

Catalytic synthesis of methylene diphenyl dicarbamate from methyl phenyl carbamate and trioxane over sulfuric acid catalyst

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Methylene diphenyl dicarbamate (MDC) was synthesized from methyl phenyl carbamate (MPC) and trioxane using sulfuric acid (H₂SO₄) as catalyst. The effects of reaction temperature, reaction time, molar ratio of reactants and the content of catalyst have been studied in details. The results showed that H₂SO₄ exhibited high catalytic activity with the merits of moderate reaction velocity. Under the conditions of $n(\text{MPC})/n(\text{trioxane})=3:1$, reaction temperature of 95°C, reaction time of 3.5 h and 30% H₂SO₄, the conversion of MPC reached 99.0% with the selectivity of MDC 81.6%. Moreover, the H₂SO₄ catalyst was reused five times without obviously activity decrease. Based on the identification of byproducts, a possible reaction mechanism was proposed.

Keywords methylene diphenyl dicarbamate, methyl phenyl carbamate, trioxane, condensation

1 Introduction

Diphenylmethane diisocyanate (MDI) is an important intermediate for the manufacture of polyurethanes, which can be used as a material of metal-adhesive, fiberglass, dope, elastomer-fiber and all kinds of leatheroid, etc. [1–3]. Commercially, MDI is manufactured by the reaction of phosgene and methylene dianiline. However, the phosgene route is not environmentally friendly due to the high toxicity of phosgene and hence generates highly corrosive

hydrochloride as byproduct. For the purpose of eliminating all these drawbacks, several non-phosgene routes [4–6] have been developed. Among them, thermal decomposition of methylene diphenyl dicarbamate (MDC) to obtain MDI is thought to be one of the most attractive ways.

Recently, studies on MDC synthesis have been mainly focused on the condensation of methyl phenyl carbamate (MPC), which can be synthesized by many methods. However, there are still some challenges to be overcome for the industrialization of this reaction. Takeshita et al. [7,8] studied the condensation of MPC using HCHO as methylene agent with sulfuric acid (H₂SO₄) (96%) as catalyst. The MDC was obtained in 73% yield with large amount of byproducts that was caused by superfluous HCHO. In the presence of acid, trioxane was decomposed to HCHO with appropriate rate to avoid the superfluous HCHO. Therefore, Wada et al. [9–11], Fukuoka et al. [12] and Clerici et al. [13] did lots of research on the condensation reaction using trioxane as methylene agent with different catalysts. The selectivity of MDC has been improved, but the highest MPC conversion was no more than 45%. Li et al. [14] worked on the MDC synthesis from trioxane and MPC using mixed acid as catalyst, resulting an MDC yield of 75.8%. However, harsh reaction conditions such as high reaction temperature (105°C) and long reaction time (5 h) are required.

In previous studies, there was neither further report about the detailed research on the condensation of MPC and trioxane nor the reaction mechanism. This prompted us to undertake the present work. In this paper, the effects of reaction conditions, the recycle of catalyst and the identification of major byproducts were studied. Based on the identification of byproducts, a possible reaction mechanism was proposed.

2 Materials and methods

2.1 Materials

Trioxane was purchased from Sinopharm Chemical Reagent Co. Ltd. H₂SO₄ was purchased from Beijing shiji Co. Ltd. MPC was synthesized from 1,3-diphenyl urea and DMC, which had been deeply studied in our laboratory [6] with the purity of 99.8%.

2.2 Experimental method

In a typical procedure for MDC synthesis, MPC (6.04 g, 0.04 mol), trioxane (1.20 g, 0.0133 mol), water (36 mL) and H₂SO₄ (16.06 g, 98.0%) were charged into a 100 mL round-bottom flask with an oil bath. Trioxane would not be added until the mixture was heated to a certain temperature with

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vigorous stirring. The reactant solution was cooled to room temperature after a certain amount of time, then filtered to separate solid from liquid. In the stability test of recycled catalyst, the H_2SO_4 solution was purified two times by active carbon. Then the loss of the H_2SO_4 was balanced by adding fresh H_2SO_4 .

