

Study on the Optimization of 1,3-Bis (Isocyanatomethyl) Benzene Synthesis with Bis (Trichloromethyl) Carbonate

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Abstract: 1,3-Bis(isocyanatomethyl)benzene is an isocyanate with high quality performance, excellent yellowing resistance and weather resistance. It has wide application in optical polymer composite materials, construction, automotive and other industries. The current production process is mainly prepared by the liquid phase reaction of m-xylylenediamine with highly toxic phosgene. Due to the particularity of phosgene, the synthesis and application of 1,3-bis(isocyanatomethyl)benzene is greatly restricted, the production threshold and the price remains high, which seriously affects the promotion of products. Exploring the non-phosgene green synthesis process for the preparation of 1,3-bis(isocyanatomethyl)benzene is one of hotspots in the isocyanate research and development. The research target of this paper is to explore a safe, convenient and environmentally friendly synthesis route for 1,3-bis(isocyanatomethyl) benzene. The synthesis optimization of 1,3-Bis(isocyanatomethyl) benzene from m-xylylenediamine and bis(trichloromethyl) Carbonate was comprehensively studied. Factors such as molar ratio of raw materials, reaction temperature, reaction time and nitrogen rate were also studied. The optimal conditions were as follows: the molar ratio of m-xylylenediamine to bis(trichloromethyl)carbonate was 1.2:1.0, the nitrogen gas velocity was 8 mL·min⁻¹, the reaction temperature was 125°C and the reaction time was 8.0 hours. Under the optimum condition, the 1,3-Bis (isocyanatomethyl) benzene yield was 83.35%. The reaction mechanism and the key steps involved in the reaction process were also deeply analyzed.

Keywords: 1,3-Bis (Isocyanatomethyl) Benzene; Bis(Trichloromethyl)Carbonate; M-Xylylenediamine; Optimization

1. Introduction

1,3-Bis(isocyanatomethyl)benzene (MXDI) is colorless, transparent liquid at room temperature. It is an aliphatic isocyanate with excellent weatherability, color retention and adhesion. It is mainly used for high-grade polyurethane paints, ophthalmic lenses, packaging softeners, outdoor sealants, elastomers, leather and adhesives and so on [1, 2]. The traditional production process of MXDI is m-Xylylenediamine (MXDA) reaction with phosgene to salt formation at low temperature [3, 4]. MXDA first reacts with dry hydrogen chloride or carbon dioxide to form a salt. The

salt reacts with liquid phosgene at a lower temperature to produce m-Xylylenediaminohydrochloride. Finally m-Xylylenediaminohydrochloride reacts with gaseous phosgene to MXDI at suitable high temperature. And there will generate a small amount of m-Chloromethyl benzyl isocyanate (CBI) [5]. The method for MXDI uses highly toxic phosgene, which is very dangerous in using, transportation and storage. It requires a variety of strict safety using measures. With the development of society and the enhancement of people's environmental protection consciousness, it is an inevitable trend of technological development of seeking for green chemical raw materials to replace phosgene [6, 7].

Bis(trichloromethyl)Carbonate (BTC) is also named solid phosgene. BTC is insoluble in water and soluble in organic solvents such as benzene, ethanol, ether, chloroform and tetrahydrofuran. It decomposes in the case of hot water or catalyst (Figure 1). BTC has similar reactivity with phosgene [8-11]. It can react with alcohol, aldehyde, amine, amide, carboxylic acid, phenol, hydroxylamine and other compounds. It can also be cyclized and condensed to prepare heterocyclic compounds, which can completely replace highly toxic in chemical reactions. The chemical products related to phosgene and diphosgene synthesis (disabled) are mainly used in the production of pesticides, pharmaceuticals, organic intermediates and high polymer intermediates. Currently, the application in the production of isocyanates such as NDI and XDI is gradually expanded. Due to its high melting point, low volatility, and low toxicity, it is only treated in industry as a general toxic substance. It is safe and convenient to use with mild conditions, good selectivity and high yields in synthesis reaction [12-15]. And it holds a similar reaction mechanism as phosgene and can participate many organic synthesis reactions [16]. So BTC can be used as an ideal substitute for phosgene.

