

Urethane Reaction Kinetics of Butanediols Catalyzed by Zr(acac)₄

Peng Fei Yang, Tian Duo Li

Shandong Provincial Key Laboratory of Fine Chemicals, Shandong Polytechnic University, Jinan 250353, People's Republic of China
 Correspondence to: P. F. Yang (E-mail: ypfyfh@gmail.com)

ABSTRACT: The urethane reaction of isocyanate was carried out with zirconium acetyl acetonate (Zr(acac)₄) as catalyst. 1,2-Butanediol and 1,4-butanediol were used as model compounds to investigate the reaction kinetics. It was shown that hydroxyl groups in 1,2-butanediol appeared to have different reaction rate when reacting with phenyl isocyanate, which was labeled as k_{fast} and k_{slow} . It was very surprising that the reaction rate of 1,4-butanediol (k_{con}) was very similar to the value of k_{slow} at the same temperature although there is only primary hydroxyl group in its molecule. Furthermore, activation energy (E_a), activation enthalpy (ΔH), and activation entropy (ΔS) for the reaction were calculated out, from which some catalytic properties of Zr(acac)₄ were revealed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2399–2403, 2013

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INTRODUCTION

Polyurethane has been widely used in many fields, and its preparation via the reaction of isocyanate with hydroxyl compound has been extensively investigated.^{1,2} One of the most important factors that affect the reaction is catalyst,³ such as organotin or tertiary amines. However, concerning the need of pro-environment, safety, and health, an important development is the replacement of organotin compound to environmentally friendly catalyst, such as metal- β -diketones (M(acac)_n).

A few researchers have reported the catalytic properties of zirconium chelate for the urethane reaction kinetics and mechanism.^{4–9} For example, Blank et al.^{4,5} investigated the reaction of alcohol or water with isocyanate with zirconium chelate as catalyst. They found that compared with organotin catalyst, the reaction catalyzed by zirconium chelate was selective and preferred to the isocyanate–water reaction. This permitted its use not only in waterborne isocyanate cross-linked two component coatings, but also in plural component gun applications. Furthermore, Benthem et al.⁶ developed the perspective in synthesis of polyurethane dendrimer catalyzed by zirconium (IV) salts, which are based on the selective reaction of alcohol with diisocyanate carrying both tertiary and primary isocyanate groups. Coating applications of that ultimate monodisperse polymer were not only restricted to perfect branching polymers, but also included isocyanate functional coating resins.

Butanediol is one of the essential materials in polyurethane industry. In the early stage, literature often reported the applica-

tion of 1,4-butanediol.¹⁰ Recently, more and more researchers changed their focus to asymmetric diols or polyols with secondary or tertiary hydroxyl groups, which could synthesize special polyurethane with different molecular structure.^{11–13} For example, Yan and Gao¹⁴ obtained hyper-branched polyurethanes from the two monomers: AA' and B_xB'. Asymmetric diol is crucial in that synthetic route and its urethane reaction data is necessary, including kinetic and thermodynamic parameters.

In this article, the urethane reaction of 1,2-butanediol and phenyl isocyanate is carried on with Zr(acac)₄ as catalyst. For comparison, 1,4-butanediol is also used as reactant. The reaction is monitored by *in situ* Fourier transform-infrared (FT-IR), followed by the kinetic and thermodynamic studies, from which some catalytic properties of Zr(acac)₄ are revealed.

EXPERIMENTAL

Materials and Instruments

Phenyl isocyanate was purchased from Sigma Aldrich (Saint Louis, MO) and 1,2-butanediol, 1,4-butanediol and Zr(acac)₄ were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China), all of which were used as received. Dichloromethane was purchased from Sinopharm Chemical Reagent Co., purified with distillation and stored over molecular sieves (5Å). The purities of all the reagents were of analytical grade (A.R.).

