



NOTE

Kinetics for the Amine-Catalyzed Carbamate Reaction of Toluylene-2,4-diisocyanate

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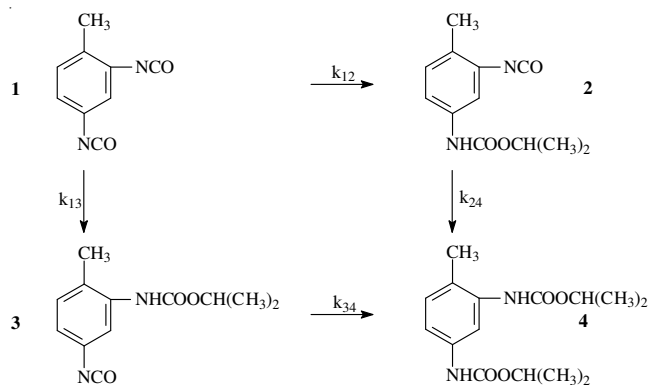
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Toluylene-2,4-diisocyanate (2,4-TDI) **1** reacts with alcohols through two simultaneous paths in the polyurethane reaction, which generate two different intermediates and one final product-toluylene-4-carbamate-2-isocyanate **2**, toluylene-2-carbamate-4-isocyanate **3** and toluylene-2,4-dicarbamate **4**. The -CH₃ chemical shifts in benzene ring in compounds **1**, **2**, **3** and **4** can be easily tested, well distinguished and quantified. Combined with the results of FT-IR *in situ*, its kinetics is investigated and four rate constants for the toluylene-2,4-diisocyanate carbamate reaction with isopropanol are calculated out.

Key Words: Toluylene-2,4-diisocyanate, Polyurethane reaction, Kinetics, Triethylamine.

The reaction of toluylene-2,4-diisocyanate (2,4-TDI) and alcohols have been reported to be a parallel and series reaction, which contains not one reaction path but two simultaneous reaction paths^{1,2} (**Scheme-I**). There are a number of researches about the reaction kinetics³⁻⁶. However, the distinction between k_{12} and k_{13} , k_{34} and k_{24} could not be easily detected when amine or tin is used as catalyst⁷. In order to acquire the rate constants for the *para*- or *ortho*-isocyanate groups, some assumptions must be made to deduce kinetic equation^{8,9}, which can not exactly describe the real reaction process.



Scheme-I: Two simultaneous paths for the 2,4-TDI-isopropanol reaction

NMR spectroscopy is a good tool to address the issue¹⁰⁻¹². For instance, Dubois *et al.*¹³ investigated the toluylene-2,4-

diisocyanate-hydroxyl terminated polybutadiene reaction with ¹³C NMR and found that the variation of carbamate groups in polyurethane could be well distinguished during the whole reaction process. Quantitative analysis for compounds **1**, **2**, **3** and **4** seems possible. Yet, test time is very long relative to reaction time. Accurate spectra is difficult to acquire, only if the reaction could be conveniently terminated at any moment.

In this contribution, ¹H NMR (Bruker, AVANCE II 400) is used to analyze the chemical shifts of methyl group in benzene ring. The -CH₃ chemical shifts for compounds **1**, **2**, **3** and **4** in CDCl₃ are well distinguished. Combined with the results of FT-IR (Mettler Toledo, React IR IC10) *in situ*, the rate constants of k_{12} , k_{13} , k_{34} and k_{24} can be, respectively calculated out.

First, 2,4-TDI (2.3 mmol, 0.33 mL), isopropanol (4.6 mmol, 0.35 mL) and triethylamine (2.4 mmol, 0.33 mL) are mixed in CDCl₃ (73 mmol, 7 mL) and reacted at 55 °C. FT-IR *in situ* is used to monitor the reaction process¹⁴. The relationship between total absorbance of -NCO (A) and time (t) can be obtained accurately (Fig. 1). According to the relationship between absorbance and concentration, the rate constants in the initial stage and final stage can be calculated out with the general nth-order expression, which is that $k_{\text{initial}} = 1.5 \times 10^{-1} \text{ L mol}^{-1} \text{ min}^{-1}$ ($0 \leq \xi \leq 8\%$) and $k_{\text{final}} = 1.3 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$ ($69\% \leq \xi \leq 75\%$), respectively. The extent of reaction (ξ) can be calculated from the total -NCO consumption.

Second, the same reaction is carried once more. When the reaction reaches certain moments (t), part of the reaction

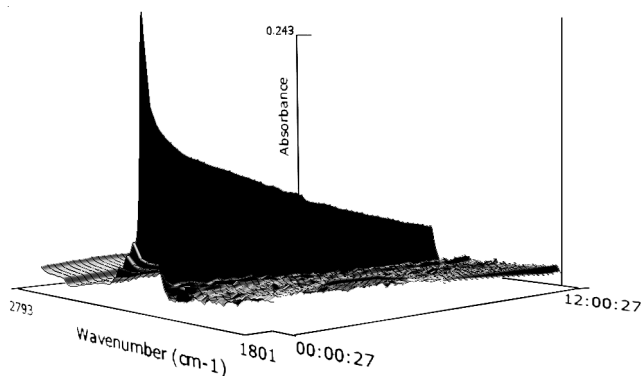


Fig. 1. Relationship between -NCO absorbance and reaction time

mixture (0.5 mL) is taken out to test ^1H NMR spectra. Thus, a series of ^1H NMR spectra is obtained at different extents of the reaction. According to Yang *et al.*¹⁵, the chemical shifts for -CH₃ in benzene ring in compounds **1**, **2**, **3** and **4** can be attributed to 2.30, 2.27, 2.21 and 2.19 ppm, respectively. Thus, the amounts of compounds **1**, **2**, **3** and **4** are determined accurately (Fig. 2).