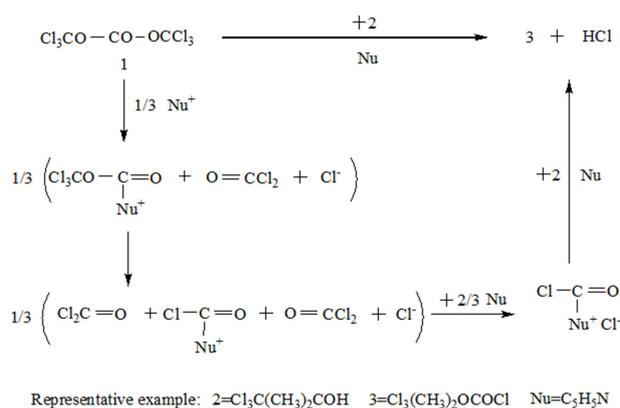


Figure 1. Reaction of BTC decomposition to COCl₂.

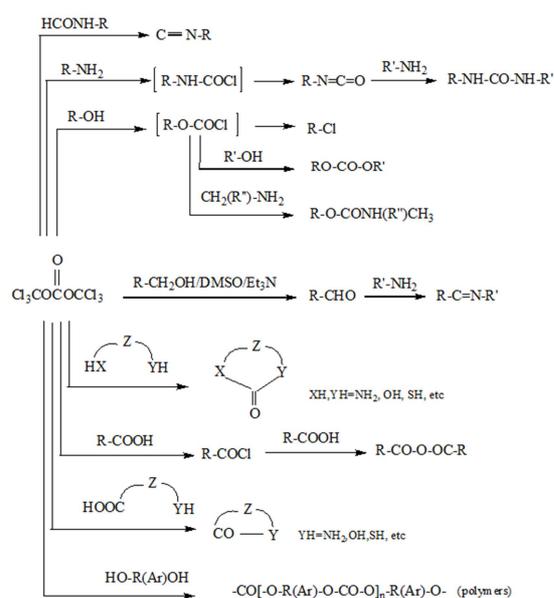


Figure 2. Application of BTC in organic synthesis reactions.

In this paper, the synthesis reaction on MXDI was researched using BTC and MXDA as raw materials. The effects of molar ratio of BTC to MXDA, reaction temperature, reaction time and nitrogen gas velocity on the reaction were investigated and optimized.

2. Experimental

2.1. Chemicals and Materials

In this study, triphosgene was purchased from Pingdingshan Shenying Chemical Technology Co., Ltd.; Pyridine, chlorobenzene, and o-dichlorobenzene were purchased from J&K Scientific Co., Ltd.; m-xylylenediamine (99%) and xylylene diisocyanate (95%) were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd.

Polaris-Q Gas Chromatograph Mass Spectrometer, Thermo Finnigan Company, USA; Agilent Technologies (China) Co., Ltd, 6820 Gas Chromatograph; Ningbo Aifa Vacuum Technology Co., Ltd., GLD-N136 Vacuum Oil Pump.

2.2. Experiment Procedure

A 500 mL four-port reaction flask was connected to a spherical condenser tube, a thermometer, and a nitrogen gas pipe. A certain amount of MXDA powder and an appropriate amount of solvent chlorobenzene were added to four-port reaction flask and stirred until completely dissolved. The dry hydrogen chloride gas was introduced at a certain gas velocity and was stopped after 3 hours. The appropriate amount of BTC chlorobenzene solution was added dropwise to the reaction mixture and the stirring was continued in one hour. After the dropwise addition, the temperature was raised to a specific temperature. The reaction bottle was purged velocity of carrier gas(N₂) was 8mL·min⁻¹ and reaction tail gas absorbed with Alkali liquor. After being purged with nitrogen gas maintaining 4-10 hours, the reaction bottle was cooled to room temperature and continued to purge with nitrogen gas for another 30min. The residue was filtered to remove and vacuum-distilled to remove most chlorobenzene at 10kPa. Then the reaction liquid was decompressed to 3.0-5.0 kPa to collect 160-168°C distillate. The MXDI product was a clear colorless and transparent liquid.

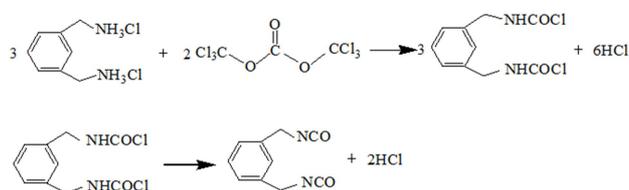


Figure 3. Reaction of BTC and MXDA to MXDI.

