Short Communication

The influence of triethylamine on the hydrodechlorination reactivity of chlorophenols over Raney Ni catalyst

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ABSTRACT

The hydrodechlorination (HDCl) of 2,4-dichlorophenol (2,4-DCP), 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP) over Raney Ni in liquid phase with triethylamine (Et$_3$N) under mild conditions was studied. The results showed that Et$_3$N together with solvents significantly affected the HDCl reactivity or selectivity, in which *ortho*-positioned Cl of chlorophenols (CPs) was easier to be dechlorinated in methanol (MeOH) and ethanol (EtOH), whereas *para*-positioned Cl was preferentially dechlorinated in water. Different species and action mechanisms of Et$_3$N in water and organic solvents possibly affected the HDCl reactivity or selectivity of CPs over Raney Ni.

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1. Introduction

Chlorophenols (CPs) have been widely used as wood preservatives, and as pesticides/herbicide precursors. Furthermore, they can also be found in effluent streams associated with the pulp and paper industries. Due to the high toxicity and hard biodegradability of these compounds, they have been long regarded as a major source of environmental pollution [1]. Therefore, development of efficient methods to dispose them is very necessary and important. In the last few years, various destructive techniques including biological, thermal and chemical treatments have been developed for the detoxification of organic pollutants [2,3]. Among them catalytic hydrodechlorination (HDCl) has received attention as one of the most promising and innovative technologies for the disposal of toxic organochlorines, which can convert the toxic organic chlorides into the corresponding hydrocarbons under mild conditions [4–6].

Usually, supported Pd catalysts were chosen in the HDCl of CPs in liquid phase [7–12], but it was limited in the practical use due to the high cost of these catalysts. In recent years, the use of low-cost catalysts such as Raney Ni has received considerable attention in the HDCl of aryl chlorides. Many studies have indicated that organochlorines could be completely HDCl in liquid system over Raney Ni under mild conditions [13–16]. In our previous studies, it was also proved that the catalytic activity of Raney Ni was comparable to that of Pd/C for the dehalogenation of 4-bromobiphenyl (4-BB) and 2-chlorophenol (2-CP) under mild conditions [17,18].

During the HDCl process of chlorinated organic compounds, HCl by-product formed, which might result in the deactivation of catalysts. So, some bases were often used as scavengers of HCl to eliminate and minimize the poison of HCl to catalysts [8,9,19]. As an organic base, triethylamine (Et$_3$N) has been used in a series of the HDCl reactions over Pd catalysts to remove HCl formed [20–24]. Additionally, Monguchi et al. [22] thought that, besides playing a role of a base in the HDCl of aryl chlorides, Et$_3$N also could act as an electron donor for the reactants and expedite the HDCl reaction.

In this work, the HDCl reactivities of CPs such as 2,4-DCP, 2-CP and 4-CP were investigated in liquid phase over Raney Ni with Et$_3$N at room temperature and atmospheric pressure. It was found that Et$_3$N obviously affected the HDCl reactivity or selectivity of CPs, and played different roles in water and organic solvents. The effect of Et$_3$N on the HDCl reactivity or selectivity of aryl chlorides has not been reported in literature.

2. Experimental

2.1. Experimental materials

Raney Ni catalyst (RTH-311) used in experiments was supplied by Dalian Tongyong Chemical Co., Ltd., Liaoning, China. The weight percentage of nickel and aluminum in the catalyst was more than 90% and less than 7%, respectively. The catalyst was not pre-treated before experiments and only kept in water-sealing storage.

All CPs used in experiments were purchased from Alfa Aesar with a minimum purity of 98%. The other analytical reagents such as methanol (MeOH), ethanol (EtOH), Et₃N and NaOH were supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. De-ionized water and high purity hydrogen and nitrogen (>99.99%) were used in experiments.

2.2. Experimental process

The reaction was carried out in a three-neck flask at 40 °C, 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. Under atmospheric pressure, 80 mL solutions (water or MeOH/EtOH) were added into the flask, containing 2,4-DCP (3.13 mmol), 2-CP/4-CP (6.22 mmol), Et₃N (9.29 mmol) or NaOH (6.85 mmol). After the air in the flask was completely replaced by nitrogen, Raney Ni (0.2 g or 0.4 g) was added. Then the reaction mixture was stirred vigorously with a magnetic stirrer and was kept at 40 °C using a thermostated water bath. During the reaction, an aliquot of the reactant was taken and centrifuged, and then analyzed by gas chromatography (GC).

