Catalytic Kinetics and Mechanism Transformation of $Fe(acac)_3$ on the Urethane Reaction of 1,2-Propanediol with Phenyl Isocyanate

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ABSTRACT: The urethane reaction of 1,2-propanediol with phenyl isocyanate was investigated with ferric acetylacetonate ($Fe(acac)_3$) as a catalyst. In situ Fourier transform infrared spectroscopy was used to monitor the reaction, and catalytic kinetics of $Fe(acac)_3$ was studied. The reaction rates of both hydroxyl groups were described with a second-order equation, from which the influence of the $Fe(acac)_3$ concentration and reaction temperature was discussed. It was very surprising that the relationship between $1/C$ and t became constant when reaction temperature increased, which indicated that there was no reactive distinction between the two hydroxyl groups. Although the phenomenon differed with the variation of temperature, it was unaffected by the $Fe(acac)_3$ concentration. It was attributed to the transformation of the reaction mechanism with the increase in temperature. Furthermore, activation energy (E_a), enthalpy (ΔH^*), and entropy (ΔS^*) for the catalyzed reaction were determined from Arrhenius and Eyring equations, which testified to the transformation of the reaction mechanism. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 623–628, 2013

INTRODUCTION

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties. PUs can be tailored to meet various demands of modern technologies, such as coatings, adhesives, fibers, foams, and thermoplastic elastomers [1,2]. In addition to their application, the reaction kinetics of hydroxyl compounds with isocyanates has been widely investigated [3,4]. Many factors affect the reaction, such as reactant [5–8], catalyst [9–13], and solvent [14,15].

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Concerning the needs of safety and health [16], an important development of the catalyst is the replacement of organotin compounds to environmentally friendly metal-β-diketones (M(acac)$_n$) [17–22]. For example, Ligabue et al. [17,18] described catalytic properties of Fe(acac)$_3$ and Cu(acac)$_2$ for the monourethane and diurethane reactions of hexamethylene diisocyanate with several monobasic alcohols. They found that different alcohols had different reaction mechanisms and underwent different transition states. Furthermore, Lima et al. [21] compared the catalytic property of metal-β-diketones complexes (Fe, Cu, Sn, and Cr) and the commercial catalyst dibutyltin dilaurate in the polyurethane synthesis. They found that when reacting with isophorone diisocyanate dibutyltin dilaurate was more effective for the urethane reaction with polyethers, and metal-β-diketones complexes were more effective for the urethane reaction with polyesters.

As far as the reaction kinetics is concerned, the structure of diisocyanates is often considered as the main factor that influences the urethane reaction. Król and Wojturska [23] reported the kinetics of a model reaction of 2,4- and 2,6-tolylene diisocyanate with 1-butanol, which was had in the reaction medium of liquid aliphatic hydrocarbons. Rate constants and activation energy were determined and presented, which were very useful in discussing the reaction mechanism. However, much less attention is paid to the reactivity of different hydroxyl groups in asymmetric diols. Therefore, reaction kinetics and thermochemical features could be investigated only with the help of computer simulation [24]. In this work, phenyl isocyanate is used as the model compound to react with 1,2-propanediol with Fe(acac)$_3$ as a catalyst. In situ Fourier transform infrared spectroscopy (FT-IR) is used to monitor the reaction to work out the rate constant, activation energy, enthalpy, and entropy, on the basis of which the catalytic properties of Fe(acac)$_3$ are investigated.

EXPERIMENTAL

Materials and Instruments

Phenyl isocyanate was purchased from Sigma-Aldrich (St. Louis, MO); 1,2-propanediol and Fe(acac)$_3$ were purchased from the Sinopharm Chemical Reagent Co. (Shanghai, China); all of these were used without further purification. Butyl acetate was also purchased from the Sinopharm Chemical Reagent Co. and was purified with distillation and stored over molecular sieves (5 Å).

