Kinetics and Mechanisms of Catalyzed and Noncatalyzed Reactions of OH and NCO in Acrylic Polyol–1,6-Hexamethylene Diisocyanate (HDI) Polyurethanes. VI

Qiwen Han, Marek W. Urban

The University of Southern Mississippi, School of Polymers and High Performance Materials, Shelby F. Thames Polymer Research Center, Hattiesburg, Mississippi 39406

ABSTRACT: Fourier transform infrared spectroscopy was used to study the kinetics of noncatalyzed and catalyzed polyurethanes. These studies show that for noncatalyzed acrylic polyol–hexamethylene diisocyanate (HDI) trimer reactions, the reactions between OH and NCO of HDI exhibit second-order kinetics, with first-order kinetics with respect to NCO and OH. On the other hand, when dibutyltin dilaurate (DBTDL) is used as a catalyst in acrylic polyol–HDI trimer reactions, the reaction rate is first order with respect to NCO and 0.5 order in OH and DBTDL concentrations. A 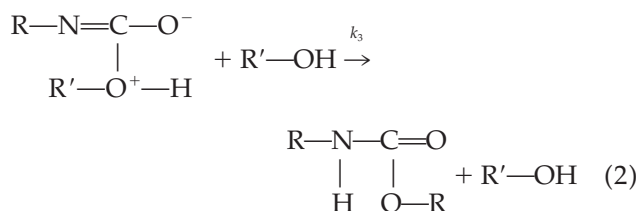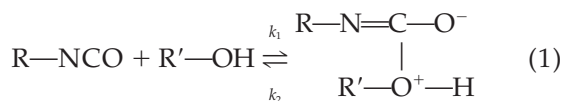mechanism for the catalyzed acrylic polyol–HDI trimer crosslinking reactions is proposed and it appears that an equilibrium involving associations between OH and DBTDL exists, resulting in the formation of an active anion, which interacts with NCO to generate polyurethanes. To further verify this mechanism, the influence of acidity on the reaction rate constant was investigated. When the acidity of the system is increased, retardation of urethane formation occurs. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2322–2329, 2002

Key words: polyurethanes; kinetics; catalysis; HDI; FTIR

INTRODUCTION

Although numerous studies have been conducted concerning reactions of isocyanates (NCO) and alcohols (OH), reaction mechanisms are still unclear,[1–9] which is primarily attributed to the complexity and sensitivity of these reactants to reaction conditions.

Baker and co-workers postulated the following steps for noncatalyzed NCO–OH reactions:[10–16]

$$
\text{R—NCO} + \text{R'—OH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{matrix} \text{R—N}{=}\text{C—O}^- \\ | \\ \text{R'—O}^+\text{—H} \end{matrix} \quad (1)
$$

$$
\begin{matrix} \text{R—N}{=}\text{C—O}^- \\ | \\ \text{R'—O}^+\text{—H} \end{matrix} + \text{R'—OH} \overset{k_3}{\rightarrow}
$$

$$
\begin{matrix} \text{R—N—C}{=}\text{O} \\ |\quad\ | \\ \text{H}\ \ \text{O—R} \end{matrix} + \text{R'—OH} \quad (2)
$$

Based on this mechanism, the reaction rate expression is follows:

$$
-\frac{d[\text{NCO}]}{dt} = k_1[\text{NCO}][\text{OH}]\frac{k_3[\text{OH}]}{k_2 + k_3[\text{OH}]} \quad (3)
$$

According to this equation, if [OH] is so small that k_2 is substantially greater than k_3 [OH], the reaction will follow third-order kinetics (first order with respect to NCO and second order with respect to OH). This situation is most likely to occur at the later stages of reaction process when alcohol concentration levels are low. On the other hand, if [OH] is large enough so that k_2 is substantially smaller than k_3 [OH], which implies the early stages of reactions, the reaction will follow second-order kinetics (first order with respect to NCO and OH).