2.3. Product analysis

The intermediate products in the HDCl of CPs were determined by GC/MS (Thermo Scientific ITQ 900) with a column of HP-5 (30 m × 0.25 mm × 0.25 μm). The composition of the reaction system was analyzed by GC/FID (Agilent 7890A) with a column of DB-1701 (30 m × 0.32 mm × 0.25 μm).

3. Results and discussion

Usually, 2,4-DCP was catalytically hydrogenated within 60 min in water with hydrogen gas over Raney Ni under mild conditions (Table 1). According to the analytical results of GC/MS, 2-CP and 4-CP were the dechlorinated intermediate products in the HDCl of 2,4-DCP, and then they could be further converted to phenol, and even, to cyclohexanone and cyclohexanol with hydrogen gas over Raney Ni. In the end, phenol was the main product, and only a small amount of cyclohexanone and cyclohexanol formed. Therefore, the HDCl of 2,4-DCP was a stepwise process and the HDCl reaction pathway of 2,4-DCP was shown in Scheme 1. Compared to CPs, phenol, cyclohexanone and cyclohexanol are less toxic and useful as intermediates in chemical manufacturing. Thus, the HDCl method with Raney Ni catalyst could effectively decrease and eliminate the toxicity and pollution of CPs.

Additionally, it was clearly observed in Table 1 that the dechlorination reactions were faster in water than that in EtOH and MeOH under the same conditions. It means that solvent effects showed a very important influence on the HDCl reaction. This result was possibly attributed to a lesser catalyst deactivation as a result of increased solubility of HCl and/or NaCl and Et₃NHCl (formed during HCl neutralization with NaOH or Et₃N) which facilitated their removal from the active surface of the catalyst in water [20–24].

In some literature, 2-CP was the only reactive intermediate product in the HDCl of 2,4-DCP in liquid system [8–10,12,25–28]. In this study, it could be seen that when NaOH was used as a base in liquid system, the amount of 2-CP formed was more than that of 4-CP in organic solvent (MeOH) and in water by GC/MS during the HDCl of 2,4-DCP (Table 1). It means that para-positioned Cl was easier to be hydrogenated than ortho-positioned Cl of 2,4-DCP, whether in water or in organic solvents. This trend was coincident with the results reported in the literature [8–10,12,25–28]. It was possibly due to the steric hindrance of hydroxyl group where the ortho-positioned Cl experienced a more restricted HDCl [8–10,12,25–28].

Table 1
The hydrodechlorination reactivity of 2,4-DCP over Raney Ni catalyst with Et₃N or NaOH in liquid phase.[a]

Base	Solvent	Time (min)	Products distribution (%)			
			DCP	2-CP	4-CP	Phenol
Et₃N	Methanol	10	81.6	3.4	6.8	8.2
		30	64.6	3.9	10.4	21.1
		60	49.3	3.7	11.4	35.6
	Ethanol[b]	10	90.9	0	5.4	3.7
		30	76.3	2.2	10.9	10.6
		60	64.3	2.6	13.9	19.2
	Water	5	70.2	4.6	0.9	24.3
		15	24.4	2.7	0	72.9
		20	7.1	0.9	0	92.0
		30	0	0	0	100
NaOH	Methanol	10	90.3	1.1	0.8	7.8
		30	80.3	1.2	0.9	17.6
		60	69.0	1.1	0.7	29.2
	Water	5	85.0	3.3	0	11.7
		15	60.8	4.0	0.8	34.4
		30	29.3	2.1	0	68.6
		50	0	0	0	100

[a] Reaction conditions: 80 mL solutions containing 2,4-DCP (3.13 mmol), Et₃N (9.29 mmol) or NaOH (6.85 mmol) and Raney Ni (0.4 g for organic solvents and 0.2 g for water), 40 °C, 10 mL H₂ min⁻¹.
[b] Et₃N (4.45 mmol).

