Catalytic hydrodechlorination reactivity of monochlorophenols in aqueous solutions over palladium/carbon catalyst

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A B S T R A C T

Monochlorophenols (CPs) were completely hydrodechlorinated with 5% Pd/C in aqueous solutions at room temperature under atmospheric pressure. In the hydrogenation process, 2-CP, 3-CP and 4-CP showed different dechlorination reactivity. It was found the C–Cl bond in the ortho position of hydroxyl group was the most difficult dechlorination in the hydrogenation of monochlorophenols in aqueous solutions compared to those in meta and para positions. Additionally, bases and solvents also had influences on the hydrodechlorination reactivity and selectivity of monochlorophenols as well as the activity of the catalyst. In aqueous solutions, it was more advantageous to the hydrodechlorination of monochlorophenols during the hydrogenation due to the cleaning function of water. Furthermore, the presence of bases, especially for sodium hydroxide, also ensured the high activity of the catalyst in water.

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1. Introduction

Heterogeneously catalytic hydrogenation is a convenient method for the dehalogenation of aryl halides in organic synthesis because of its experimental simplicity, good yields and high purity of products [1]. In recent years, because the disposal of chlorinated organic waste becomes a serious environmental problem, catalytic hydrodehalogenation methods have been developed in the treatment of chlorinated organic waste [2–9] and a wide variety of hydrodehalogenation systems have been used in the environmental catalysis [10–18].

In most hydrogenation reactions of aromatic halides in liquid phase, organic solvents are usually used as the reaction medium. However, water, being cheaper, safer and more environmentally amicable than organic solvents, is seldom utilized in the hydrodechlorination of aryl halides [17–20]. We have reported the heterogeneously catalytic hydrodechlorination of aromatic halides in the liquid phase. It was found that the addition of water greatly improved the dechlorination rates of the hydrodechlorination reactions [21–22]. Recently, the hydrodehalogenation of aromatic halides, PCBs and dioxins in aqueous solution has been studied in our group [23–25]. Here, we reported the hydrodechlorination reactivity of monochlorophenols (2-CP, 3-CP and 4-CP) in aqueous solutions at room temperature under atmospheric pressure. Additionally, it was also found that bases and solvents also had influences on the hydrodechlorination reactivity of monochlorophenols.

2. Experimental section

5% Pd/C catalyst used in experiments was purchased from C&P Chemical Co., China. The catalyst was not pre-treated before experiments and only hermetically-sealed kept in a desiccator. 2-Chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) (purity ≥ 98%) were obtained from Aldrich. Water used in the reaction was deionized. The purities of hydrogen and nitrogen used in the experiments were more than 99.99%.

The reaction was carried out in a three-necked flask, which was attached with a thermometer, a condenser and a hydrotreater (including a hydrogen cylinder, hydrogen flowmeter, three-way valve and a nitrogen cylinder), with a magnetic stirrer at room temperature. Under atmospheric pressure, 50 ml aqueous solution of monochlorophenols (4.0 mmol), stoichiometric NaOH (160 mg, 4.0 mmol) and 5% Pd/C (30 mg, 14.2 × 10−3 mmol) were added into the flask. At room temperature, monochlorophenols were treated with hydrogen gas and 5% Pd/C in aqueous solutions.

The intermediate products in the hydrodechlorination reaction of monochlorophenols (2-CP, 3-CP and 4-CP) were determined by GC/MS (Finnigan trace 2000 GC/MS-Trap) with a column of HP-
The different catalyst used in the dechlorination of chlorophenols. This difference was possibly relevant to the positions of the hydroxyl group. In Table 2, 2-CP, 3-CP and 4-CP exhibited different dechlorination reactivity in aqueous solutions over 5% Pd/C. It can be clearly observed that the turnover frequencies (TOFs) of the dechlorination of monochlorophenols followed the order of 4-CP > 3-CP > 2-CP, which was consistent with the results reported by Felis et al. [26]. Felis found the ortho and para chlorine atoms were equally reactive whereas the meta position chlorine was more difficult to hydrogenolyis in monochlorophenols. This difference was possibly relevant to the different catalyst used in the dechlorination of chlorophenols.

### Table 1

<table>
<thead>
<tr>
<th>CPs</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>TOF (min⁻¹)</th>
<th>DC (%)</th>
<th>Compositions of Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-CP</td>
<td>H₂O</td>
<td>60</td>
<td>4.7</td>
<td>100</td>
<td>99.8 0.20 No detection</td>
</tr>
<tr>
<td>3-CP</td>
<td>H₂O</td>
<td>35</td>
<td>8.1</td>
<td>100</td>
<td>99.5 0.49 0.01</td>
</tr>
<tr>
<td>4-CP</td>
<td>H₂O</td>
<td>33</td>
<td>8.6</td>
<td>100</td>
<td>99.5 0.48 0.02</td>
</tr>
</tbody>
</table>

* a Reaction conditions: 50 ml aqueous solution of monochlorophenol (0.51 g, 4.0 mmol); 160 mg NaOH (4.0 mmol); 30 mg 5% Pd/C; 25°C; under atmospheric pressure.

* b TOF: turnover frequency.