Catalysis utilizing organotin compounds for polyurethane/polyurea formation reactions has been of interest, and various intermediates were proposed in an attempt to elucidate the reaction mechanisms.[17,18] For example, existence of tin–alcohol complexes[19–22] as well as complexation of tin compounds with isocyanates[22,23] were detected. Thus, it was proposed[24–28] that ternary complexes involving tin compounds were formed. Other mechanisms were also proposed that involved rapid equilibrium formation of a complex between a tin compound and an alcohol[29] or isocyanate,[30] followed by a slow bimolecular reaction of the complex with other reactant.

Based on the literature data, it is quite apparent that reaction kinetics leading to polyurethane formation depends not only on reactivity and conditions of the

TABLE I
Condition Levels and Reaction Rates for NCO and OH Groups
in Acrylic Polyol/HDI Trimer System[a]

Series	$[NCO]_0$ (mol L^{-1} · E2)	$[OH]_0$ (mol L^{-1} · E2)	Reaction rate (mol L^{-1} min^{-1} · E-5)	Log R
1	5.00	5.00	1.683	−4.77
2	2.00	5.00	0.688	−5.16
3	2.00	2.00	0.280	−5.55
n		0.97		
h		1.03		
k		6.67×10^{-3} L mol^{-1} min^{-1}		

[a] Solvent: XY/BA, 1 : 1, w/w, 30°C.

primary reactants, but also on catalysts, which may vary in structure and reactivity. Furthermore, the majority of previous studies utilized simple model molecules, which often do not completely represent actual crosslinking reactions, although there were attempts to investigate kinetics/mechanisms for practical polyurethane systems.[31,32] In this study we focus on acrylic polyol–hexamethylene diisocyanate (HDI) trimer reactions containing dibutyltin dilaurate (DBTDL) as a catalyst, as well as the differences, if any, between noncatalyzed and catalyzed reaction kinetics and mechanisms.

EXPERIMENTAL

Starting materials and reactions

Acrylic polyol [50%; Desmophen A-450A; in 1:1 (w/w) xylene (XY)/butyl acetate (BA) solvent; **1**] and 1,6-hexamethylene diisocyanate (HDI) trimer (Desmodur N3300; **2**) were provided by Bayer Corporation. Dibytyltin dilaurate (DBTDL; 98%; **3**), anhydrous xylene (purity, 99+%; **4**) and anhydrous butyl acetate (purity, 99+%; **5**) were purchased from Aldrich Chemical Company, Inc.

In an effort to determine the order of reactions and the reaction rate constant, isocyanate (NCO) concentration changes were monitored during polyurethane formation. Based on the experimental design, **1**, **2**, and/or **3** were diluted with 1:1 (w/w) **4/5** solvent and mixed in a series of concentrations and ratios. Reactants were placed in a 0.011-cm thick KRS-5 infrared (IR) transmission cell. NCO concentration changes were determined by measurement of the intensities of the NCO stretching band (2273 cm^{-1}) intensity, and actual concentrations were calculated based on the Beers–Lambert Law.

Spectroscopic analysis

Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna-IR® 850 spectrometer. The spectrometer was continuously purged with dry air supplied from a Balston Type 75-60 air purification system. In a typical experiment, FT-IR spectra were collected at a 4 cm^{-1} resolution using 200 co-added scans that were collected and compared with a background of 200 co-added scans of the transmission cell filled with 1:1 (w/w) **4/5** solvent. NCO concentrations were determined by constructing a calibration curve based on the measurement of a series of standard NCO solutions, which allowed correlation of the band intensity at 2273 cm^{-1} to the NCO concentration.

