.

![Figure 1: The Mass Contents of CH₃CO₂H and H₂O₂ in Mixture: at Room Temperature (about 20°C); Reagent A: Reagent B = 1:1(V/V)](image)

![Figure 2: The Effect of Different Oxidants: m(2-MN) = 2.5g, T = 60°C, v(CH₃CO₂H) = 55mL, v(oxidant) = 28mL, Reaction Time = 3h](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The Effect of Different Temperatures in Different Oxidants[^d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. No.</td>
<td>Oxidant</td>
</tr>
<tr>
<td>1</td>
<td>30%H₂O₂</td>
</tr>
<tr>
<td>2</td>
<td>30%H₂O₂</td>
</tr>
<tr>
<td>3</td>
<td>30%H₂O₂</td>
</tr>
<tr>
<td>4</td>
<td>30%H₂O₂</td>
</tr>
<tr>
<td>5</td>
<td>Mixture</td>
</tr>
<tr>
<td>6</td>
<td>Mixture</td>
</tr>
<tr>
<td>7</td>
<td>Mixture</td>
</tr>
<tr>
<td>8</td>
<td>Mixture</td>
</tr>
</tbody>
</table>

[^d]: m(2-MN)=2.5g, v(oxidant)=28mL, v(CH₃CO₂H)=55mL, reaction time=3h
Sulfric Acid as Effective Catalyst for the Oxidation of 2-Methyl Naphthalene by Hydrogen Peroxide

We kept other conditions same except the temperatures when 30% H$_2$O$_2$ and the mixture as oxidants respectively. In the former result shows the conversion of raw material increased to 95.2% as the temperature increases while the best selectivity was founded at 60°C in 52.0%. Probably there was critical over-oxidation in reaction when temperature high as the explanation.

It showed different case when he mixture as oxidant instead of 30% H$_2$O$_2$. The conversions varied slightly in 50% while the selectivity decreased sharply with temperature increasing. So we consider the decomposability of CH$_3$CO$_2$H, which change into CH$_3$CO$_2$H and O$_2$ and enhanced by higher temperature, will account for it. As a result it gave a yield of 2-MNQ in 36.6% at 40°C.

From the two tables of temperature’s effect, we can see the trends of conversion and selectivity of reaction are contradictory. We hope to improve the conversion at lower temperature by adding sulfuric acid through the aromatic substituted pathway. Followed are the researches of different parameters we studied.

The Effect of Different Dosage of Sulfuric Acid as Catalyst

It was clearly shown that the conversion of 2-MN was improved greatly because of sulfuric acid, mainly above 94% as the dosage of sulfuric acid in volume fraction to acetic acid more than 0.5%. At the same time selectivity of 2-MNQ was also enhanced to 86.4% as the highest one when 1.0% of sulfuric acid used. The aromatic substituted pathway is speculated as the dominated oxidation pathway with a higher conversion than the epoxidation one due to the activity of CH$_3$CO$_2$H$^+$ formed by acetic acid and H$^+$ supplied from sulfuric acid. More than 1.0% of sulfuric acid could no longer bring much more effective impact for the oxidation of 2-MN.

The Effect of Different Dosage of Oxidant

Obviously larger dosage of 30% H$_2$O$_2$ could bring about higher conversion as well as lower selectivity due to the over-oxidation in reaction. There was a highest point both for selectivity and yield when the dosage of 30% H$_2$O$_2$ is 28mL with 1.0% of sulfuric acid in solvent as catalyst. More than 28mL of 30% H$_2$O$_2$ can no longer lead to evident improve of conversion and the yield, to the contrary which often gave a worse yield as a comprehensive result.
**The Effect of Different Reaction Time**

The last factor we studied on this reaction is the time. Among all of the time we adopt for research selectivitis are fluctuating around 80% while the conversion was continually increased as time elapsed. It was speculated that the forming 2-MNQ could be oxidized into other side-products in further, so we can forecast the selectivity probably will decrease with reaction time longer. However the conversion of 2-MN was above 90% after 3h.

**CONCLUSION**

Oxidation of 2-methylnaphthalene with hydrogen peroxide in the acetic acid yields 2-methyl-1,4-naphthoquinone at 60 °C with 1.0% sulfuric acid as catalyst in a higher yield of 81.3% than other traditional methods, which will also can avoid the serious chromium-pollution. From the detailed studies, especially for research on those comparisons between two kinds of oxidant, we suppose the aromatic substituted pathway as the dominated oxidation pathway with a higher conversion than the epoxidation one due to the activity of CH\(_3\)CO\(_2\)H\(_2\) formed by acetic acid and H\(^+\) supplied from sulfuric acid. The use of acetic acid and hydrogen peroxide with sulfuric acid as catalyst clearly represents advancement for an oxidation process under economically and environmentally acceptable conditions, which hitherto used chromium and manganese salts for oxidation of this reaction.

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**REFERENCES**


