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^{1}H NMR analysis of the tolylene-2,4-diisocyanate–methanol reaction

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Abstract

Tolylene-2,4-diisocyanate (2,4-TDI) **1** reacts with methanol through two simultaneous paths in the polyurethane reaction, which involve two different intermediates – tolylene-4-carbamatic-2-isocyanate **2** and tolylene-2-carbamatic-4-isocyanate **3**, and the final product is tolylene-2,4-dicarbamate **4**. The –CH_3 chemical shifts in benzene ring in compounds **1**, **2**, **3** and **4** can be easily tested and well distinguished, through which those four compounds are quantified and their kinetics are investigated. It shows that four rate constants for the tolylene-2,4-diisocyanate–methanol reaction in CCl_4 at 50 °C are $k_1 = 9.6 \times 10^{-2}$ h^{-2} mol^{-2} min^{-1}, $k_2 = 1.4 \times 10^{-2}$ h^{-2} mol^{-2} min^{-1}, $k_3 = 4.0 \times 10^{-3}$ h^{-2} mol^{-2} min^{-1}, $k_4 = 1.4 \times 10^{-3}$ h^{-2} mol^{-2} min^{-1}. (k_1 is the reaction rate constant from compounds **1** to **2**; k_2 is the reaction rate constant from compounds **1** to **3**; k_3 is the reaction rate constant from compounds **3** to **4**; k_4 is the reaction rate constant from compounds **2** to **4**).

Keywords: Tolylene-2,4-diisocyanate; Polyurethane reaction; Kinetics

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The reaction kinetics of tolylene-2,4-diisocyanate (2,4-TDI) and methanol have been reported to be a parallel and series reaction containing two simultaneous reaction paths instead of one reaction path [1,2] (Scheme 1). There are a lot of researches about the reaction kinetics [3–5]. However, the distinction between k_1 and k_3, k_2 and k_4 could not be easily detected by that way [6] and some assumptions must be done to deduce the kinetic equation [7,8]. NMR spectroscopy is a good way to solve the problem [9]. For instance, Dubois et al. [10] investigated the 2,4-TDI–hydroxyl terminated polybutadiene reaction with ^{13}C NMR and found that the variation of carbamate groups in polyurethane could be well distinguished during the whole reaction process. Yet, quantitative study seems impossible because the test time is too long to acquire accurate spectra.

In this contribution, ^{1}H NMR (Bruker, AVANCE II 400) is used to analyze the chemical shifts of methyl group in benzene ring during the 2,4-TDI–methanol reaction. The –CH_3 chemical shifts for compounds **1**, **2**, **3** and **4** in $CDCl_3$ can be well distinguished.

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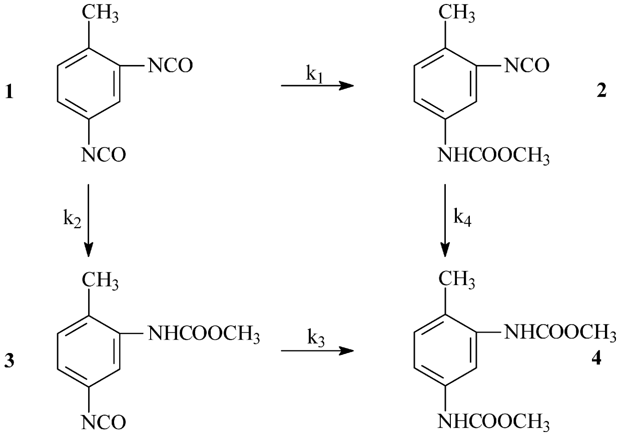

Scheme 1. Two simultaneous paths for the 2,4-TDI–methanol reaction.

