

Catalysis, Kinetics and Reaction Engineering

# Efficient synthesis of 1,6-hexamethylene diurethane through coupling transesterification and methoxycarbonylation with methyl phenyl carbonate as intermediate☆

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## ABSTRACT

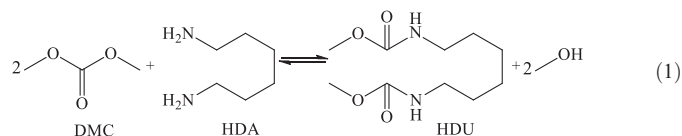
A reaction coupling system of transesterification and methoxycarbonylation with methyl phenyl carbonate (MPC) as intermediate was established to efficiently prepare 1,6-hexamethylene diurethane (HDU) from 1,6-hexamethylene diamine (HDA). The feasibility of the system was explored using the thermodynamics analysis, the reaction mechanism and the experiment results. The optimal reaction was carried out to get higher HDU yield. The thermodynamic analysis showed that the methoxycarbonylation of HDA with MPC, the Gibbs free energy of which was negative, was a spontaneous process. Furthermore, the equilibrium constant of the methoxycarbonylation of HDA with MPC was much greater than that of the transesterification of dimethyl carbonate (DMC) with phenol, so the reaction coupling could be realized under mild conditions. The reaction mechanism analysis indicated that phenoxy anion was the key species for reaction coupling. Higher MPC concentration was detected when sodium phenoxide was used as transesterification reactant with DMC, since the phenoxy anion of sodium phenoxide could be dissociated more easily. Sodium phenoxide was more suitable to prepare HDU through reaction coupling. A yield of HDU as high as 98.3% could be reached under the optimal conditions of  $m_{\text{PhONa}}/m_{\text{DMC}} = 0.027$  and  $n_{\text{DMC}}/n_{\text{HDA}} = 8/1$  at 90 °C in 2 h.

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## 1. Introduction

1,6-Hexamethylene diisocyanate (HDI) is one of the most important aliphatic diisocyanates widely used to prepare abrasion, chemical resistance and no yellowing polyurethane paints [1]. HDI is commercially prepared from 1,6-hexamethylene diamine (HDA) and phosgene [2,3], which is highly toxic and corrosive. Moreover, serious environmental problems can be caused due to the formation of byproduct HCl. Recently, a green two-step process for HDI production has attracted much attention, in which 1,6-hexamethylene diurethane (HDU) is first prepared from HDA, and then HDI can be produced through the thermolysis of HDU. The technologies for HDU production without phosgene include the carbonylation of

HDA [4–6] and urea alcoholysis [7–9], which need high temperature and pressure, and are difficult to commercially industrialize. Preparation of HDU through methoxycarbonylation of HDA using green dimethyl carbonate (DMC) under mild conditions has been a hot research topic [10–16]. The reaction is as follows [Eq. (1)].



Unfortunately, polar solvents and delicate catalysts are essentially applied in the reaction, and the long reaction time, low yield of target product and heavy metal pollution are difficult to overcome in this process.

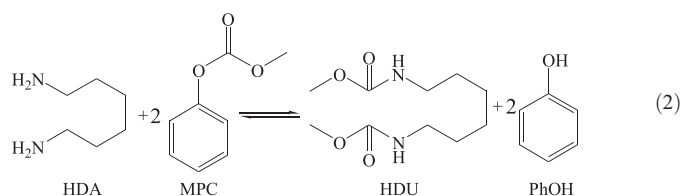
Methyl phenol carbonate (MPC) was reported as the methoxycarbonylation reagent to prepare HDU from HDA for the first time by Yoshida [17]. In our prior work, HDU had been synthesized from

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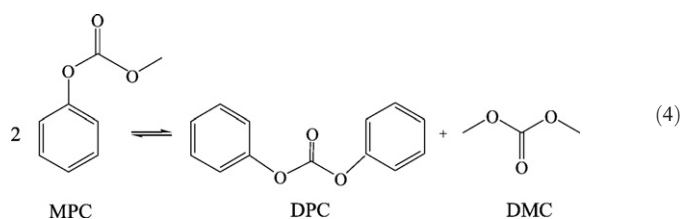
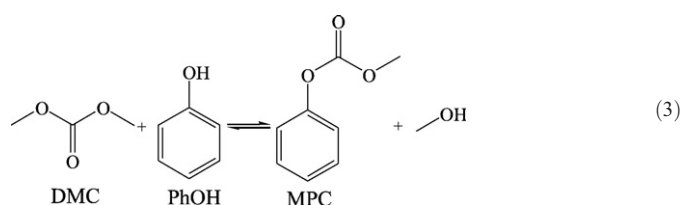
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HDA and MPC without solvent, and a high HDU yield realized quickly under mild conditions [18]. The reaction is as follows [Eq. (2)].



However, the synthesis and separation of MPC are difficult, and there is no industrial process for MPC production. The reaction conditions of DMC with PhOH to MPC are very rigorous, and more importantly, the yield of MPC is even low due to both the limitation of equilibrium and the disproportionation reaction of MPC to diphenyl carbonate (DPC) [19–21]. The reactions [Eqs. (3) and (4)] are as follows.