The *in situ* FT-IR spectrometer, React IR IC10, was manufactured by Mettler Toledo (Columbia, MD). Air purification

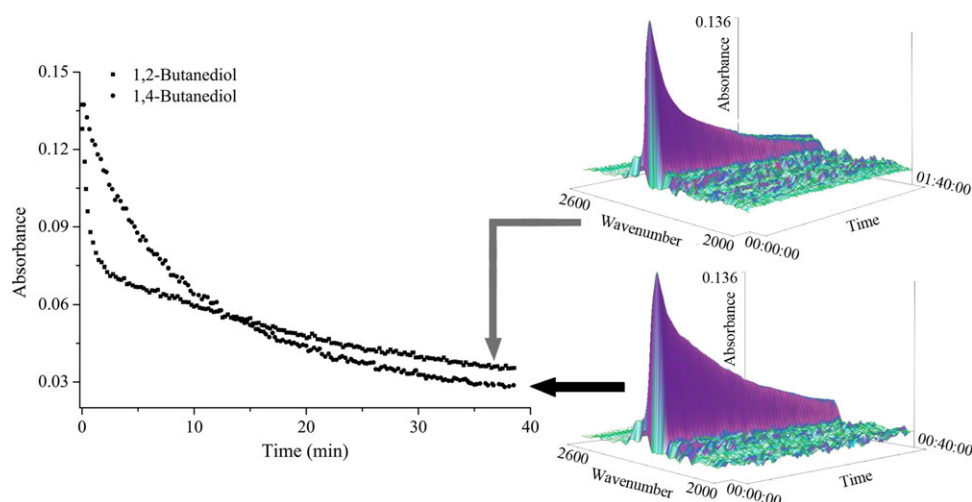


Figure 1. Plot of $-\text{NCO}$ absorbance versus t for the butanediol–phenyl isocyanate reaction (20°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

system, XYA-5000G, was manufactured by Shanghai XiYou Analytical Instrument Co..

Calibration for Concentration from Absorbance

Different concentrations of phenyl isocyanate in dichloromethane were prepared. FT-IR spectroscopy was used to measure their absorbance. Thus, the relationship between absorbance and concentration was obtained in highly concentrated solutions.

Kinetic Studies for the Urethane Reaction

Using air-purification system, clean and dry air was flowed into the instrument continuously until the absorbance of all impurities was constant. Then, the background spectra were recorded with *in situ* FT-IR spectrometer. After that, butanediol (1.38 mmol, 0.124 g), dichloromethane (53.0 mmol, 7.00 mL), and catalytic amount of $\text{Zr}(\text{acac})_4$ were poured into a three-neck flask with magnetic stir. The probe of *in situ* FT-IR spectrometer was immersed into the reactants to monitor the variation of IR spectra. When the reaction temperature reached the set

point, stoichiometric amount of phenyl isocyanate (2.76 mmol, 0.30 mL) ($-\text{NCO}/-\text{OH} = 1$) was added and the reaction began. Data were collected every minute until the reaction was terminated at a certain extent of conversion. The resolution was 8 cm^{-1} and the scan region was $4000\text{--}650\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Polyurethane can be dissolved in many solvents, but good solvent of $\text{Zr}(\text{acac})_4$ is limited. Therefore, dichloromethane is selected to dissolve $\text{Zr}(\text{acac})_4$ and its concentration in our experiment is $4 \times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$. As a powerful tool for the investigation of reaction kinetics,^{15–17} *in situ* FT-IR spectroscopy is used to monitor the urethane reaction catalyzed by $\text{Zr}(\text{acac})_4$. The absorption of isocyanate groups at 2270 cm^{-1} is the most useful peak to monitor the reaction progress and reliable for kinetic analysis. To visualize changes near the region of 2270 cm^{-1} better, a plot of $-\text{NCO}$ absorbance versus reaction time is depicted in Figure 1 (20°C).

It can be found from the data in Figure 1 that the initial reaction rate of 1,2-butanediol is much faster than that of 1,4-butanediol. When reaction time goes on, the reaction rate of 1,2-butanediol decreases and becomes similar to that of 1,4-butanediol. It maybe lies in the molecular structure of butanediols, which will be illuminated later on.