2.3 Analytical methods

The products were analyzed by high performance liquid chromatography (HPLC, Agilent 1100 series) equipped with a UV detector and Zorbax Extented-C18. The mobile phase of $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 55/45$ (v/v) was used at a flow of $1.0 \text{ mL} \cdot \text{min}^{-1}$. The yield of MDC was calculated based on MPC.

Mass spectroscopy (MS) analysis was run on Waters micromass ZQ-4000 (USA). An HPLC coupled with tandem mass spectrometry (HPLC-MS/MS) was run on a Q-Trap LC-MS system with a turbo ion spray source and a Zorbax SB-C18 column (radius of 2.1 mm, length of 150 mm). Parameters of electrospray ionization were: ion spray voltage of 5500 V, source temperature of 623 K, Cur Gas 25 V, Gas1 55 V, Gas2 45 V, DP 90 V, respectively.

3 Results and discussion

3.1 Effect of reaction temperature

Figure 1 shows the relationship between the temperature and the conversion, selection and yield. The conversion of MPC increases with the rising of the temperature. Complete conversion of MPC can be achieved at temperatures over 95°C . The selectivity and yield of MDC increase while the temperature rise. They all reach maximum values at 95°C , then the selectivity and yield of MDC decrease with the further rising of the temperature. At the lower temperature range, the rising of MDC yield indicates that MDC formation is sensitive

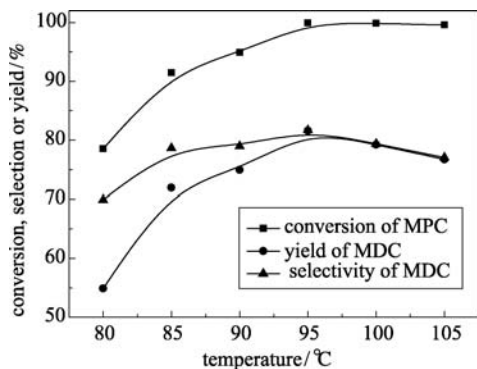


Figure 1 Effect of temperature on condensation reaction ($n(\text{MPC})/n(\text{trioxane}) = 3$, $W_{\text{H}_2\text{SO}_4} = 30\%$, $t = 3.5 \text{ h}$).

to the temperature. When the temperature is above 95°C , the decreasing of MDC selectivity is caused by the augment in byproducts because the higher temperature is favor for the byproducts formation. This result is coincident with literatures [15–17] in different reaction system. As a conclusion, the optimum temperature should be controlled at 95°C .

3.2 Effect of reaction time

The investigation of reaction time is illustrated in Figure 2. It is fully consistent with the expected results. The conversion of MPC only increases with the rising of reaction time and reaches 100% after 3 h. The MDC yield first goes through a high value and then drops. The maximum (81.6%) is achieved at 3.5 h. The selectivity of MDC appears to be rather complicated and varies between 75% and 81%. Fukuoka et al. [4] suggested that the conversion of MPC to MDC maybe go through a certain intermediate before MDC formation. The detail about the intermediate is presented in the discussion part of the reaction mechanism. According to our results, the optimum time should be controlled at 3.5 h.

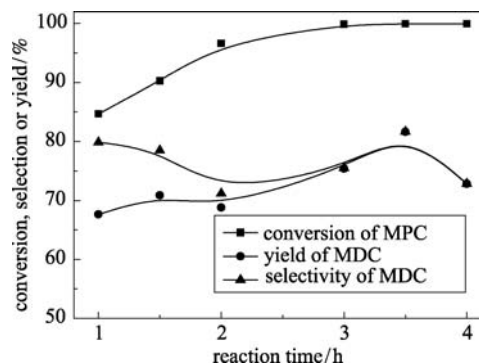


Figure 2 Effect of reaction time on condensation reaction ($n(\text{MPC})/n(\text{trioxane}) = 3$, $W_{\text{H}_2\text{SO}_4} = 30\%$, $T = 95^\circ\text{C}$).