Recently, reaction coupling technology has shown perfect efficiency and atomic economy in the chemical production process.  $\gamma$ -Butyrolactone was prepared by coupling the endothermic dehydrogenation of ethanol with the exothermic hydrogenation of maleic anhydride to effectively utilize the reaction heat and improve the selectivity [22]. Furthermore, the coupling process greatly reduced the use of inflammable and explosive hydrogen. DMC reacting with aniline can produce benzene methyl carbonate and methanol, and methanol reacting with biphenyl urea can produce benzene methyl carbonate and aniline. Using DMC and biphenyl urea as feedstock, through coupling the above two reactions, the atomic economy can be greatly improved because of the application of the byproducts methanol and aniline [23]. Thus, the appropriate intermediate is the key to realizing the reaction coupling.

Apparently, when phenol is added into the reaction system of DMC with HDA [Eq. (1)], phenol may react with DMC to produce DPC [Eq. (3)], and then MPC may react with HDA to produce HDU [Eq. (2)]. Although the equilibrium conversion of Eq. (3) is extremely low, the Eq. (2) can quickly occur and decrease the concentration of MPC in the system. Then, the equilibrium of Eq. (3) is shifted and Eq. (3) may be promoted. In short, a small amount of phenol in the reaction system of DMC with HDA may realize the coupling of Eqs. (1) and (2) with MPC as intermediate. In the present work, a reaction coupling system is built into the reaction system of DMC and HDA with MPC as intermediate. The feasibility of MPC production from DMC and phenol or sodium phenoxide in the reaction system of DMC with HDA under mild conditions was verified by theory and experiment. Finally, the reaction conditions of HDU preparation through reaction coupling were optimized.

## 2. Experimental

### 2.1. Reagents

HDA (analysis pure), phenol (PhOH, analysis pure), sodium phenoxide (PhONa, analysis pure), anisole (An, analysis pure) and acetonitrile (chromatographical pure) were purchased from China National Medicines Corporation Ltd.  $\text{CH}_3\text{OH}$  (chromatographically pure) was purchased from Shandong Yuwang Corporation Ltd. DPC (analysis pure) was provided by Tonglin Jintai Chemical Corporation Ltd., deionized water was from Hangzhou Wahaha Corporation Ltd. and DMC (industrial pure) was provided by Changzhou Yabang Chemical Corporation Ltd.

MPC was prepared by the method in the literature [24] and purified by distillation under vacuum prior to use with a final purity of 99.95% determined by gas chromatography.

### 2.2. Analysis methods

#### 2.2.1. Analysis instruments

Nicolet 5700 smart Fourier infrared spectrometer (Nicolet Instrument Company in the United States), TRACE DSQ gas chromatography–mass spectrometry (GC–MS) with DP-5 capillary column (the THERMO Fisher Company) and Agilent 1100 Series high performance liquid chromatography (HPLC) with CZORBAX SB-C18 column and ultraviolet detector (Agilent Company in the United States) were used in this study.

#### 2.2.2. Analysis conditions

The scanning range of infrared analysis was from 400 to 4000  $\text{cm}^{-1}$ . Pure He was used as a carrier in GC–MS with a flow rate of 10  $\text{ml} \cdot \text{min}^{-1}$ . The temperatures of vaporizer and connector were 300 °C and 250 °C, respectively. The column temperature of GC stayed at 150 °C for 2 min, and then rose to 290 °C with a rate of 10 °C  $\cdot \text{min}^{-1}$ , and finally stayed at 290 °C for 6 min. The double voltage and emission current of MS with an EI power source were 1500 V and 20.0 A, respectively. The scanning range of MS was from 45 to 450 amu. The column temperature of HPLC was room temperature (RT), and the carrier of HPLC was a mixture of acetonitrile and deionized water (0.8  $\text{ml} \cdot \text{min}^{-1}$ ) with a volume ratio of 55:45.

#### 2.2.3. Qualitative analysis of HDU

Qualitative analysis of the sample, after steaming out the light component in the reaction liquid and taking two recrystallization times, was carried out using GC–MS and FTIR. The molecular fragments with mass to charge ratio of 41, 44, 55, 67, 74, 82, 88, 97, 102, 114, 126, 130, 141, 156, 168, 173, 200 and 232 were detected by GC–MS. The mass to charge ratio of the molecular ion of the sample was 232, consistent with HDU. The infrared spectrum of the sample is shown in Fig. 1.

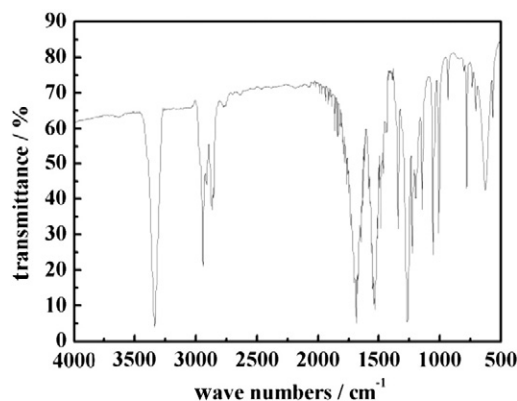


Fig. 1. Infrared spectrum for synthesis sample of HDU.

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