1. Results and discussion

First, 2,4-TDI (2.3 mmol, 0.33 mL) and methanol (4.6 mmol, 0.19 mL) are mixed in CCl_4 (73 mmol, 7 mL) and reacted at 50 °C. FT-IR (Mettler Toledo, React IR IC10) *in situ* is used to monitor the reaction process [11]. The relationship between total amount of –NCO and time (t) can be obtained accurately and the rate constants can be calculated out. As a result, the rate constant in the initial stage is $k_{\text{initial}} = 1.1 \times 10^{-1}\ \text{h}^{-2}\ \text{mol}^{-2}\ \text{min}^{-1}$ ($0 \leq \xi \leq 19\%$) and that in the final stage is $k_{\text{final}} = 5.4 \times 10^{-3}\ \text{h}^{-2}\cdot\text{mol}^{-2}\cdot\text{min}^{-1}$ ($62\% \leq \xi \leq 70\%$). The extent of reaction (ξ) can be calculated from the extent of total –NCO consumption.

Second, the same reaction is carried on again. When the reaction reaches certain moments (t), part of the reaction mixture (0.5 mL) is taken out at corresponding intervals to test ^{1}H NMR spectra. Thus, a series of ^{1}H NMR spectra is obtained with different extents of the reaction. According to the references [12], the chemical shifts for $-CH_3$ 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. 1).

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

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

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 in the 2,4-TDI–methanol reaction are shown in Fig. 2.

The amount of compound **1** decreases and the amount of compound **4** increases continuously. But, in sharp contrast, there is a maximum mol percentage of compounds **2** (ξ = 60%) and **3** (ξ = 40%), which are 74% and 12%, respectively.

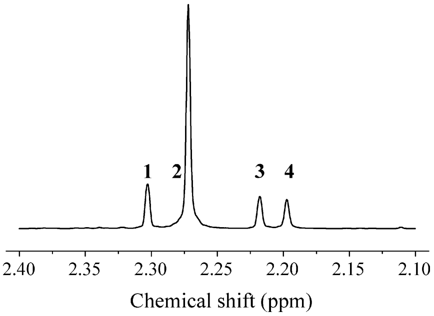

Fig. 1. ^{1}H NMR spectra of 2,4-TDI–methanol reaction for 1.5 h.

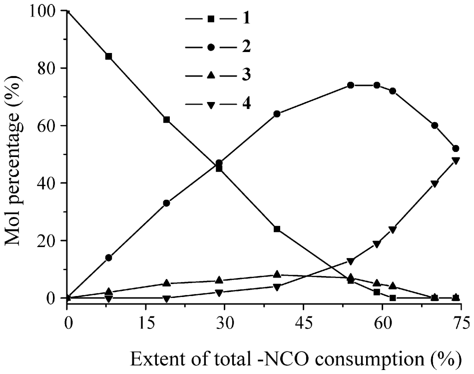

Fig. 2. The variation of **1**, **2**, **3** and **4** mol percentage to ξ.

Moreover, there is no compound **4** in the reaction system when ξ is lower than 19%. Only k_1 and k_2 take effect, so the relationship between k_1 and k_2 in the parallel reaction can be calculated:

$$\frac{k_1}{k_2} = \frac{\Delta I_2}{\Delta I_3} = \frac{I_{2,\xi=19\%} - I_{2,\xi=0}}{I_{3,\xi=19\%} - I_{3,\xi=0}} = 6.6$$

Likewise, there is no compound **1** in the reaction system when ξ is higher than 62% and lower than 70%. Only k_3 and k_4 take effect, so the relationship between k_3 and k_4 in the parallel reaction can be calculated:

$$\frac{k_3}{k_4} = \frac{\Delta I_2}{\Delta I_3} = \frac{I_{2,\xi=70\%} - I_{2,\xi=62\%}}{I_{3,\xi=70\%} - I_{3,\xi=62\%}} = 3$$

Finally, considering the relationship of $k_{\mathrm{initial}} = k_1 + k_2$ and $k_{\mathrm{final}} = k_3 + k_4$, the four rate constants for the 2,4-TDI–methanol reaction in CCl_4 at 50 °C can be calculated: $k_1 = 9.6 \times 10^{-2}\ h^{-2}\ mol^{-2}\ min^{-1}$; $k_2 = 1.4 \times 10^{-2}\ h^{-2}\ mol^{-2}\ min^{-1}$; $k_3 = 4.0 \times 10^{-3}\ h^{-2}\ mol^{-2}\ min^{-1}$; $k_4 = 1.4 \times 10^{-3}\ h^{-2}\ mol^{-2}\ min^{-1}$.

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