2.3. Sample Analysis

Gas chromatographic conditions: gas chromatographic capillary column SE-30 (30m×0.53mm×0.50μm), FID detector, vaporization chamber temperature 270°C, detector temperature 270°C, column oven, initial 80°C, hold 5min,

programmed at 15°C min⁻¹ to 200°C, and then 10°C min⁻¹ to 250°C, hold 5min; carrier gas nitrogen (purity 99.99%) pressure 200kPa, hydrogen Pressure 200kPa, air pressure 500kPa. Decane was internal standard and 2 µl decane was added to 1 mL sample.

Mass spectrometry conditions: gas chromatographic capillary column HP-5 (30m×0.25mm×0.25µm), vaporization chamber temperature 270°C, ion source temperature 270°C, ion trap temperature 260°C; ionization source: EI, initial 80°C, hold 1min, programmed at 10°C·min⁻¹ to 260°C.

3. Results and Discussion

3.1. Effect of Molar Ratio of Mxda to Btc

It theoretically produced 3 mol of phosgene from 1 mol of BTC and 1 mol of MXDA complete reaction theoretically required 2 mol of phosgene. Because the reaction process of BTC and MXDA was more complex, the actual consumption was not according to the reaction ratio. It can be seen in the table 1 that the yield of MXDI first increased slowly and then decreased as the molar ratio of MXDA to BTC increased. When the amount of BTC was excessively high (Entry 1 and 2), the amount of by-products increased resulting in a lower yield of MXDI. And when the molar ratio of MXDA to BTC exceeded the reaction equivalent ratio, the reaction was not complete due to the gas-liquid reaction system. Raw materials did not participate in the reaction leading to lower MXDI yields (Entry 4 and 5). Therefore, the optimal molar ratio of MXDA to BTC was 1.20:1.

Table 1. Effects of molar ratio of MXDA /BTC on the title reaction.

Entry	n _{m-XDA} : n _{BTC}	Yield _{m-XDI} /%
1	1:1.5	72.16
2	1:1	81.24
3	1.2:1	83.35
4	1.5:1	80.16
5	1.75:1	70.28

3.2. Effect of Reaction Temperature

MXDA and BTC can react at lower temperature, while MXDA can be better dissolved in chlorobenzene at high temperature and discharged more HCl. Making this comprehensive consideration, the reaction temperature was controlled at 60°C when was dropping the chlorobenzene solution of MXDA. The meta-(dimethylamino)benzoyl chloride decomposed to MXDI at a relatively high temperature, which was relatively influenced by the temperature. Table 2 showed the effect of different decomposition temperatures on the reaction. It can be seen from table 2 that as the temperature increased, the yield of MXDI first increased and then decreased. At a temperature of 125°C, the MXDI yield reached a maximum of 83.35% (Entry3). The possible cause of this phenomenon was the lower temperature (Entry1), where most of the meta-(dimethylamino) benzoyl chloride did not react, resulting in a minimum yield of 55.78% of MXDI. And when the temperature was higher (Entry5), the amount of

by-product CBI increased. At the same time, MXDI and phosgene generated a little of urea, which resulted in the reduction of the MXDI yield to 70.26%. Therefore, the optimal reaction temperature was 125°C.

Table 2. Effect of reaction temperature on the title reaction.

Entry	Temperature/°C	Yield _{m-XDI} /%
1	110	55.78
2	120	80.26
3	125	83.35
4*	140	77.15
5*	150	70.26

Note: o-dichlorobenzene as solvent.

3.3. Effect of Reaction Time

Table 3 showed the effect of reaction time on the reaction. As can be seen from Table 3, the yield of MXDI first reached the highest yield of 83.35% (Entry3) and then decreased as the reaction time increased. It may be due to the slow decomposition reaction of m-xylylenediy chloride. When the reaction time was too short, the yield of MXDI (Entry1) decreased to 78.62%. The meta-xylylenedicarboxylic acid chloride was incomplete reaction. When the reaction time was too long, the yield of MXDI decreased (Entry5) to 76.60% and the amount of by-products increased. Therefore, the optimal reaction time was 8 hours.

