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Study on the synthesis of toluene-2,4-diisocyanate via amine and carbonyl fluoride

Ni Zhang [a], Xiaomeng Zhou [b], Hengdao Quan [a,b,*], Akira Sekiya [b]

[a] School of Chemical Engineering & Environment, Beijing Institute of Technology, 5 South Zhongguangcun Street, Haidian District, Beijing 100081, PR China
[b] National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

We presented recently a synthesis of toluene-2,4-diisocyanate (TDI) as one of the nine examples to verify the feasibility of an industrial appealing two-step method for isocyanates synthesis via amines and carbonyl fluoride (COF_2). Because more investigation was considered to be necessary for future industrial application, the two-step synthesis processes of TDI were studied in detail herein. The total yield of TDI increased 5.6% under the optimized experimental conditions. The influence of the excess COF_2 left in the reaction system was studied carefully according to a one-pot method.

1. Introduction

Toluene-2,4-diisocyanate (TDI) is the major raw material for synthesis of both flexible and rigid polyurethane, which could be used as automotive cushions, carpet underlay, furniture, insulators in construction, pipeline, etc. [1]. Presently, the phosgenation of the 2,4-diaminotoluene (TDA) or its salt precursors is still the main production method in a commercial scale [1–3], but several alternative methods have been developed to reduce or eliminate its security and environment risks, such as the one-step carbonylation of 2,4-dinitrotoluene (DNT) [4,5]. During the recent two decades, many researchers paid their attentions to one such method that involves the production of carbamate esters by oxidative carbonylation of TDA [6–9] or reductive carbonylation of DNT [10,11], dealcoholysis of which gives TDI. But to the best of our knowledge, none of them are applied in industry so far due to several drawbacks.

We showed recently a facile two-step method that reaction of amines and COF_2 to yield the corresponding isocyanates could be facilitated under relatively mild conditions and in good yields, by which the TDI was synthesized as an example in 87.4% yield based on TDA [12]. It is well known that COF_2 is an attractive and important compound as a semiconductor etching gas, cleaning gas, and a chemical intermediate to prepare other fluorinated compounds [13–15] and generally more expensive than phosgene. Using COF_2 instead of phosgene to react with amines for isocyanates production will inevitably increase the raw material costs, but the costs of equipment, facilities, security and environmental protection, etc. will be decreased accordingly due to the relatively lower potential risk of COF_2. Besides, the novel synthesis method of COF_2 invented by our laboratory [16] and the recycle of by-product HF and raw material COF_2 could decrease the total costs further [12]. Synthetically, there is no much difference about the total costs between the COF_2 method and phosgene method if the total yields are basically the same.

However, the investigation for the synthesis of TDI via TDA and COF_2 was not detailed in the previous report [12], in which the other eight different isocyanates were synthesized and the focus was placed on the verification about the feasibility of COF_2 method. Herein, six main factors of the experimental conditions for the two-step method are further studied and optimized, and the influence of the excess COF_2 left in the reaction system is discussed carefully via a one-port method.

2. Results and discussion

2.1. Synthesis of TDI via two-step method

The method is consisted of two steps. The first step is the reaction between COF_2 and TDA at the room temperature or near. The second step is the decomposition of the intermediate

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[*] Corresponding author at: National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
E-mail address: hengdao-quan@aist.go.jp (H. Quan).

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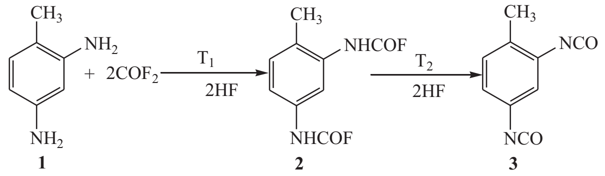

Scheme 1. The main reactions of TDA with COF_2.

produced in the first step at a higher temperature. According to our previous report [17], the whole process mainly took place by way of Scheme 1.

2.1.1. The reaction between TDA and COF_2

Several factors, for example reaction time, may affect the results of the first step reaction. To check their relevance for the yield of target intermediate **2**, several experiments were conducted and the results are shown as Table 1.

From Table 1 – (1), we can know that when *n* (TDA): *n* (COF_2) was 1:1, there was no **2** produced. With the increase of COF_2, the yield of **2** was growing up until *n* (TDA): *n* (COF_2) reached 1:4, at which the highest yield was obtained. Whereas when *n* (TDA): *n* (COF_2) was 1:6, the yield of **2** was decreased, which may be explained that the excess COF_2 addition at the '$C{=}O$' double bond of **2** were happened and generated a by-product with 'C (F)–O–COF' structure [15]; and we do not believe that this decrease was caused by the reverse reaction of **2** with HF owing to the no detected TDA in the products. Compare the experimental results in Table 1 – (2), it is known that with the increase of TDA amount, the yield of **2** was growing up. Because the mole ratio of TDA and COF_2 was fixed, when TDA amount increased, the COF_2 amount will also increase, which means the pressure in the reactor will increase correspondingly. Thus, the yield cannot be increased indefinitely just by adding more substrates because higher requirement for the pressure tolerance of the reactor and the resulting increase of apparatus cost and dangerousness should be considered; and for the 10 ml stainless reactor used here, the amount of TDA was preferred to be 4 mmol. Based on the results of Table 1 – (3), the preferable reaction time was 2 h. The possible reason about the yield decrease of **2** after 2 h is considered to be similar to the result of Table 1 – (1) at 1:6 mole ratio of TDA and COF_2.