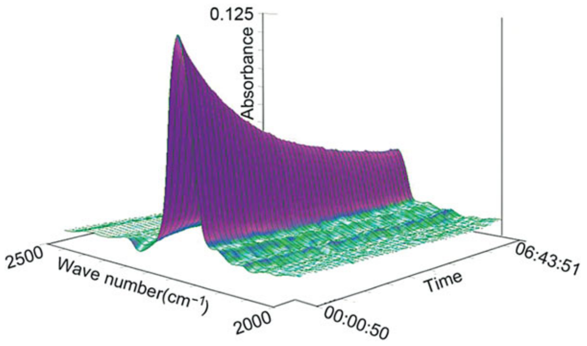


Figure 1 3D FT-IR spectra for the reaction of 1,2-propanediol with phenyl isocyanate ($T = 10°\mathrm{C}$, [Fe(acac)$_3$] $= 10^{-3}$ mol·L^{-1}) (color reproduction on wileyonlinelibrary.com).

The in situ FT-IR spectrometer React IR IC10, manufactured by Mettler Toledo (Columbia, MD), was used for all kinetic studies.

Kinetic Studies of the Urethane Reaction

Clean and dry air was flowed through the instrument continuously until the absorbance of all impurities became constant. The background spectra were recorded to eliminate interference by air. After that, 1,2-propanediol (1.38 mmol, 0.105 g), butyl acetate (53.0 mmol, 7.00 mL), and different amounts of Fe(acac)$_3$ were poured into the flask. The probe of the 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, the stoichiometric amount of phenyl isocyanate (2.76 mmol, 0.329 g) (–NCO/–OH = 1) was added and the reaction began. Data were collected every half minute until the reaction was terminated at certain extent of conversion. The resolution was 8 cm^{-1}, and the scan region was 4000–650 cm^{-1}.

RESULTS AND DISCUSSION

Spectral analysis is an important tool for discussing reaction kinetics and dynamics [25,26]. The isocyanate peak at the region of 2270 cm^{-1} was most useful and reliable to monitor the reaction progress [27]. A waterfall plot of the in situ FT-IR spectra is depicted in Fig. 1, which clearly shows the changes in isocyanate absorbance versus reaction time ($T = 10°\mathrm{C}$, [Fe(acac)$_3$] $= 10^{-3}$ mol·L^{-1}).

It is well known that Beer's law (Eq. (1)) can be used only for low-concentration solutions. As far as high-concentration solutions are concerned, it is

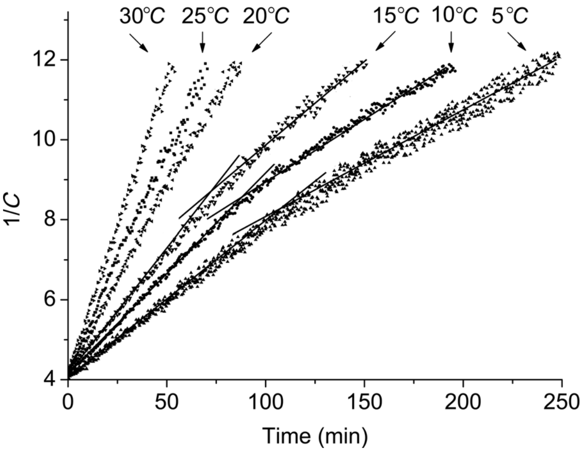


Figure 2 Relationship between $1/C$ and t for the reaction of 1,2-propanediol with phenyl isocyanate ($[\mathrm{Fe(acac)_3}] = 10^{-3}$ mol·L^{-1}).

necessary to examine the relationship between –NCO absorbance (A) and concentration (C). In our previous paper [28], it was reported that Beer's law holds true when the –NCO concentration is lower than 0.4 mol/L. Because of the linear relationship between A and C, the value of k_0 is conveniently obtained from the initial absorbance (A_0) and concentration (C_0):

$$A = k_0 \cdot C \tag{1}$$

where $k_0 = A/C = A_0/C_0 = 0.495\ \mathrm{L \cdot mol^{-1}}$:

$$1/C = 1/C_0 + kt \tag{2}$$

To work out kinetic constants, it is assumed that there is no side reaction. When the stoichiometric ratio is used, the total isocyanate concentration can be given by the general second-order expression [8] as a relationship of time dependence (Eq. (2)). The relationship between absorbance (A) and reaction time (t) can be acquired from in situ FT-IR, and the relationship between absorbance (A) and the concentration (C) can be acquired from Beer's law, from which the $1/C$ versus t curve is plotted.