3.3 Effect of MPC to trioxane molar ratio

The effect of molar ratio of MPC to trioxane is also studied in the range of 2.5 to 12. Results are shown in Figure 3. From Figure 3, it can be found that the conversion of MPC decreases with the rising of the molar ratio, whereas the selectivity and yield of MDC passes a maximum of 79.4% and 78.5% at the ratio of 3. When the molar ratio is lower than 3, polycondensations of the byproducts are easily formed [14,18], which attributes to the higher concentration of HCHO decomposed by trioxane. When the ratio is more than 3 (which means the concentration of trioxane is low in reaction system), the yield and selectivity of MDC decrease due to the lack of methylene agent. Therefore the optimal molar ratio of MPC to trioxane is 3:1.

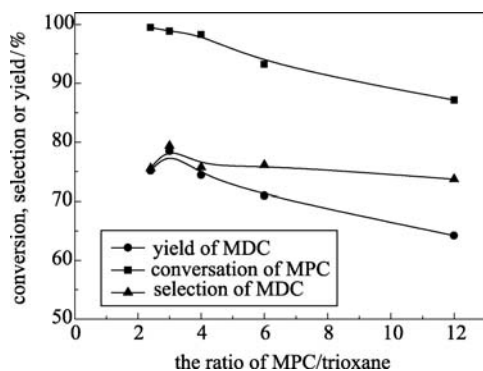


Figure 3 Effect of the molar ratio of MPC to trioxane on condensation reaction ($W_{\text{H}_2\text{SO}_4}=30\%$, $T=95^\circ\text{C}$, $t=3.5\text{ h}$).

3.4 Effect of the H_2SO_4 concentration

Figure 4 shows the relationship between the results of reaction and the concentration of H_2SO_4 . The conversion of MPC increases with the amount rising of H_2SO_4 . The curve of MDC-yield appears to be a reversed V-shape against the amount of H_2SO_4 . The proper concentration of H_2SO_4 is 30%. In the condensation process of MPC and trioxane, H_2SO_4 acts as two roles: one is the catalysis for synthesis of MDC, the other is contribution H^+ to the decomposition of trioxane. Hence the low amount of H^+ is not enough to realize these two roles at the same time. When the concentration of H_2SO_4 is over 30%, the byproducts are easily formed in the form of polynuclear compounds and *N*-phenmethyl compounds. The HPLC analysis results also conform that the amount of byproducts increases as the H_2SO_4 amounts increases. Similar results are also confirmed by Ref. [19].

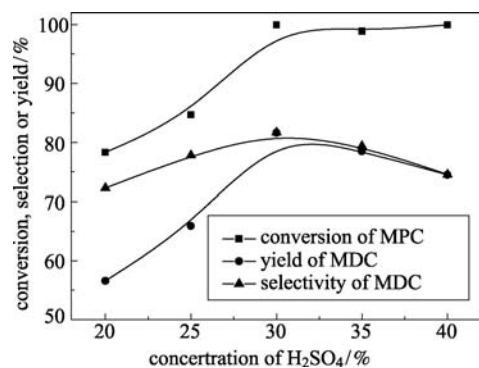


Figure 4 Effect of concentration of H_2SO_4 on condensation reaction ($n(\text{MPC})/n(\text{trioxane})=3$, $T=95^\circ\text{C}$, $t=3.5\text{ h}$).

3.5 Recycling of H_2SO_4

The effect of recycled H_2SO_4 is studied under optimum conditions. The results are shown in Figure 5. The conversion of MPC has a little fluctuation, but the MDC yield and

selectivity is steady on the whole. In a word, the H_2SO_4 catalyst shows a good stability without significant decrease in the activity after recycling for five times.