RESULTS AND DISCUSSION

The first step in the kinetic studies of acrylic polyol–HDI trimer reactions is to determine the order of reactions. Generally, the kinetic equation of this system can be expressed as follows:

$$R = -d[NCO]/dt = k[NCO]^n[OH]^h \qquad (4)$$

where R is the reaction rate, t is reaction time, k is the rate constant, and n and h are orders of NCO and OH, respectively. By measuring the initial reaction rate R_0, we have

$$R_0 = k[NCO]_0^n[OH]_0^h \qquad (5)$$

and

$$\log R_0 = \log k + n \log[NCO]_0 + h \log[OH]_0 \qquad (6)$$

where the subscript 0 denotes $t = 0$.

Three series of reaction conditions with respect to the reagent concentration are summarized in Table I. According to eq. 6, the following relations hold:

$$\log R_{01} = \log k + n \log[NCO]_{01} + h \log[OH]_{01} \qquad (7)$$

$$\log R_{02} = \log k + n \log[NCO]_{02} + h \log[OH]_{02} \qquad (8)$$

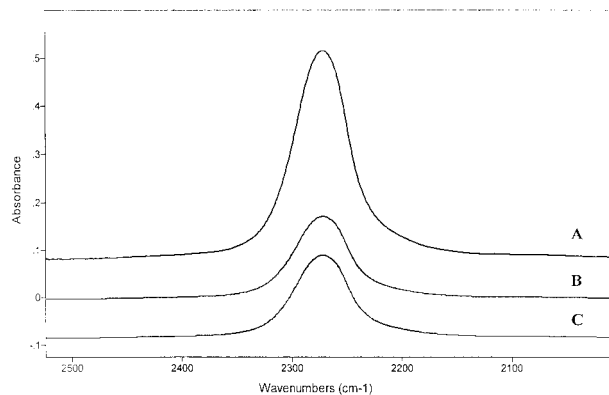$$\log R_{03} = \log k + n \log[NCO]_{03} + h \log[OH]_{03} \qquad (9)$$

Because

Figure 1 FT-IR transmission spectra of acrylic polyol–HDI trimer reaction systems in the NCO stretching region (2273 cm^{-1}). Reaction conditions were CY/BA (1:1 w/s) solvent; 30 °C; and (A) [NCO] = 0.0500 mol L^{-1} and [OH] = 0.0500 mol L^{-1}, (B) [NCO] = 0.0200 mol L^{-1} and [OH] = 0.0500 mol L^{-1}, and (C) [NCO] = 0.0200 mol L^{-1} and [OH] = 0.0200 mol L^{-1}.

$$[OH]_{01} = [OH]_{02} \qquad (10)$$

$$[NCO]_{02} = [NCO]_{03} \qquad (11)$$

eqs. 7, 8, and 9 can be simplified and the following expressions hold:

$$n = [\log(R_{02}/R_{01})]/[\log([NCO]_{02}/[NCO]_{01})] \quad (12)$$

$$h = [\log(R_{03}/R_{02})]/[\log([OH]_{03}/[OH]_{02})] \quad (13)$$

Because [NCO]$_{01}$, [NCO]$_{02}$, [OH]$_{02}$, and [OH]$_{03}$ are known, determining the initial reaction rates R_{01}, R_{02}, and R_{03} allows us to solve for reaction orders n and h.
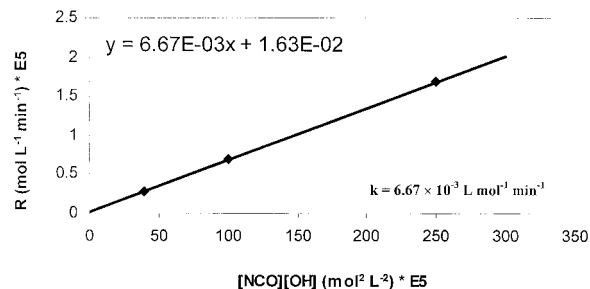

Figure 3 [NCO][OH] plotted as a function of R for the NCO + OH system [solvent: XY/BA (1:1 w/w); temperature: 30 °C].

