



An effective oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethylbenzoquinone using Fenton's reagent under mild conditions

Ying Li^{a,b}, Pei Zhang^a, Mingzhu Wu^a, Wei Liu^{a,b,*}, Zhongzhou Yi^{a,b},
Min Yang^a, Jucheng Zhang^a, Guowei Zhang^a, Zhanhong Bai^a

^a Department of Chemistry, Honghe University, Mengzi, 661100, PR China

^b Key Laboratory of Natural Pharmaceutical & Chemical Biology of Yunnan Province, Honghe University, Mengzi, 661100, PR China

ARTICLE INFO

Article history:

Received 17 March 2008

Received in revised form 6 September 2008

Accepted 17 September 2008

Keywords:

Oxidation

2,3,6-Trimethylphenol

2,3,5-Trimethylbenzoquinone

Fenton's reagent

FeSO₄

Catalyst

ABSTRACT

The oxidation of 2,3,6-trimethylphenol with Fenton's reagent has been investigated under mild conditions in aqueous phase. 2,3,5-Trimethylbenzoquinone was obtained with a selectivity of nearly 99.9% at 100% conversion of 2,3,6-trimethylphenol at 45 °C for 3 h. The different parameters like: the performance of different catalysts, the effect of catalyst concentration, reaction time, and reaction temperature has been investigated. Moreover, our new catalytic system was found also to be active in the oxidation of *o*-methylphenols to the corresponding benzoquinones by 5% H₂O₂ under mild conditions. In order to further study this reaction system, the possible mechanism was proposed. An important advantage of this catalytic system, apart from the organic solvent-free conditions, is that it is nontoxic, inexpensive and water-soluble.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

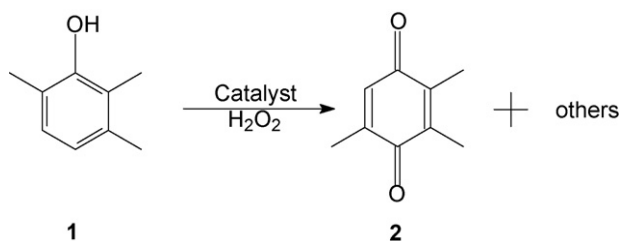
During recent years, in the wake of increasingly stringent environmental legislation, attention has been focused on the development of catalytic oxidations for the manufacture of fine chemicals [1]. The oxidation of phenols to quinones, for example, is a ubiquitous reaction in organic chemistry. These transformations are of great importance not only in the laboratory but also in industry, where they account for most of the applied processes in bulk and fine chemistry. Natural products having a benzoquinone structure also show biologically important properties such as cardiovascular, antitumour, antibacterial, antigerminative, and antiprotozoan activities [2–4]. Furthermore, benzoquinones are important fine chemicals in industry and are used to synthesize many pharmaceuticals [5]. For example, 2,3,5-trimethyl-1,4-benzoquinone (TMQ), as with a number of other benzoquinones, is an especially valuable starting material for the synthesis of V_E and other pharmaceuticals. The oxidation of 2,3,5-trimethylphenol (TMP) or 2,3,6-trimethylphenol is the key step for the production of 2,3,5-trimethylbenzoquinone. In industry, a current method of TMQ production is *para*-sulfonation of TMP,

followed by oxidation with manganese dioxide. This method, however, is not suitable for continuable industrialized manufacture because of the contamination of inorganic salts and wastewater. Previously, various oxidation methods for trimethylphenol have been reported [6–14]. These different methods, however, show varying degrees of success as well as limitations due to the need for equimolar catalysts, high reaction temperatures, and the use of large quantities of organic solvents in reaction system with the possibility of explosion. Among these, CuCl₂ has been the most favored catalyst when used with an equimolar amount of TMP. Takehira [15] and Bodnar et al. [16] reduced the amount of the catalyst by employing nitrogen-containing organic compounds as co-catalysts. However, the co-catalysts were partly consumed in the reaction system. Recently, we reported that the catalyst CuCo₂O₄ showed high activity and selectivity in the oxidation of 2,3,5-trimethylphenol to 2,3,6-trimethylbenzoquinone with aqueous hydrogen peroxide at room temperature. However, the excessive use of H₂O₂ is unrealistic in an industrial process [17].