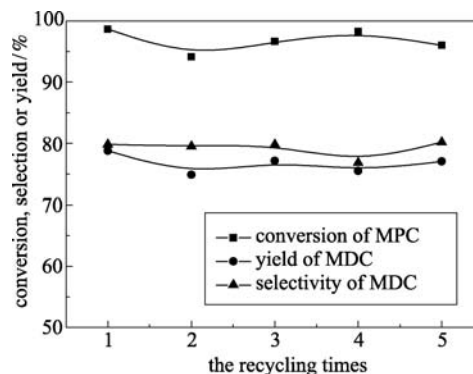


Figure 5 Effect of recycled H_2SO_4 ($n(\text{MPC})/n(\text{trioxane})=3$, $T=95^\circ\text{C}$, $t=3.5\text{ h}$, $W_{\text{H}_2\text{SO}_4}=30\%$).

3.6 Analysis on byproducts and mechanism

Since the byproducts are complexes in the condensation of MPC with trioxane, there is little work on the identification of byproducts. In order to have an explicit understanding on the reaction process, the byproduct identification is emphatically studied by HPLC-MS/MS and the results are listed in Figure 6 and Figure 7. The liquid chromatogram (Figure 6) shows that over six kinds of compounds have been detected in the products. The MPC and MDC can be directly identified by pure samples. Their corresponding times are 8.21 min (MPC) and 30.32 min (MDC), respectively. The major byproduct is detected at 19.79 min. The MS spectra are shown in Figure 7. The high abundance is at $m/z = 313.10$ via the loss of H. It indicates that the molecular weight is 314. Further reaction/fragmentation of the ion at $m/z = 281.09$ is from $(313.10 - \text{CH}_3\text{OH})$, the fragmentation at $m/z = 249.08$ ($281.09 - \text{CH}_3\text{OH}$) appears in the spectrum. It means that the byproduct is one of the isomers of MDC. It is well known that there are three isomers of MDC: 4,4'-MDC, 2,4'-MDC, and 2,2'-MDC. In our work, the MDC mentioned above is 4,4'-MDC, other isomers are byproducts relative to it. But when the ion $\text{H}_2\text{C}^+\text{OH}$ attacks MPC to substitute H^+ , the first location

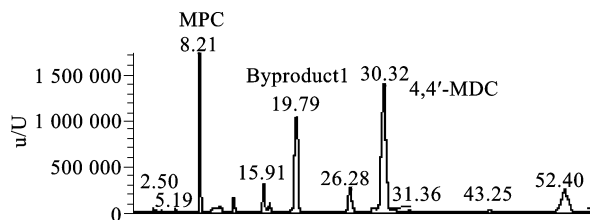


Figure 6 The liquid chromatogram of byproducts.

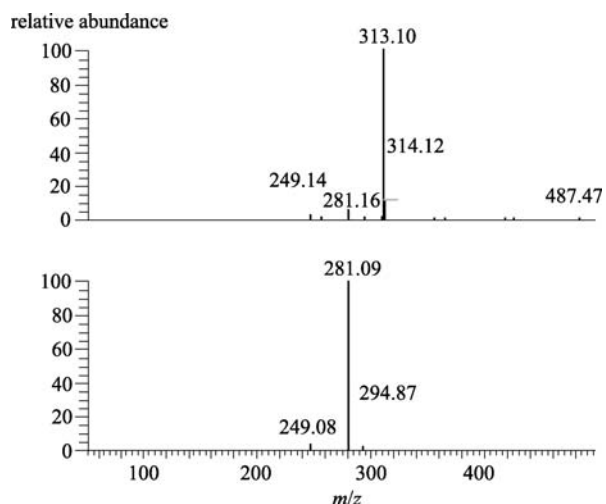


Figure 7 MS spectra of 2,4'-MDC.

is 4-H⁺ and the second is 2-H⁺. What's more, the group “-NHCOOCH₃” is bulky, the steric hindrance is huge so that 2,2'-MDC is difficult to form. Thus we can confirm that the major byproduct at 19.79 min is 2,4'-MDC. As for other byproducts, their total amount is very tiny so that the analysis is difficult. Therefore, the detailed research about them isn't discussed in the section.