As shown in Figure 1, measuring the 2273 cm^{-1} band intensity allows us to calculate the NCO concentration as a function of time, which is given in Figure 2, and the slope represents $-R = d[NCO]/dt$. Using eqs. 12 and 13 and measuring the initial reaction rates under the conditions listed in Table I, the orders of reactions for NCO and OH were determined. The results listed in Table I indicate that the reaction is first order with respect to NCO and OH. Therefore, the reaction rate equation is

$$R = k[NCO][OH] \qquad (15)$$

The reaction rate constant was determined by measuring the slope of the R versus [NCO][OH] curve. As shown in Figure 3, $k = 6.67 \times 10^{-3}$ L mol^{-1} min^{-1} at 30 °C. Experimental results indicates that, at least at the early stages of reaction, k_3[OH] is much greater than k_2, if eq. 3 holds.

It is often assumed that there are no differences in the reaction order for reactions with and without cat-
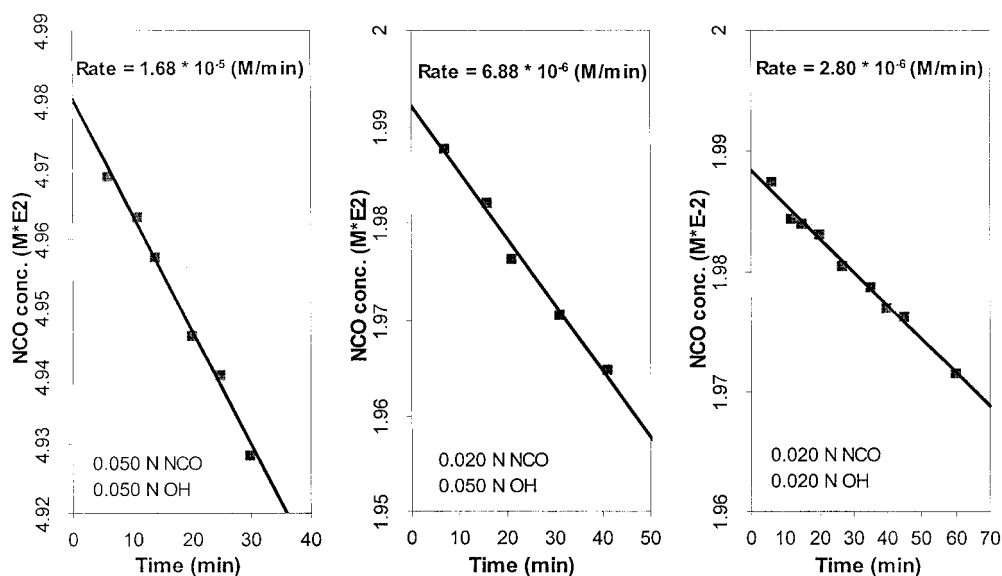

Figure 2 NCO concentration plotted as a function of time for various initial OH concentrations at the early stages of reaction for NCO + OH system [solvent: XY/BA (1:1 w/w); temperature: 30 °C].

TABLE II
Condition Levels and Reaction Rates for NCO and OH Groups in Acrylic Polyol/HDI Trimer/DBTDL System[a]

Series	$[NCO]_0$ (mol L^{-1} · E2)	$[OH]_0$ (mol L^{-1} · E2)	$[DBTDL]_0$ (mol L^{-1} · E42)	Reaction rate (mol L^{-1} min^{-1} · E-5)	Log R
4	2.50	2.50	1.88	3.14	−4.50
5	2.50	2.50	3.75	4.44	−4.35
6	5.00	2.50	3.75	8.85	−4.05
7	2.50	5.00	3.75	6.20	−4.21
n'			0.98		
h'			0.48		
d			0.48		
k			5.76×10^{-1} L mol^{-1} min^{-1}		

[a] Solvent: XY/BA, 1 : 1, w/w, 30°C.