One hundred years ago, H.J.H. Fenton reported that ferrous ions strongly promote the oxidation of maleic acid by hydrogen peroxide [18]. Study has shown that the combination of H₂O₂ and a ferrous salt, "Fenton's reagent", is an efficient oxidant of a wide variety of organic substrates [19]. Subsequently Fenton's and like-Fenton's reagents were used in wastewater treatment under acidic conditions [20–24]. Although the use of Fenton's reagent

* Corresponding author at: Department of Chemistry, Honghe University, Mengzi, 661100, PR China. Tel.: +86 873 3694921; fax: +86 873 3694921.

E-mail address: wzm800929@yahoo.com (W. Liu).



and related reactions are potentially useful oxidation processes for organic compounds in water, there are few reports in which Fenton's reagent was used for organic synthesis [25–28].

We report in this work a very simple, efficient and selective oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethylbenzoquinone with 5% H_2O_2 catalyzed by FeSO_4 (Fenton's reagent), developed under mild conditions. The reaction can take place in the aqueous phase and can be applied to the oxidation of *o*-methylphenols to the corresponding benzoquinones. As a water-soluble catalyst, FeSO_4 can be easily separated from the reaction products by simple disposal. In addition, the products are not contaminated with traces of metal catalyst.

2. Experimental

2.1. Materials

Methylphenols were donated by J&K Chemical Ltd. H_2O_2 (30%) and metal salts were analytical grade from Aldrich or Fluka.

2.2. General procedure for the oxidation of 2,3,6-trimethylphenol

The catalytic oxidation reactions of TMP were carried out using a 100 mL three-necked flask equipped with a reflux condenser, magnetic stirrer, super constant temperature oil bath and thermometer. In a typical reaction, TMP (1 mmol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5 mol%) and deionized water (10 mL) were placed in the flask, and then 5% H_2O_2 (4.1 mmol) was added dropwise to the stirred mixture at 45 °C. Ten microlitres of fresh chloroform was added and then separated. The selectivities and conversions were determined by GC and GC–MS.

2.3. Physical measurements

GC analyses were performed using a gas chromatograph (GC-2010, Shimadzu) equipped with a flame ionization detector and a quartz capillary column (25 m \times 0.3 mm) filled with Carbowax 20M. GC–MS analyses of the products were carried out using a HP 5973/6890 system (electron impact ionization at 70 eV, He carrier gas, 30 m \times 0.25 mm cross-linked 5% PHME siloxane (0.25 μm coating) capillary column; HP-5MS) or a VG-7070 instrument.

3. Results and discussion

3.1. Catalytic oxidation of 2,3,5-trimethylphenol

3.1.1. Performance of Fenton's and like-Fenton's reagents

The catalytic performance of Fenton's reagent and several prevailing like-Fenton's reagents for the oxidation of TMP by 5% H_2O_2 (Scheme 1) was compared under the same conditions with the results shown in Table 1. The oxidation of TMP (1 mmol) was carried out with 4.1 mol H_2O_2 (5%) as oxidant in the presence of a catalytic amount of various metal salts (5 mol%) in

Table 1
Oxidation of TMP with different catalysts.

Catalyst	Conversion (mol%)	Selectivity (mol%)	Isolated yield (mol%)
–	0.0	0.0	0.0
$\text{Cr}(\text{NO}_3)_3$	66.2	78.6	51.1
$\text{Cr}_2(\text{SO}_4)_3$	66.7	99.3	66.0
$\text{Mn}(\text{NO}_3)_2$	80.3	85.6	68.7
MnSO_4	80.2	98.2	78.7
$\text{Fe}(\text{NO}_3)_3$	98.7	88.6	87.4
$\text{Fe}_2(\text{SO}_4)_3$	100.0	99.9	99.7
FeSO_4	100.0	99.9	99.8
FeCl_3	96.3	84.3	81.1
FeCl_2	96.7	98.3	95.0
$\text{Co}(\text{NO}_3)_3$	98.5	60.5	59.5
$\text{Co}_2(\text{SO}_4)_3$	97.5	85.5	83.3
$\text{Ni}(\text{NO}_3)_2$	91.3	72.9	66.5
NiSO_4	91.7	92.5	84.6
$\text{Cu}(\text{NO}_3)_2$	83.6	80.5	62.2
CuSO_4	82.9	90.3	74.7

Reaction conditions: 1 mmol TMP, 5 mol% catalyst, 10 mL deionized water, 4.1 mol 5% H_2O_2 , reaction time = 3 h, reaction temperature = 45 °C.