Influence of Temperature

The relationship between $1/C$ and t at different temperatures is shown in Fig. 2. Detailed data are summarized in Table I. The concentration of $\mathrm{Fe(acac)_3}$ was set as 10^{-3} mol·L^{-1} to acquire the appropriate reaction rate.

There were two different hydroxyl groups in 1,2-propanediol, a primary hydroxyl and a secondary hydroxyl. Therefore, it could be concluded that the reaction should be divided into two stages and the $1/C$ versus t curve would behave as two consecutive straight lines with different slopes. The assumption was testified when reaction temperature was lower than 15°C (Fig. 2). At 5, 10, and 15°C, the reaction rate of the primary hydroxyl (k_{prim}) and the secondary hydroxyl (k_{sec}) was different and increased with rising temperature. The value of $k_{\mathrm{prim}}/k_{\mathrm{sec}}$, namely the selectivity of different hydroxyl groups in 1,2-propanediol, nearly remained constant.

However, after the reaction temperature reached 20°C or higher, the second-order rate plots became quite constant and no significant deviation was found. That is, the reaction rate of the primary hydroxyl and secondary hydroxyl became equal. It was quite surprising that reaction temperature greatly affected the urethane kinetics as well as the reaction mechanism. Either the deceleration of the reaction rate of the primary hydroxyl or the acceleration of the reaction rate of the secondary hydroxyl might have led to that result, and this will be discussed later on the basis of thermodynamic parameters.

Influence of Catalyst Concentration

To check the surprising phenomenon caused by temperature and to get rid of the influence of the catalyst

Table I Rate Constants for the Reaction of 1,2-Propanediol with Phenyl Isocyanate at Different Temperatures ($[\mathrm{Fe(acac)_3}] = 10^{-3}$ mol·L^{-1})

T (°C)	k_{prim} (L·mol^{-1}·min^{-1})	Linear Correlation Coefficient (R)	k_{sec} (L·mol^{-1}·min^{-1})	Linear Correlation Coefficient (R)	$k_{\mathrm{prim}}/k_{\mathrm{sec}}$
5	1.49×10^{-2}	0.996	9.11×10^{-3}	0.951	1.64
10	2.59×10^{-2}	0.999	1.59×10^{-2}	0.964	1.63
15	4.28×10^{-2}	0.998	2.85×10^{-2}	0.952	1.50
20	5.60×10^{-2}	0.997	5.60×10^{-2}	0.997	1.00
25	9.66×10^{-2}	0.997	9.66×10^{-2}	0.997	1.00
30	1.61×10^{-1}	0.998	1.61×10^{-2}	0.998	1.00

Table II Rate Constants (k_{prim} and k_{sec}) for the 1,2-Propanediol–Phenyl Isocyanate Reaction of Different Fe(acac)$_3$ Concentrations