Table 3. Effect of reaction time on the title reaction.

Entry	Time/h	Yield _{m-XDI} /%
1	6	78.62
2	7	80.34
3	8	83.35
4	9	79.76
5	10	76.60

3.4. Effect of Gas Velocity

Table 4 showed the effect of nitrogen gas velocity on the reaction. As it can be seen from Table 4, the nitrogen gas velocity had a certain influence on the reaction. When the nitrogen gas velocity increased (Entry1-3), the XDI yield reached 83.35% (Entry3). It promoted the discharge of hydrogen chloride gas and facilitated the generation of XDI. And when the nitrogen gas velocity further increased (Entry 4 and 5), the yield of XDI began to decline to 75.20% (Entry5). When the nitrogen gas velocity was too large, a amount of phosgene would be carried out so that the MXDA hydrochloride unreacted completely leading to the yield of XDI decrease. In summary, the optimal nitrogen gas velocity was 8 mL·min⁻¹.

Table 4. Effect of nitrogen gas velocity on the title reaction.

Entry	Nitrogen Rate mL·min ⁻¹	Yield _{MXDI} /%
1	0	70.55
2	5	78.30
3	8	83.35
4	15	80.66
5	25	75.20

3.5. Reaction Mechanism

According to the actual research results, combined with the existing literature and theory, the possible reaction process of MXDA with BTC to MXDI was shown in Figure 3. As it can be seen from Figure 4, there were six main reactions in the MXDA and BTC reactions to MXDI. At room temperature, MXDA reacted firstly with hydrogen chloride to the hydrochloride salt, and then the solid phosgene chlorobenzene solution was dropwise added to the salt for reducing the formation of urea. The reaction of m-xylyldiaminocarbonyl chloride to generate MXDI required appropriate high temperature. The reaction rate was relatively slow and the reaction was the key reaction in the whole reaction. The temperature was too high to inhibit m-xylylenediyldichloride generating CBI. Therefore, the key reaction was in promoting the reaction d and suppressing the reaction f. Selecting the appropriate reaction temperature and reaction time can promote the production of MXDI and inhibit the formation of CBI, thereby increasing the yield of MXDI [17].

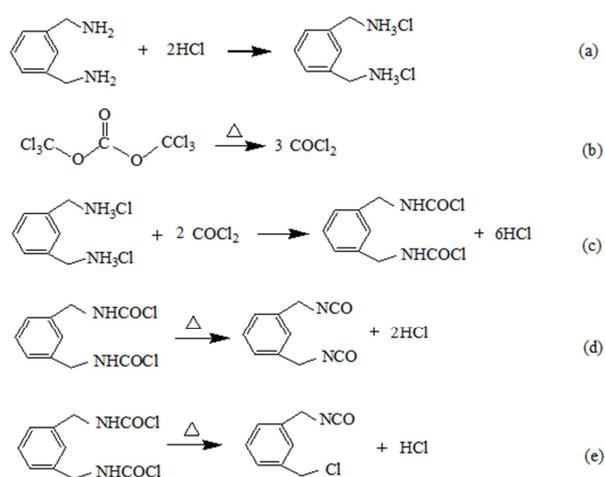


Figure 4. Reaction process of MXDA and BTC to MXDI.

4. Conclusions

In this paper, the reaction process of BTC with MXDA to MXDI was studied. The influencing factors and reaction mechanism were investigated. A safe and convenient route for organic synthesis was provided in the future of BTC application.

Through the study in experiments, it was found that there were multiple correlation reactions in the reaction process of MXDA and BTC to MXDI. The molar ratio of BTC to MXDA, reaction temperature, reaction time and nitrogen gas velocity on the reaction were investigated and optimized. The optimal reaction conditions were as follows: the molar ratio of MXDA to BTC was 1.2:1.0, the mass fraction of MXDA in chlorobenzene was 10%, the mass fraction of BTC in chlorobenzene was 10%, the nitrogen gas velocity was $8\text{ mL}\cdot\text{min}^{-1}$, the reaction temperature was 125°C and the reaction time was 8 hours. The MXDI yield was 83.35% under the optimal reaction conditions. The reaction

mechanism and the key steps involved in the reaction process were also deeply analyzed.

Support

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