The Relationship Between Absorbance and Concentration

To calculate out rate constant, the absorbance of $-\text{NCO}$ must be calibrated to its concentration. As is known to all, Beer–Lambert law can only be used for solutions of low concentration. As far as common concentrated solutions are concerned, linear relationship between absorbance and concentration must be testified. According to the method reported in our previous paper,¹⁸ various concentration of $-\text{NCO}$ in dichloromethane is analyzed with *in situ* FT-IR to obtain its absorbance at 2270 cm^{-1} . The linear relationship appears correct only for concentration lower than $0.4\text{ mol}\cdot\text{L}^{-1}$ (Figure 2). According to that, the range of $0\text{--}0.4\text{ mol}\cdot\text{L}^{-1}$ is used in the following studies, and the relationship between absorbance and concentration is shown in eq. (1).

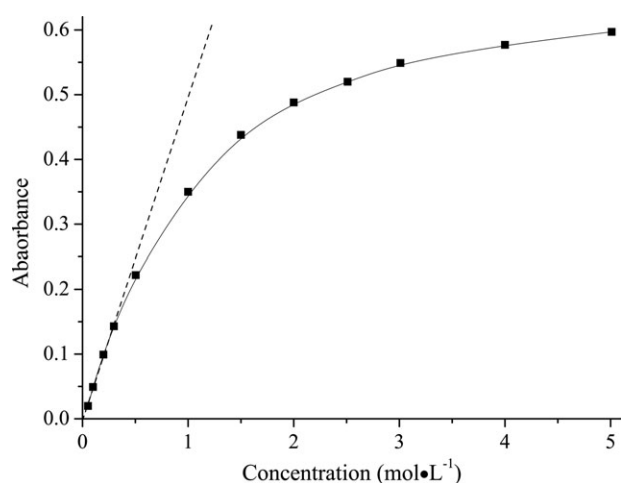
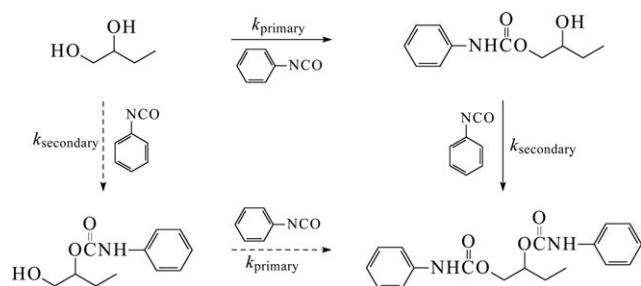


Figure 2. Calibration of absorbance to concentration for $-\text{NCO}$ in dichloromethane.



Scheme 1. Two simultaneous paths for the 1,2-butanediol–phenyl isocyanate reaction.

$$A_{-NCO} = k_0 \cdot C_{-NCO} (k_0 = 0.498 \text{ L} \cdot \text{mol}^{-1}) \quad (1)$$

Kinetic Studies

There are two hydroxyl groups in the molecule of 1,2-butanediol. Therefore, the reaction kinetics of 1,2-butanediol with phenyl isocyanate is a parallel and series reaction containing two simultaneous reaction paths (Scheme 1). It is very like the reaction of tolylene-2,4-diisocyanate with methanol, which we have reported before.¹⁹

It can be found in Scheme 1 that the rate constants of primary hydroxyl group and secondary hydroxyl group are named as k_{primary} and $k_{\text{secondary}}$, respectively. The dashed reaction route in Scheme 1 cannot perform easily because k_{primary} is much larger than $k_{\text{secondary}}$. So it can be ignored to work out kinetic parameters for simplicity. It has been reported that the reaction is in accordance with 2nd-order kinetics.⁵ Thus, the relationship between $1/C$ and t in dichloromethane at 20°C is shown in Figure 3, from which rate constant can be work out from the slope of curve.

It can be found from the data in Figure 3 that the urethane reaction of 1,2-butanediol appears to be divided into two stages, which generates two reaction rate constants. We name the rate constants as k_{fast} and k_{slow} , which is very similar to the rate constants of k_{primary} and $k_{\text{secondary}}$, respectively. That is, $k_{\text{fast}} \approx$