Concentration (mol·L^{-1})	k_{prim} (L·mol^{-1}·min^{-1})			k_{sec} (L·mol^{-1}·min^{-1})			$k_{\mathrm{prim}}/k_{\mathrm{sec}}$		
	10°C	15°C	20°C	10°C	15°C	20°C	10°C	15°C	20°C
2×10^{-3}	4.40×10^{-2}	6.39×10^{-2}	8.91×10^{-2}	3.04×10^{-2}	4.14×10^{-2}	8.91×10^{-2}	1.45	1.54	1.00
4×10^{-3}	4.85×10^{-2}	7.87×10^{-2}	1.24×10^{-1}	3.33×10^{-2}	5.30×10^{-2}	1.24×10^{-1}	1.46	1.49	1.00
6×10^{-3}	5.89×10^{-2}	9.50×10^{-2}	1.45×10^{-1}	3.65×10^{-2}	6.24×10^{-2}	1.45×10^{-1}	1.61	1.52	1.00
8×10^{-3}	7.52×10^{-2}	1.25×10^{-1}	1.58×10^{-1}	4.63×10^{-2}	7.97×10^{-2}	1.58×10^{-1}	1.63	1.57	1.00
10×10^{-3}	8.42×10^{-2}	1.39×10^{-1}	1.71×10^{-1}	5.45×10^{-2}	9.01×10^{-2}	1.71×10^{-1}	1.55	1.53	1.00

concentration, the concentration of Fe(acac)$_3$ was varied from 2×10^{-3} to 10×10^{-3} mol·L^{-1} and each series was run at different temperatures (10, 15, and 20°C). Detailed results are presented in Table II.

As shown in Table II, the reaction rates of primary and secondary hydroxyls were enhanced with the increase in the Fe(acac)$_3$ concentration. Similarly, there were two different reaction rates at 10 and 15°C but only one reaction rate at 20°C. The value of $k_{\mathrm{prim}}/k_{\mathrm{sec}}$ also changed very little with the variation of the concentration at 10 and 15°C. Hence, it could be concluded that, when reacting with phenyl isocyanate, the selectivity of the urethane reaction in 1,2-propanediol was independent of the Fe(acac)$_3$ concentration but strongly dependent on reaction temperature.

Thermodynamic Parameters

Thermodynamic studies were based on the rate constant (Table I). Activation energy (E_a), enthalpy (ΔH^*), and entropy (ΔS^*) were determined using Arrhenius (Eq. (3)) and Eyring (Eq. (4)) laws:

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{3}$$

$$\ln \frac{k}{T} = \ln \frac{R}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \tag{4}$$

where k is the reaction rate constant, T is the reaction temperature, A is the preexponential factor, R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), N is the Avogadro's constant (6.02×10^{23}), and h is the Planck's constant (6.62×10^{-34} J·s). The plots are shown in Fig. 3, and detailed results are presented in Table III.

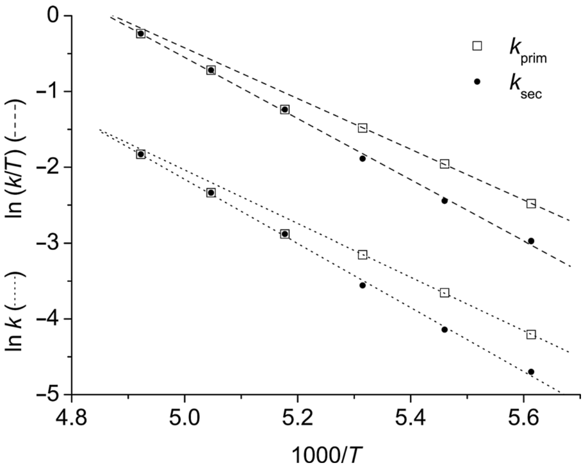
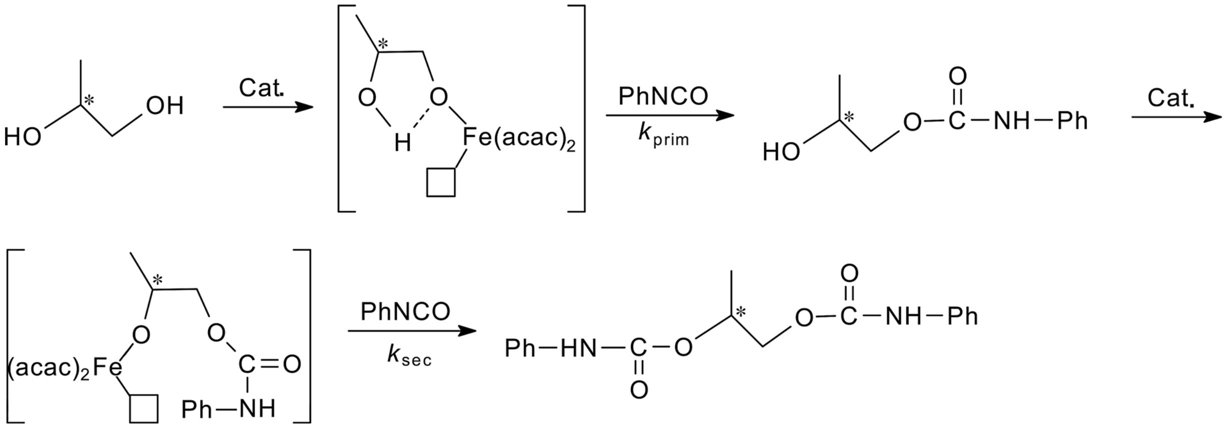