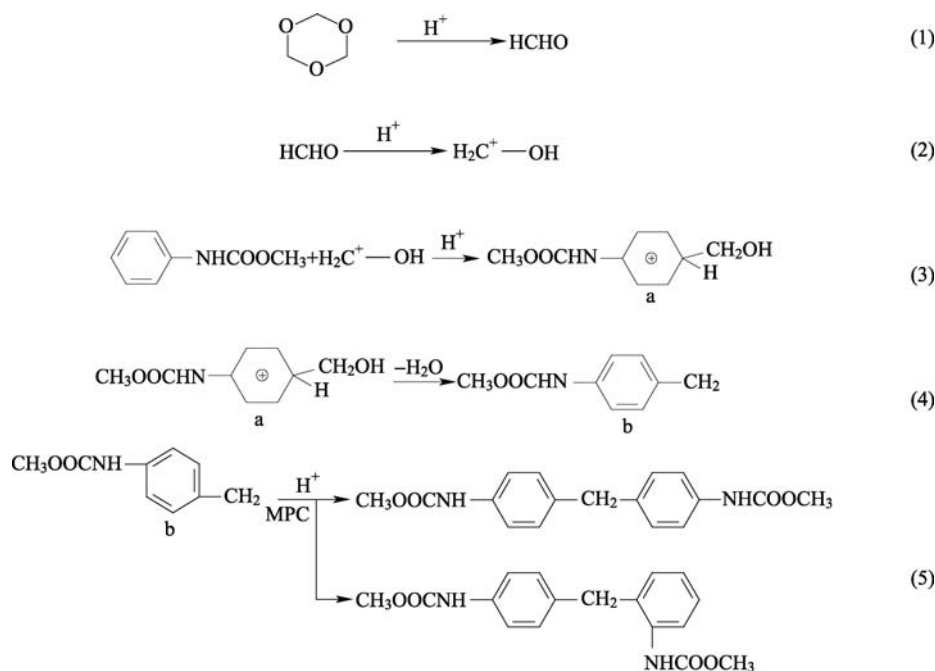
Based on our work, a possible mechanism is proposed as follows. The process of products formation includes five steps, as shown in Scheme 1. The first step is that trioxane is depolymerized into HCHO in the present of H⁺ (Eq. (1)). In

the second step, HCHO is transformed into proton alcohol (Eq. (2)). Furthermore, the proton alcohol attacks the benzene ring of MPC to form an intermediate (a) (Eq. (3)) at the third step. Then intermediate (a) is transformed to an intermediate (b) (Eq. (4)). Finally, the intermediate (b) combines with other MPC to produce 4,4'-MDC or 2,4'-MDC (Eq. (5)).

Among the five steps, the first step has been studied a lot and has been proven by Cui et al. [20] and Wang et al. [21]. This step is very important because it is relatively slow and hence controls the rate of the condensation reaction. Besides, MPC can be perfectly transformed into MDC under such condition. The products are pulverous so that the reaction materials can be mixed very well. As a result, these greatly overcome the adhesive phenomenon and slack the byproducts formation in whole process. Meanwhile, two kinds of intermediates (a) and (b) are present in the third and fourth step. The formation of intermediate products requires a certain amount of reaction time which is the main reason for the minimum selectivity of MDC at 2 h in the effect of reaction time (Figure 2). On the contrary, the phenomenon is a good evidence that the third and fourth steps are the only way for the MDC synthesis. The mechanisms of the third and fourth steps are also supported by Hou et al. [22,23].

4 Conclusions

In this work, MDC was synthesized from MPC using trioxane as methylene agent over H₂SO₄ catalyst. Since trioxane can be



Scheme 1 Proposed reaction mechanism in five steps.

decomposed to HCHO and hence avoid the parcel of superfluous HCHO, it shows kinds of merits in moderate reaction velocity and great improvement of the MDC yield. Under suitable reaction conditions, the yield of MDC reached 81.6%. Moreover, H₂SO₄ can be reused for five times while no significant loss in catalytic activity was observed. The major byproduct 2,4'-MDC was identified and a possible reaction mechanism was proposed in the end.

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