However, when Et₃N as a base was used, more 2-CP as an intermediate product was produced in water, and more 4-CP was formed in MeOH and EtOH (Table 1). It indicated that in the presence of Et₃N, ortho-positioned Cl of 2,4-DCP was easier to be dechlorinated by Raney Ni in organic solvents; on the contrary, para-positioned Cl was easier to be dechlorinated in water. The result in organic solvents with Et₃N was inconsistent with those of previous studies, where 2-CP was the only reactive intermediate product in the HDCl of 2,4-DCP in liquid system [8–10,12,25–28].

Consequently, we concluded that Et₃N together with solvents affected greatly the HDCl reactivity or selectivity of CPs over Raney Ni, where the ortho-positioned Cl was easier to be dechlorinated in organic solvents, whereas para-positioned Cl was easier to be dechlorinated in water. Scheme 1 described the HDCl process of 2,4-DCP affected by Et₃N/NaOH and solvents. In order to further understand the influence of Et₃N on the HDCl reactivity of CPs, the HDCl processes of single and mixed 2-CP and 4-CP were investigated.

The HDCl processes of single 2-CP and 4-CP over Raney Ni with Et₃N in different solvents under mild conditions were shown in Fig. 1. It was seen that the HDCl of 2-CP was always faster than that of 4-CP in organic solvents (MeOH and EtOH), whereas the HDCl reactivity was just the opposite in water. In order to more visually display the effect of Et₃N on the HDCl reactivity of 2-CP and 4-CP, we further researched the HDCl processes of mixed 2-CP and 4-CP under the same reaction conditions, as shown in Fig. 2. It was clearly observed that there was the same trend as Fig. 1, that is, the HDCl of 2-CP was always faster than that of 4-CP in organic solvents, whereas the HDCl of 4-CP was always faster than that of 2-CP in water. In a word, whether in single system or in mixed system of 2-CP and 4-CP, ortho-positioned Cl was easier to be dechlorinated in organic solvents, whereas the priority HDCl of para-positioned Cl occurred in water, which was the same as the results obtained in the HDCl of 2,4-DCP.

As an organic base, Et₃N possibly played different roles in water and organic solvents. It is easy to ionize to form ammonium ion and hydroxyl ion in water. And then, HCl formed in the HDCl processes can be neutralized by hydroxyl ion (Scheme 2). So, it could eliminate the poison of HCl to catalysts, and promote the catalytic HDCl processes [20–24]. In any case, Et₃N played an important role of a base in water, the same as NaOH. However, in organic solvents such as MeOH and EtOH, Et₃N is usually difficult to ionize and present in molecular state. As a base, it could directly react with HCl to form triethylamine-hydrochloride in the HDCl of
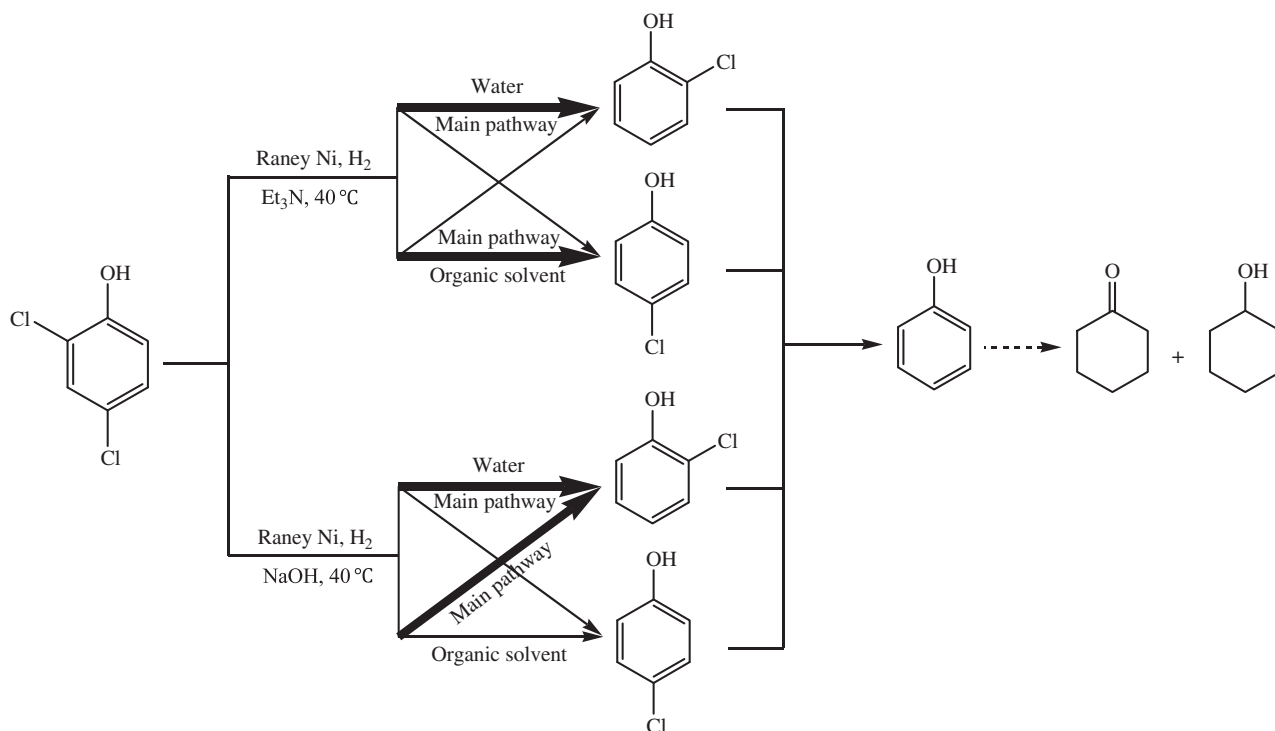
Scheme 1. The hydrodechlorination process of 2,4-DCP over Raney Ni catalyst.