Figure 3 Arrhenius and Eyring plots for the reaction of 1,2-propanediol with phenyl isocyanate ([Fe(acac)$_3$] = 10^{-3} mol·L^{-1}).

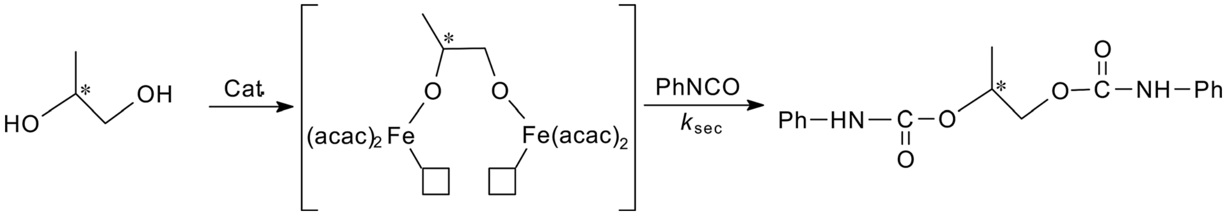
For the secondary hydroxyl group (k_{sec}), activation energy or activation enthalpy was invariant (35.1 and 33.6 kJ·mol^{-1}) and did not change with the increase in temperature, which was similar to other normal reactions. However, as for the primary hydroxyl group (k_{prim}), activation energy or activation enthalpy was quite lower at low temperature ($T \leq 15$°C; 29.4 and 27.8 kJ·mol^{-1}) and then became a little higher at high temperature ($T \geq 20$°C; 35.1 and 33.6 kJ·mol^{-1}). It could be concluded that when temperature increased

Table III Thermodynamic Parameters for Different Hydroxyl Groups in 1,2-Propanediol

Run	E_a (kJ·mol^{-1})	A (L·mol^{-1}·min^{-1})	ΔH^* (kJ·mol^{-1})	ΔS^* (J·mol^{-1}·K^{-1})
k_{prim}	29.4	6.07×10^{6}	27.8	–61.9
k_{sec}	35.1	1.73×10^{8}	33.6	–34.3



Scheme 1 Two-stage reaction route at low temperature.



Scheme 2 One-stage reaction route at high temperature.

the reaction rate of the primary hydroxyl group slowed, yet the reaction rate of the secondary hydroxyl group remained invariable. Furthermore, the large negative values of the activation entropy indicated an associative mechanism in the transition states, which was reviewed by Jayakumar et al. [29].

Discussion of Reaction Mechanism

It had been reported that 1,2-propanediol could form a five-centered transition state by its intramolecular hydrogen bond [17,18], which greatly affected the mechanism of the urethane reaction. When Fe(acac)$_3$ was used as a catalyst, the hydroxyl group in 1,2-propanediol interacted with the acetylacetonate ligand through the hydrogen bond and then eliminated an acetylacetone molecule [30]. As a result, a chemical bond formed between the oxygen atom in 1,2-propanediol and the iron atom that possessed a vacant site (□). That transition state is shown in Schemes 1 and 2 along with the proposed reaction mechanism.