In order to further evaluate the dechlorination reactivity of monochlorophenols, the equal amounts of 2-CP, 3-CP and 4-CP were mixed in aqueous solution and were catalyzed hydrogenated with hydrogen gas over 5% Pd/C. The results are shown in Fig. 1. For the mixtures of monochlorophenols, the dechlorination rates of 2-CP, 3-CP and 4-CP show the same order as that in the former experiments: 4-CP > 3-CP > 2-CP. So, 2-CP was the most difficult dechlorination in the catalytic hydrogenation of monochlorophenols with H₂ over 5% Pd/C in aqueous solutions. In other words, chlorine atoms, which are away from hydroxyl group in 2-CP, 3-CP and 4-CP, are much easier to be hydrogenated than that in the neighboring position in aqueous solutions over Pd/C. It was indicated that the steric hindrance effect of the hydroxyl group possibly affected the hydrogenolyis of ortho position C–Cl bond [13,27–28]. Recently, Aramendia et al. [8] also found that the steric effect of the methyl group could inhibit the dechlorination rate during the hydrogenation of o-chlorotoluene.

Additionally, we also research the effects of bases and solvents on the reactivity of monochlorophenols in the catalytic hydrodechlorination over 5% Pd/C. Here the mixtures of 2-CP and 4-CP were used as models and different bases were added into aqueous solutions. The results are listed in Table 2.

During the hydrodechlorination of organic chlorides, hydrochloric acid (HCl) is generated and can cause catalytically active metal to poison [29]. In the liquid-phase system the presence of a base acts as a proton scavenger, maintaining the catalytic metal in a reduced state and limiting Cl interaction(s) [14,30]. Therefore, when there was no base in the dechlorination reaction, because of the inhibitory effect of HCl on Pd/C catalyst, the dechlorination rates of 2-CP and 4-CP were lower than those using bases, such as NaOH, Et₃N (Table 2).
Furthermore, it was also observed that the dechlorination rates of 2-CP and 4-CP were different in aqueous solutions and in ethanol systems when the bases were different in the reactions. The rates of 4-CP and 2-CP were much higher when using NaOH than those with Et3N in aqueous solutions. However, in ethanol, the rates of 4-CP and 2-CP were much higher when using Et3N as a proton scavenger. The reasons of these results were possibly relevant to the solubility and basicity of the bases. Contrast to triethylamine (Et3N), a weak organic base, NaOH is a stronger base and much easier to react with HCl produced in the dechlorination of chlorophenols than Et3N. However, in ethanol, Et3N, as an organic base, is easier to dissolve than NaOH. Therefore, it was more advantageous to eliminate the poison of HCl to Pd/C for Et3N in ethanol.

Additionally, both dechlorination rates of 2-CP and 4-CP were similar when using NaOH and Et3N in ethanol, which was completely different to the results in water (Table 2). These variations of the rates illustrated that the bases could affect the reactivity of the dechlorination of organic chlorides in liquid phases. It also implied that the roles of the bases were not limited to neutralize hydrochloric acid produced in the hydrodechlorination of monochlorophenols. The bases possibly had some influences on the activity of the catalyst and the selectivity of the dechlorination [30–32].

It was also found in Table 2 that the change of the solvent system had an obvious influence on the dechlorination reactivity of 2-CP and 4-CP. Using water as the solvent, it was advantageous to the dechlorination of 4-CP and 2-CP. However, in ethanol, the dechlorination rates of 2-CP and 4-CP were much lower than those in water. We thought that sodium chloride (NaCl) formed by the neutralization of HCl and NaOH could accumulate on the surface of Pd/C during the hydrodechlorination in aqueous solutions. Ukisu et al. [10] in their studies on hydrogenation of aromatic chlorides over Rh–Pt/C have observed the activity of the catalyst gradually decreased due to accumulation of sodium chlorides on its surface and water could wash away these salts.

Thus, the nature of solvents was considerably important to the hydrodechlorination of organic chlorides in liquid phase. These facts encourage us to believe that accurately choosing proper reaction environments is essential, where both the reaction rate and reactivity may be favored. In this way, a useful hydrodechlorination method could be coupled to the destruction of chlorinated organic wastes, such as PCBs and dioxins.

In conclusion, monochlorophenols (CPs) were completely hydrodechlorinated with hydrogen gas over 5% Pd/C in aqueous solutions at room temperature under atmospheric pressure. 2-CP, 3-CP and 4-CP showed different dechlorination reactivity and the rates of the dechlorination followed the order of 4-CP ≈ 3-CP > 2-CP in aqueous solutions. Furthermore, it was found that the natures of bases and solvents also had obvious influences on the hydrodechlorination reactivity and selectivity of monochlorophenols as well as the activity of the catalyst. In aqueous solutions, it was more advantageous to the hydrodechlorination of monochlorophenols during the hydrogenation due to the cleaning function of water. Furthermore, the presence of bases, especially for sodium hydroxide, also ensured the high activity of the catalyst in water.

Table 2
The base and solvent effects on the dechlorination reactivity of 2-CP and 4-CP.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Bases</th>
<th>Solvents</th>
<th>Yields of Phenol (%)</th>
<th>Compositions of substrates (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>NaOH</td>
<td>Water</td>
<td>50</td>
<td>0.25 g 2-CP (2.0 mmol)</td>
</tr>
<tr>
<td>10</td>
<td>Et3N</td>
<td>Water</td>
<td>49</td>
<td>0.25 g 4-CP (2.0 mmol)</td>
</tr>
<tr>
<td>15</td>
<td>No base</td>
<td>Water</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>NaOH</td>
<td>Ethanol</td>
<td>45</td>
<td>0.25 g 2-CP (2.0 mmol)</td>
</tr>
<tr>
<td>45</td>
<td>Et3N</td>
<td>Ethanol</td>
<td>44</td>
<td>0.25 g 4-CP (2.0 mmol)</td>
</tr>
</tbody>
</table>

**References**