Moreover, the solvent is indispensable for the first synthesis step, thus the investigation about the effects of different solvents is necessary. The intermediate **2** is soluble in acetone, ethanol, DMF, DMSO, and THF; and it is insoluble in toluene, dichloromethane, chlorobenzene, and *m*-dichlorobenzene. According to synthesis procedure that descried in Section 4.3.1.1, we selected four different solvents for comparison under the experimental conditions optimized above. The results are shown in Table 2.

Table 1
The yields of intermediate **2** under different experimental conditions.

(1) in different mole ratio of TDA and COF_2[a]					
n (TDA):*n* (COF_2)	1:1	1:1.5	1:2	1:4	1:6
Yield of **2** (%)	0	6.74	24.4	52.5	37.8
(2) in different TDA amount[b]					
TDA amount (mmol)	2	4	6		
Yield of **2** (%)	48.4	52.5	83.4		
(3) in different reaction time[c]					
Reaction time (hour)	1	2	4	12	
Yield of **2** (%)	70.9	94.5	70.9	52.5	

Reaction temperature: room temperature; Solvent: chlorobenzene, 7.5 g; the yield of intermediate **2** was determined by ^1H NMR.

[a] Amount of TDA: 4 mmol; reaction time: 12 h.

[b] *n* (TDA): *n* (COF_2) = 1:4; reaction time: 12 h.

[c] Amount of TDA: 4 mmol; *n* (TDA): *n* (COF_2) = 1:4.

Table 2
The experimental results by using different solvents[a].

Entry	TDA (mmol)	COF_2 (mmol)	Solvent	Solvent amount (g)	Yield of **2** (%)
1	8	32	Toluene	15	59.6
2	8	32	Chlorobenzene	15	90.3
3	8	32	Dichloromethane	15	96.2
4	8	32	THF	15	0

[a] Reaction temperature: room temperature; reaction time: 2 h; the yield of intermediate **2** was determined by ^1H NMR.

From Table 2, the intermediate **2** could be produced in different yields except Entry 4 although THF can dissolve TDA. Among the other three Entries, the yield of **2** was the highest when dichloromethane was used as the solvent; besides, due to the lower boiling point of dichloromethane (40 °C) than chlorobenzene (132 °C), dichloromethane was more easy to be taken away and could gain purer intermediate. So, dichloromethane was a kind of preferable solvent than chlorobenzene. For toluene as the solvent, not only was the yield of **2** unsatisfactory, but also a foam-liked material was generated with intermediate **2** together, when we discharged the excess COF_2, the solution will be sprayed out. Moreover, when intermediate **2** was dissolved in acetone a night later or in DMF for 6 h, the quantity were decreased, of which the possible causes are still on study.

Actually, the reactions could happen at other temperature, such as 40 °C, 60 °C, etc. But the room temperature could keep the energy consumption low and made the application of a solvent with low boiling point possible, which is considered to be the best reaction temperature.

In sum, the optimized experimental conditions of the first step are: amount of TDA: 4 mmol; *n* (TDA): *n* (COF_2) = 1:4; reaction temperature: room temperature; reaction time: 2 h; solvent: dichloromethane.

2.1.2. Thermolysis of the carbamyl fluoride intermediate

The investigation of the decomposition process of intermediate **2**, which was produced in the first step under the optimized experimental conditions, was conducted herein under different decomposition temperature.

The intermediate solid was added into a PTFE tube after weighting precisely, the tube was sealed by rubber stopper. The gases that produced during the decompose process was taken away by N_2. The tube was put into oil bath with different temperature, the decomposed process could be observed clearly and the phenomena are as Table 3 shown.

Based on Table 3, the intermediate solid began to crack obviously at the temperature of 160 °C; and about 30 min later, there was no bubble generated in the tube, a yellowish brown viscous liquid was gained. Meanwhile, the intermediate **2** was analyzed by TG-DTA (shown in Section 4.3.1.3 Fig. 2), from which the loss of weight was mainly happened between 100 °C and

Table 3
The decomposition phenomena of intermediate solid under different temperature.

Temperature	Phenomenon
120 °C	There was no obvious visible change.
140 °C	The surface of the intermediate was becoming yellow after 2 min.
160 °C	The intermediate liquefied very quickly and some gases were generated.
180 °C	The intermediate liquefied very quickly and some gases were generated.