At low temperature, a two-stage reaction mechanism was assumed as shown Scheme 1. The Fe(III)–primary OH complex was generated when Fe(acac)$_3$ was added to the reaction system and then the complex reacted with phenyl isocyanate. The interaction was not strong enough to overcome the activation energy barrier of the intramolecular hydrogen bond. After that, the secondary hydroxyl formed the Fe(III)–secondary OH complex and reacted with another phenyl isocyanate. At high temperature, a one-stage reaction mechanism was assumed as shown in Scheme 2. The intramolecular hydrogen bond of 1,2-propanediol became so weak that Fe(acac)$_3$ could coordinate with two hydroxyls simultaneously, followed by the urethane reaction with phenyl isocyanate. However, the above explanations for the reaction mechanism were two ideal situations. As far as the actual urethane reaction was concerned, both of the mechanisms may have played a part. The transformation from Scheme 1 to Scheme 2 happened when reaction temperature was increased from 5 to 30°C.

The above-mentioned mechanism could be proved by the variation of the reaction rate. There were two rate constants when the temperature was low, which were called as k_{prim} and k_{sec}. They were, respectively, assigned to the urethane reaction of Fe(III)—the primary OH complex with the intramolecular hydrogen bond and Fe(III)—the secondary OH complex without the intramolecular hydrogen bond. When reaction temperature increased, both hydroxyls in 1,2-propanediol coordinated with Fe(acac)$_3$ and there was no intramolecular hydrogen bond. It led to only one reaction rate constant, equal to k_{sec}.

Another proof was the activation entropy. According to transition state theory [31], the activation entropy was popularly regarded as the degree of disorder in the system. Breaking of the ring structure may have led to the increase in the activation entropy. When temperature was low ($\leq$15°C), the five-membered ring of transition state in 1,2-propanediol was not opened. That is, the reaction system was relatively ordered, which led to a relatively lower activation entropy (–61.9 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$). On the contrary, activation entropy would have increased (–34.3 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) and the reaction system would have become out of order if the intramolecular hydrogen bond in 1,2-propanediol was broken. The break of the intramolecular bond may be derived from the increase in reaction temperature ($\geq$20°C) or the coordination of secondary hydroxyl ($\leq$15°C). In fact, we are planning to further characterize the Fe(III)–OH complex, but it is very difficult because of its high activity.

SUMMARY

The urethane reaction kinetics of 1,2-propanediol with phenyl isocyanate was studied using in situ FT-IR spectroscopy with $Fe(acac)_3$ as the catalyst. The urethane formation was well described by the second kinetic model, which considered not only the reactivity of primary and secondary hydroxyls (k_{prim}, k_{sec}) but also the selectivity of those hydroxyls ($k_{\mathrm{prim}}/k_{\mathrm{sec}}$) in 1,2-propanediol. It was demonstrated that the reactivity of primary and secondary hydroxyl groups increased with the increase in temperature, and the selectivity was nearly unchanged at 5, 10, and 15°C. However, it was very surprising that the relationship between $1/C$ and t became constant at 20, 25, and 30°C, which indicated that there was no reactive distinction between the two hydroxyl groups. The phenomenon differed with the variation of reaction temperature but was unaffected by the $Fe(acac)_3$ concentration.

Thermodynamic parameters were determined using Arrhenius and Eyring equations. It was found that activation energy and enthalpy for the primary hydroxyl group was lower than that of the secondary hydroxyl group at low temperature ($\leq$15°C). However, the activation energy or activation enthalpy for primary and secondary hydroxyl groups became the same at high temperature ($\geq$20°C). Finally, transition state theory was used to propose an appropriate reaction mechanism, which was based on the data of the reaction rate and activation entropy.

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