CPs (Scheme 2), by which the poison of HCl to catalysts could be effectively removed [20–24]. Furthermore, triethylamine-hydrochloride formed in the HDCl could be a modifier to coat the catalyst, which possibly influenced the outcome of the reactions by mediating the substrate–catalyst interactions [29]. Tundo et al. [29,30] had found that some amines and onium salts could change significantly the reactivity and regio-, chemo- and stereoselectivities of Pt/C, Pd/C and Raney Ni in the hydrodehalogenation reactions of haloaromatics.

Additionally, Et_3N having an electron pair on N-atom, can provide an electron pair to the surface and the active sites of the metal catalysts such as Pt, Pd, Rh and Ni [31,32]. Due to the interaction between Et_3N and Ni, the electron transfer from N to d orbital of Ni probably occurred, thereby changing the surface properties of the Ni catalyst, which might influence the reactivity or selectivity toward ortho- and para-positioned Cl of 2,4-DCP in the HDCl processes. In a

word, Et_3N not only played an important role of bases but also acted as an organic modifier in the HDCl processes in organic solvents.

In conclusion, it was believed that the different existing species and action mechanisms of Et_3N in water and organic solvents possibly affected and determined the HDCl reactivity or selectivity of CPs over Raney Ni.

4. Conclusions

In the presence of Et_3N, ortho-positioned Cl was easier to be dechlorinated over Raney Ni under mild conditions in organic solvents, whether for dichlorophenol (2,4-DCP) or for monochlorophenols (2-CP and 4-CP); however, the priority dechlorination of para-positioned Cl occurred in water. That is, Et_3N had a significant influence on the HDCl reactivity or selectivity in different solvents.
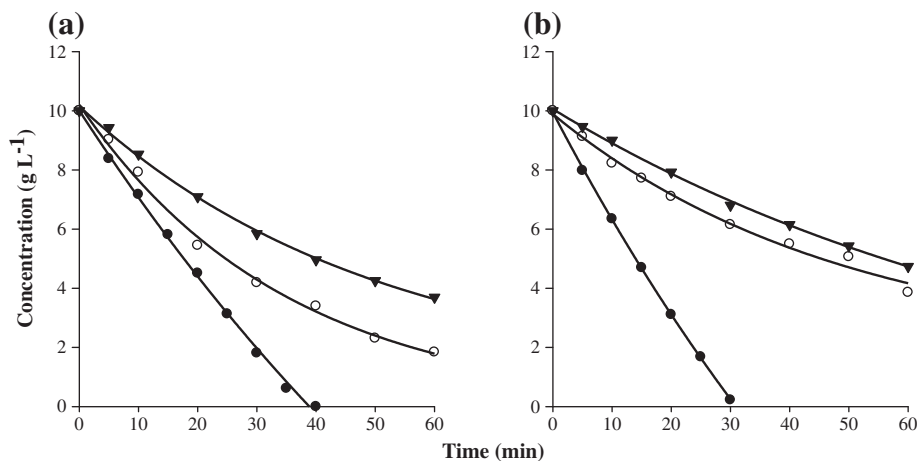