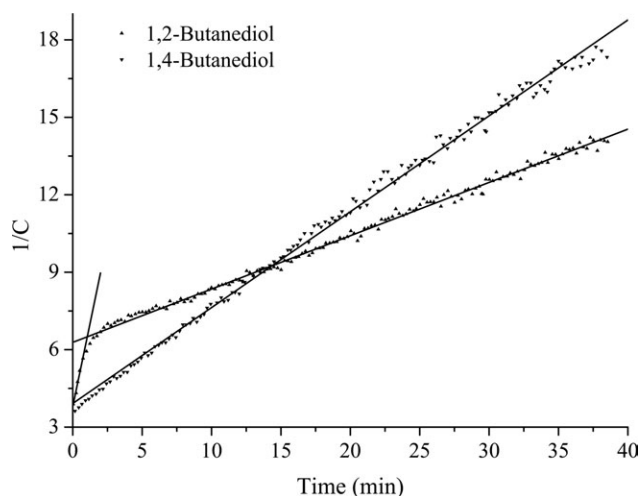


Figure 3. 2nd-Order kinetic plots for the butanediol–phenyl isocyanate reaction (20°C).

Table I. Rate Constant for the Reaction of Phenyl Isocyanate and Butanediols at Different Temperature

T(°C)	1,2-Butanediol (L·mol ⁻¹ ·min ⁻¹)			1,4-Butanediol (L·mol ⁻¹ ·min ⁻¹)
	k_{fast}	k_{slow}	$k_{\text{fast}}/k_{\text{slow}}$	k_{con}
15	1.09	0.10	10.4	0.14
20	1.93	0.21	9.24	0.27
25	3.58	0.40	8.86	0.54
30	5.93	0.76	7.78	1.01

k_{primary} and $k_{\text{slow}} \approx k_{\text{secondary}}$. In contrast to that, reaction rate of 1,4-butanediol (k_{con}) remains unchanged when reaction time goes on. Detailed values of k_{fast} and k_{slow} in 1,2-butanediol, as well as k_{con} in 1,4-butanediol, are shown in Table I at different temperature.

Zr(acac)₄ is a very effective catalyst for the reaction of isocyanate with alcohol. Compared with amine catalyst, reaction catalyzed by Zr(acac)₄ is substantially faster.^{20,21} It is very interesting that 1,2-butanediol reacts much faster than 1,4-butanediol. That is, although the value of k_{slow} and k_{con} is very similar, the value of k_{fast} is much larger than that of k_{con} . An insertion mechanism has been proposed previously, which involves activation of hydroxyl groups by Zr(acac)₄, followed by insertion of isocyanate groups.^{4,5}

Furthermore, it is observed that both values of k_{fast} and k_{slow} in 1,2-butanediol rise greatly with the increase of temperature, and the value of $k_{\text{fast}}/k_{\text{slow}}$ drops from 10.4 to 7.78. That is, reaction temperature affects the reaction rate of secondary hydroxyl group more greatly than that of primary hydroxyl group. Therefore, the selectivity of urethane reaction in 1,2-butanediol decreases.

Thermodynamic Studies

Thermodynamic parameters, such as activation energy (E_a), activation enthalpy (ΔH), and entropy (ΔS), can be determined

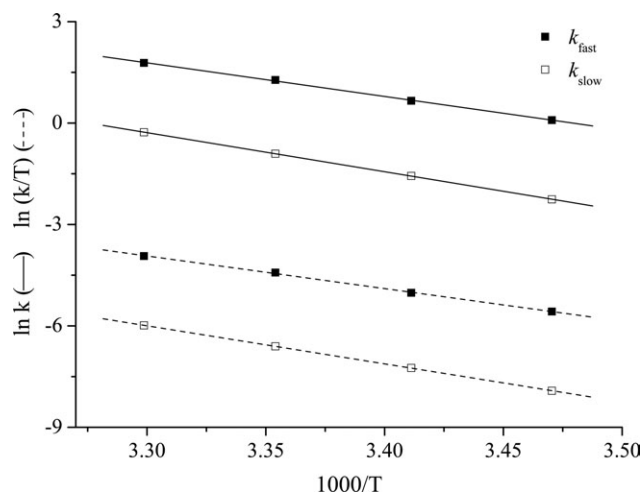


Figure 4. Arrhenius and Eyring plots for the 1,2-butanediol–phenyl isocyanate reaction.