alysts, as long as other conditions, such as reagents and solvent, are the same. However, because reaction mechanisms may be altered when catalysts are present, the reaction order may also change. In view of these aforementioned considerations, let us examine how reaction rates are affected by the presence of DBTDL catalyst. The reaction rate for the catalyzed system can be expressed as follows:

$$R = -d[NCO]/dt = k[NCO]^{n'}[OH]^{h'}[DBTDL]^{d} \quad (16)$$

where R is the reaction rate, t is reaction time, k is the rate constant, and n', h', and d are orders in NCO, OH, and DBTDL, respectively. By measuring the initial reaction rate R_0, we have

$$R_0 = k[NCO]_0^{n'}[OH]_0^{h'}[DBTDL]_0^{d} \quad (17)$$

and

$$\log R_0 = \log k + n' \log[NCO]_0 + h' \log[OH]_0$$
$$+ d \log[DBTDL]_0 \quad (18)$$

where the subscript 0 represents $t = 0$.

For four series of reactions with different reagent concentrations, we have

$$\log R_{04} = \log k + n' \log[NCO]_{04} + h' \log[OH]_{04}$$
$$+ d \log[DBTDL]_{04} \quad (19)$$

$$\log R_{05} = \log k + n' \log[NCO]_{05} + h' \log[OH]_{05}$$
$$+ d \log[DBTDL]_{05} \quad (20)$$

$$\log R_{06} = \log k + n' \log[NCO]_{06} + h' \log[OH]_{06}$$
$$+ d \log[DBTDL]_{06} \quad (21)$$

$$\log R_{07} = \log k + n' \log[NCO]_{07} + h' \log[OH]_{07}$$
$$+ d \log[DBTDL]_{07} \quad (22)$$

In this experiment, four series of reaction conditions, as shown in Table II, were set so that the following conditions hold:

$$[OH]_{04} = [OH]_{05} = [OH]_{06} \quad (23)$$

$$[NCO]_{04} = [NCO]_{05} = [NCO]_{07} \quad (24)$$

$$[DBTDL]_{05} = [DBTDL]_{06} = [DBTDL]_{07} \quad (25)$$

Based on eqs. 19, 20, 21, and 22, we have

$$h' = (\log R_{04} - \log R_{02})/(\log[OH]_{04} - \log[OH]_{02}) \quad (26)$$

$$n' = (\log R_{03} - \log R_{02})/(\log[NCO]_{03} - \log[NCO]_{02}) \quad (27)$$

$$d = (\log R_{02} - \log R_{01})/(\log[DBTDL]_{02}$$
$$- \log[DBTDL]_{01}) \quad (28)$$

Because $[NCO]_{0i}$ ($i = 2, 3$), $[OH]_{0j}$ ($j = 2, 4$), and $[DBTDL]_{0k}$ ($k = 1, 2$) are known, after determining the initial reaction rates R_{01}, R_{02}, and R_{03}, and R_{04}, reaction orders h', n', and d can be computed. Following the same method as that developed for the study of a noncatalyzed system, the NCO concentration changes as a function of reaction time for each reaction system was measured, and [NCO] as a function of time (Figure 4) was determined. The negative slope at the initial stages corresponds to the reaction rate at the beginning of the reaction.

Measuring the initial reaction rates under the conditions shown in Table II and using eqs. 26, 27, and 28 the reaction orders in OH, NCO, and DBTDL, respectively, were determined. The experimental results, listed in Table II, indicate that the reaction is first order in NCO, but 0.5th in both OH and DBTDL. This relation is represented as