Fig. 1. In the presence of Et_3N the hydrodechlorination of single 2-CP (a) and 4-CP (b) over Raney Ni in different solvents under mild conditions (● water; ○ methanol; ▼ ethanol). Reaction conditions: 80 mL solution, 2-CP or 4-CP (6.22 mmol), Et_3N (9.29 mmol) and Raney Ni (0.4 g for organic solvent and 0.2 g for water), 40 °C, 10 mL H_2 min^{-1}.
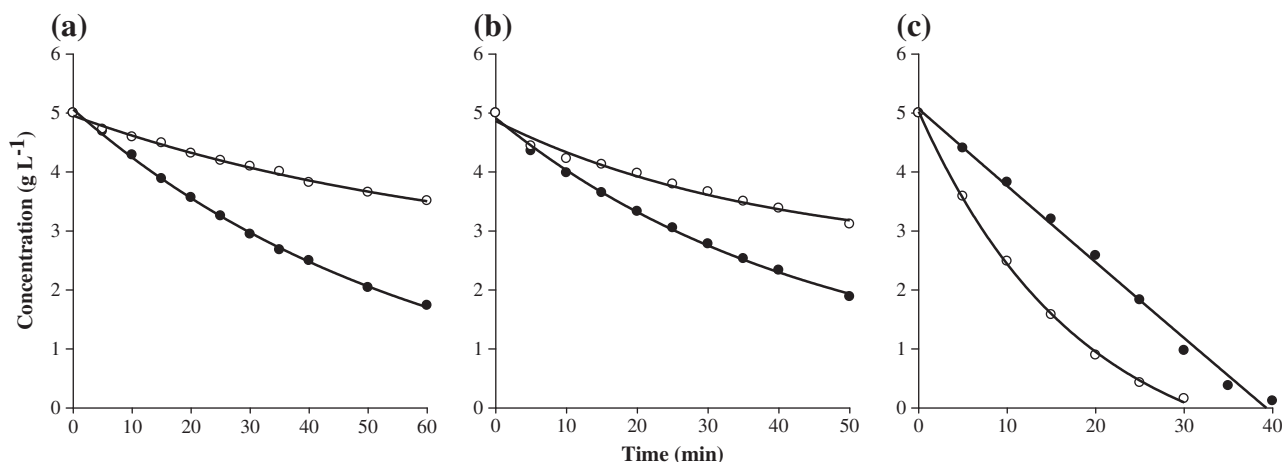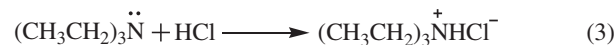
Fig. 2. In the presence of Et$_3$N the hydrodechlorination of mixed 2-CP and 4-CP over Raney Ni under mild conditions in methanol (a) ethanol (b) and water (c) (● 2-CP and ○ 4-CP). Reaction conditions: 80 mL solution, 2-CP (3.11 mmol) and 4-CP (3.11 mmol), Et$_3$N (9.29 mmol) and Raney Ni (0.4 g for organic solvent and 0.2 g for water), 40 °C, 10 mL H$_2$ min^{-1}.

In water

$$(CH_3CH_2)_3\ddot{N} + H_2O \rightleftharpoons (CH_3CH_2)_3\overset{+}{N}H + OH^- \quad (1)$$

$$OH^- + HCl \longrightarrow H_2O + Cl^- \quad (2)$$

In organic solvent

$$(CH_3CH_2)_3\ddot{N} + HCl \longrightarrow (CH_3CH_2)_3\overset{+}{N}HCl^- \quad (3)$$

Scheme 2. The reaction of Et$_3$N with HCl in water and organic solvents.

This novel phenomenon was attributed to the different existing species and action mechanisms of Et$_3$N in water and organic solvents.

Acknowledgements

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