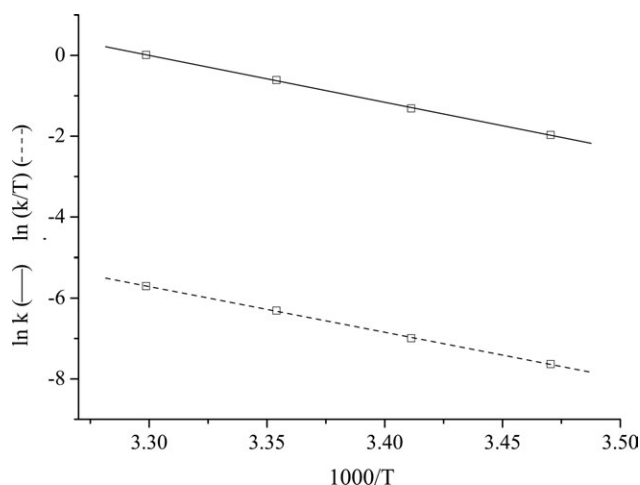


Figure 5. Arrhenius and Eyring plots for the 1,4-butanediol-phenyl isocyanate reaction.

with Arrhenius Law (eq. (2)) and Eyring Law (eq. (3)). Arrhenius plot and Eyring plot of urethane reaction for 1,2-butanediol are shown in Figure 4. Arrhenius plot and Eyring plot of urethane reaction for 1,4-butanediol are shown in Figure 5.

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (2)$$

$$\ln \frac{k}{T} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \frac{R}{Nh} \quad (3)$$

where R is the universal gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), N is the Avogadro's constant ($N = 6.02 \times 10^{23}$), h is the Planck's constant ($h = 6.62 \times 10^{-34} \text{ J} \cdot \text{s}$).

From Figures 4 and 5, activation energy (E_a), activation enthalpy (ΔH), and activation entropy (ΔS) can be calculated out as Table II, which are very useful to understand the reaction mechanism.

It can be found from the data in Table II that the values of E_a , ΔH , and ΔS for k_{con} in 1,4-butanediol are very different from those for k_{fast} in 1,2-butanediol, but very similar to those for k_{slow} in 1,2-butanediol. That is, when $\text{Zr}(\text{acac})_4$ is used as catalyst, the primary hydroxyl group in 1,2-butanediol and 1,4-butanediol shows different reaction rate. It has been testified that weak association between hydroxyl groups in butanediols was different, which was supposed before by Raspoet²² and Draye.^{23,24} Although it has been reported that steric effect and hydrogen bond in 1,2-butanediol affect the urethane reaction kinetics,^{25–27} more detailed research should be done to testify.

Table II. E_a , ΔH , and ΔS of 1,4-Butanediol with Phenyl Isocyanate

	E_a (kJ · mol ⁻¹)	ΔH (kJ · mol ⁻¹)	ΔS (J · mol ⁻¹ · K ⁻¹)
1,2-butanediol (k_{fast})	82.7	80.3	34.6
1,2-butanediol (k_{slow})	96.0	93.6	61.5
1,4-butanediol (k_{con})	96.5	94.0	65.3

CONCLUSION

Using $\text{Zr}(\text{acac})_4$ as catalyst, *in situ* FT-IR is used to monitor the urethane reaction of 1,2-butanediol with phenyl isocyanate. 1,4-Butanediol is used for comparison. Catalytic properties of $\text{Zr}(\text{acac})_4$ are described and reaction rates are calculated out. It is shown that $\text{Zr}(\text{acac})_4$ is a very effective catalyst for the urethane reaction. Primary hydroxyl group in 1,2-butanediol (k_{fast}) and 1,4-butanediol (k_{con}) shows different reaction rate, but secondary hydroxyl group in 1,2-butanediol (k_{slow}) reacts as fast as primary hydroxyl group in 1,4-butanediol (k_{con}).

Furthermore, Activation energy, activation enthalpy, and activation entropy are calculated out. The values of E_a , ΔH , and ΔS for k_{con} in 1,4-butanediol are very different from those for k_{fast} in 1,2-butanediol, but very similar to those for k_{slow} in 1,2-butanediol. It probably derives from the influence of steric effects and hydrogen bond, but more detailed research should be done to testify.

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