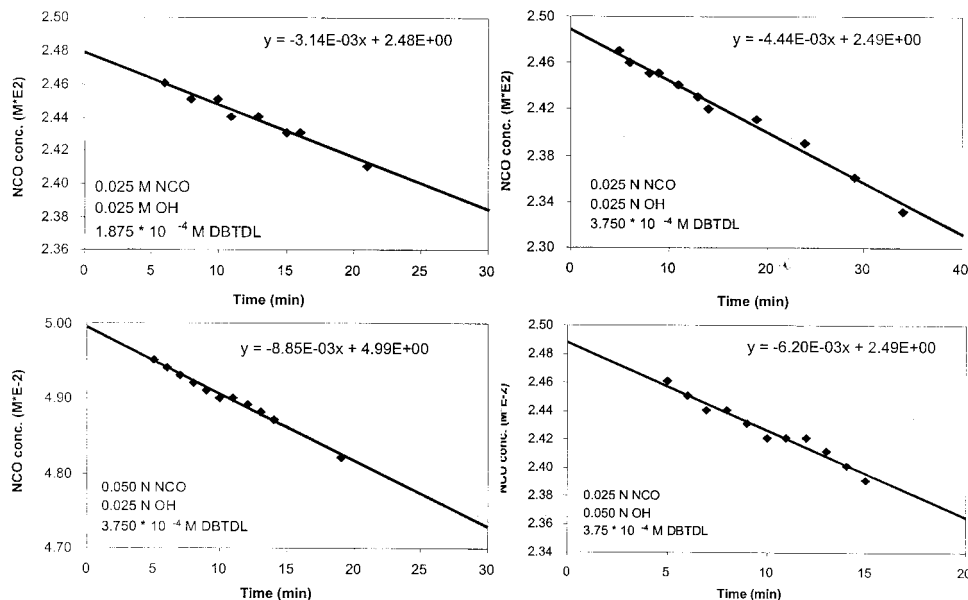$$R = k[NCO][OH]^{1/2}[DBTDL]^{1/2} \quad (29)$$

Figure 4 NCO concentration plotted as a function of time for different reactant/catalyst concentrations at the early stages of reaction for acrylic polyol/HDI trimer/DBTDL system [solvent: XY/BA (1:1 w/w); temperature: 30 °C].

The reaction rate constant for this system was determined by measuring the slope of the R versus $[NCO][OH]^{1/2}[DBTDL]^{1/2}$ curve. As shown in Figure 5, $k = 5.76 \times 10^{-1}$ L mol^{-1} min^{-1} at 30 °C.

Comparison of catalyzed and noncatalyzed polyurethane systems show that the reaction orders as well as the rate constants vary. Based on these experiments and the previous studies,[17–23] it is apearent that the reaction mechanisms are affected by the presence of DBTDL. Efforts have been made to explain the catalysis mechanism in various reaction systems. Bloodworth and co-workers[35] reported that mixtures of isocyanates and trialkyltin methoxide yield methyl trialkylstannyl carbamates, and these compounds are susceptible to protonic agents, yielding urethanes and regenerating trialkyltin methoxide. Based on these results, it was proposed that the reaction between isocyanate and alcohol, in the presence of a tin catalyst, proceeds through an intermediate formation of tin
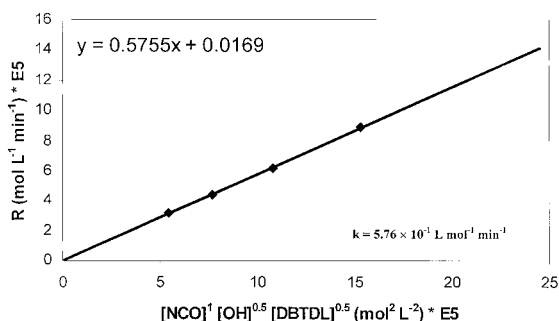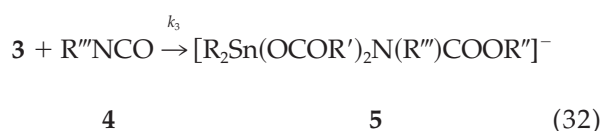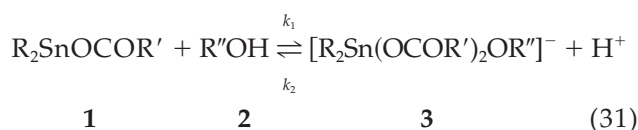
alkoxides from alcohol and the tin compound. It has also been reported[36] that in the 4, 4′-diphenylmethane diisocyanate (MDI)/methanol/DBTDL/dimethyl formamide (DMF) system, the reaction rate is proportional to the concentration of alcohol and to the square root of the concentration of the catalyst. Borkent explained this phenomenon by proposing the dissociation of the catalyst into ions:

$$R_2Sn(OCOR')_2 \rightleftharpoons [R_2SnOCOR']^+ + R'COO^- \quad (30)$$

The formation of urethane involves the action of the tin-containing cation.[36] A similar mechanism that deals with an equilibrium involving active ion intermediates was proposed by Richter and Macosko for the poly(ε-caprolactone)/MDI/DBTDL system.[37]

In view of the results for acrylic OH/NCO/DBTDL reaction system examined in this study, reaction rate is proportional to the NCO concentration and the square root of DBTDL concentration, which agrees with the literature data.[36] However, in contrast to the literature,[36] the reaction rate is not proportional to the OH concentration but to its square root. Thus, the following reaction steps are proposed:

$$R_2SnOCOR' + R''OH \overset{k_1}{\underset{k_2}{\rightleftharpoons}} [R_2Sn(OCOR')_2OR'']^- + H^+$$

$$\mathbf{1} \qquad \mathbf{2} \qquad \qquad \mathbf{3} \qquad (31)$$

$$\mathbf{3} + R'''NCO \overset{k_3}{\rightarrow} [R_2Sn(OCOR')_2N(R''')COOR'']^-$$

$$\mathbf{4} \qquad \qquad \mathbf{5} \qquad (32)$$

Figure 5 $[NCO][OH]^{0.5}[DBTDL]^{0.5}$ plotted as a function of R for the acrylic polyol/HDI trimer/DBTDL system [solvent: XY/BA (1:1 w/w); temperature: 30 °C].

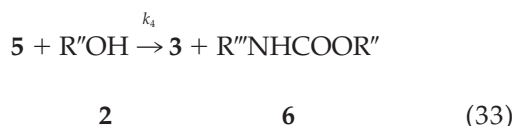$$5 + R''OH \xrightarrow{k_4} 3 + R'''NHCOOR''$$

$$\mathbf{2} \qquad\qquad \mathbf{6} \qquad\qquad (33)$$

where the first step of reactions is the interaction between the catalyst (**1**) and alcohol (**2**) to form a complex anion (**3**) and a proton. This complex anion interacts with NCO (**4**) to form another complex anion (**5**), which will rapidly react with another alcohol (**2**) to form urethane (**6**) and regenerate the catalyzing complex anion (**3**). The steps depicted in eqs. 32 and 33 will become a repeating cycle thereafter as long as NCO and OH groups are present. It should be noted that the proposed complexes between **1** and **2** are known and have been reported.[19–22] Because [**3**] = [H$^+$] under equilibrium conditions, the following equation holds:

$$[\mathbf{3}] = (k_1/k_2)^{1/2}[\mathbf{1}]^{1/2}[\mathbf{2}]^{1/2} \qquad (34)$$

When the reaction depicted in eq. 33 is fast, species **5** rapidly reaches a steady-state level, and the following equations holds:

$$d[\mathbf{5}]/dt = k_3[\mathbf{3}][\mathbf{4}] - k_4[\mathbf{5}][\mathbf{2}] = 0 \qquad (35)$$

and thus,

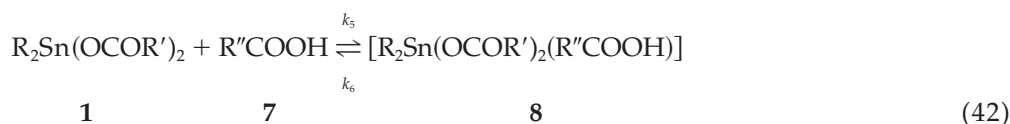$$[\mathbf{5}] = (k_3[\mathbf{3}][\mathbf{4}])/(k_4[\mathbf{2}]) \qquad (36)$$