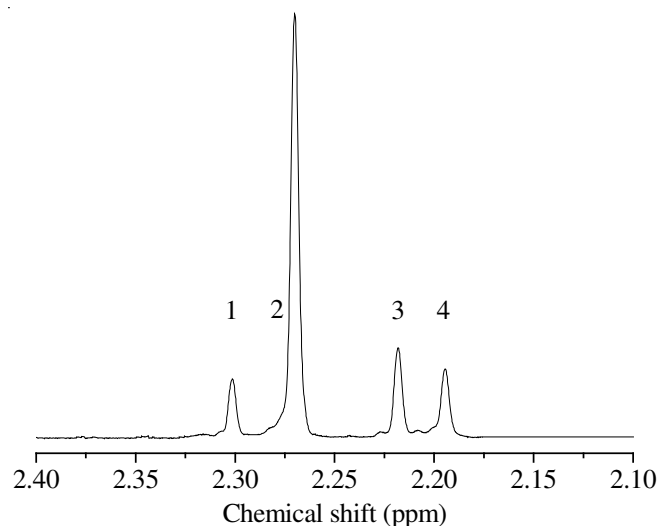


Fig. 2. ^1H NMR spectra of amine-catalyzed 2,4-TDI-isopropanol reaction after 17 min

The extent of reaction (ξ) can also be calculated out from ^1H NMR spectra

$$\xi = \frac{I_2 + I_3 + 2I_4}{2(I_1 + I_2 + I_3 + I_4)} \quad (1)$$

where I_1 , I_2 , I_3 and I_4 are the integrations of peak areas for compounds **1**, **2**, **3** and **4** and they can represent the amounts of these four compounds. The mol percentages of compounds **1**, **2**, **3** and **4** to ξ are shown in Fig. 3.

The amount of compounds **1** decreases and the amount of compounds **4** increases constantly. But, in sharp contrast, there is a maximum mol percentage of compounds **2** ($\xi = 55\%$) and **3** ($\xi = 50\%$), which are 68 and 13 %, respectively.

Moreover, there are no compounds **4** in the reaction system when ξ is lower than 8 %. Only k_{12} and k_{13} take effect, so the relationship between k_{12} and k_{13} in the parallel reaction can be calculated:

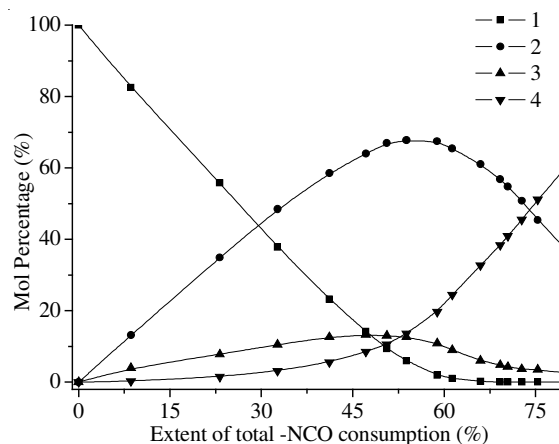


Fig. 3. Variation of compounds **1**, **2**, **3** and **4** mol percentage to ξ

$$\frac{k_{12}}{k_{13}} = \frac{\Delta I_2}{\Delta I_3} = \frac{I_{2,\xi=8\%} - I_{2,\xi=0}}{I_{3,\xi=8\%} - I_{3,\xi=0}} = 3.3 \quad (2)$$

Likewise, there are no compounds **1** in the reaction system when ξ is higher than 69 % and lower than 75 %. Only k_{34} and k_{24} take effect, so the relationship between k_{34} and k_{24} in the parallel reaction can be calculated:

$$\frac{k_{34}}{k_{24}} = \frac{\Delta I_2}{\Delta I_3} = \frac{I_{2,\xi=75\%} - I_{2,\xi=69\%}}{I_{3,\xi=75\%} - I_{3,\xi=69\%}} = 8.8 \quad (3)$$

Finally, considering the relationship of $k_{\text{initial}} = k_{12} + k_{13}$ and $k_{\text{final}} = k_{34} + k_{24}$, the four rate constants for the amine-catalyzed 2,4-TDI-isopropanol reaction in CDCl_3 at 55 °C can be calculated: $k_{12} = 1.2 \times 10^{-1} \text{ L mol}^{-1} \text{ min}^{-1}$, $k_{13} = 3.5 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$, $k_{34} = 1.1 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$, $k_{24} = 1.3 \times 10^{-3} \text{ L mol}^{-1} \text{ min}^{-1}$.

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