10 mL deionized water at 45 °C within 3 h. As seen in Table 1, the reaction did not proceed in the absence of catalyst although autocatalysis by the reactor wall is often observed in oxidations [29]. We can also see that the selectivity of TMQ varied considerably although catalysts composed of the same metal ion and different anions (NO_3^- , SO_4^{2-} and Cl^-) yielded similar values of TMP conversion. On the other hand, different metal ions had a dramatic effect on the catalytic activity even when these catalysts have the same anions. It was found that the selectivity of TMQ decreased in the order $\text{FeSO}_4 \approx \text{Fe}_2(\text{SO}_4)_3 > \text{Cr}_2(\text{SO}_4)_3 > \text{FeCl}_2 \approx \text{MnSO}_4 > \text{NiSO}_4 > \text{CuSO}_4 > \text{Fe}(\text{NO}_3)_3 > \text{Mn}(\text{NO}_3)_2 > \text{Co}_2(\text{SO}_4)_3 > \text{FeCl}_3 > \text{Cu}(\text{NO}_3)_2 > \text{Cr}(\text{NO}_3)_3 > \text{Ni}(\text{NO}_3)_2 > \text{Co}(\text{NO}_3)_2$. At the same time the conversion of TMP reduced in the order $\text{FeSO}_4 \approx \text{Fe}_2(\text{SO}_4)_3 > \text{Fe}(\text{NO}_3)_3 \approx \text{Co}(\text{NO}_3)_2 > \text{Co}_2(\text{SO}_4)_3 > \text{FeCl}_2 \approx \text{FeCl}_3 > \text{NiSO}_4 \approx \text{Ni}(\text{NO}_3)_2 > \text{CuSO}_4 \approx \text{Cu}(\text{NO}_3)_2 > \text{Mn}(\text{NO}_3)_2 \approx \text{MnSO}_4 > \text{Cr}_2(\text{SO}_4)_3 \approx \text{Cr}(\text{NO}_3)_3$. It is interesting to point out that the FeSO_4 catalyst shows the highest conversion and selectivity in the same operating conditions. However, 4-chloro-2,3,5-trimethylphenol was detected when metal salts containing Cl^- were used as the catalyst. Among these, FeCl_2 and FeCl_3 yielded the most 4-chloro-2,3,5-trimethylphenol. The amount of 4-chloro-2,3,5-trimethylphenol clearly increased and the selectivity of TMQ was markedly reduced when FeCl_2 was replaced by FeCl_3 . From Table 1, it was found that the catalytic activity of FeCl_2 was more effective than that of FeCl_3 [30], but both of them are lower than FeSO_4 . Therefore, we suggest FeSO_4 (Fenton's reagent) as the most suitable catalyst.

3.1.2. Effect of catalyst concentration

In order to lucubrate the catalytic performance of Fenton's reagent, the oxidative effect of TMQ by FeSO_4 was investigated using 4.1 mol 5% H_2O_2 as oxidant in 10 mL deionized water at 45 °C within 3 h. Fig. 1 displays the conversion of TMP and the selectivity of TMQ under the same conditions as a function of the FeSO_4 to TMP ratio. An initial steep increase in the conversion of TMP was observed when the amount of FeSO_4 was increased up to 5 mol%; beyond this amount, the conversion of TMP levelled off in the reaction system (up to 100%). The selectivity of TMQ was clearly reduced when the amount of FeSO_4 is greater than 5 mol%. Other products were detected by GC–MS when the amount of catalyst added was 8 mol%. Muconic acid, maleic acid and oxalic acid were found to be present in this reaction system. This point is in accordance with most of the literature [20,31–32]. Therefore, 5 mol% FeSO_4 would appear to be the optimum amount of catalyst for selectively producing TMQ.

Download English Version:

<https://daneshyari.com/en/article/152671>

Download Persian Version:

<https://daneshyari.com/article/152671>

[Daneshyari.com](https://daneshyari.com)