If the production rate of urethane (**6**) is defined to be the reaction rate R_1, then we have

$$R_1 = d[\mathbf{6}]/dt = k_4[\mathbf{5}][\mathbf{2}] \qquad (37)$$

Incorporating eq. 36 into eq. 37, the following relation is obtained:

$$R_1 = k_3[\mathbf{3}][\mathbf{4}] \qquad (38)$$

On the other hand, if we define the depletion rate of NCO (**4**) to be the reaction rate R_2, then

$$R_2 = -d[\mathbf{4}]/dt = k_3[\mathbf{3}][\mathbf{4}] \qquad (39)$$

Comparing eqs. 38 and 39, it is evident that the two definitions of the reaction rate lead to the same values. The reaction rate R is then expressed as follows:

$$R = k_3[\mathbf{3}][\mathbf{4}] \qquad (40)$$

Incorporating eq. 34 into eq. 40 yields

$$R = \frac{k_1^{1/2}k_3}{k_2^{1/2}}[\mathbf{1}]^{1/2}[\mathbf{2}]^{1/2}[\mathbf{4}] = k[\mathbf{1}]^{1/2}[\mathbf{2}]^{1/2}[\mathbf{4}] \qquad (41)$$

Equation 41 agrees with the reaction rate expression (eq. 29) obtained from the experiment data, thus indicating the proposed reaction mechanism agrees with the kinetic studies.

Although the kinetic data agrees with the proposed mechanism, further experimental verification is required. If the equilibrium shown by eq. 31 is indeed the case and represents the fist step of the entire process, then by increasing the acidity, the equilibrium should shift towards the starting reagent side. This shift will result in the concentration decrease of the active anion (**3**), thus decreasing the reaction rate constant. To examine the NCO consumption rate as a function of acid concentration, isolated kinetic studies were conducted in which [OH]$_0$ was significantly higher than [NCO]$_0$, and therefore $k[OH]^{1/2}[DBTDL]^{1/2} = k'$ is constant. Determination of the pseudo-first-order reaction constant k' allows us to investigate the acid influence on the NCO consumption rate:

$$R_2Sn(OCOR')_2 + R''COOH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [R_2Sn(OCOR')_2(R''COOH)]$$

$$\mathbf{1} \qquad\qquad \mathbf{7} \qquad\qquad\qquad \mathbf{8} \qquad\qquad (42)$$

These experiments showed that the addition of strong acid, such as HCl, even at significantly smaller levels than DBTDL concentration, virtually stops the catalyzed reaction. This result is illustrated in Figure 6 (Curve F), which is a plot of the NCO concentration changes as a function of time. When acetic acid (HAc) was added, however, the inhibiting effect was less pronounced, although a reaction rate decreases with the increase of HAc concentration, as shown in Figure 6 (curves B–E), was observed. These data indicate that the presence of protons, rather than the undissociated acid, causes a retarding effect on the reaction kinetics between NCO and OH. As a matter of fact, the reaction rate k' is proportional to the reciprocal of the square root of [HAc]. As shown in Figure 7, the relationship k' versus $1/[HAc]^{1/2}$ remains linear until [HAc] reaches a significantly high value, 3.33×10^{-3} mol L^{-1} ($1/[HAc]^{1/2} = 1.73 \times 10^1$ L$^{1/2}$ mol$^{-1/2}$), after which the reaction rate constant is similar to that of a noncatalyzed reaction system (4.45×10^{-4} min^{-1}). This behavior is attributed to the fact that when acetic acid is added to the reaction system, there is another equilibrium involving the catalyst and acid, as shown by eq. 42, which competes with the equilibrium in eq. 31.
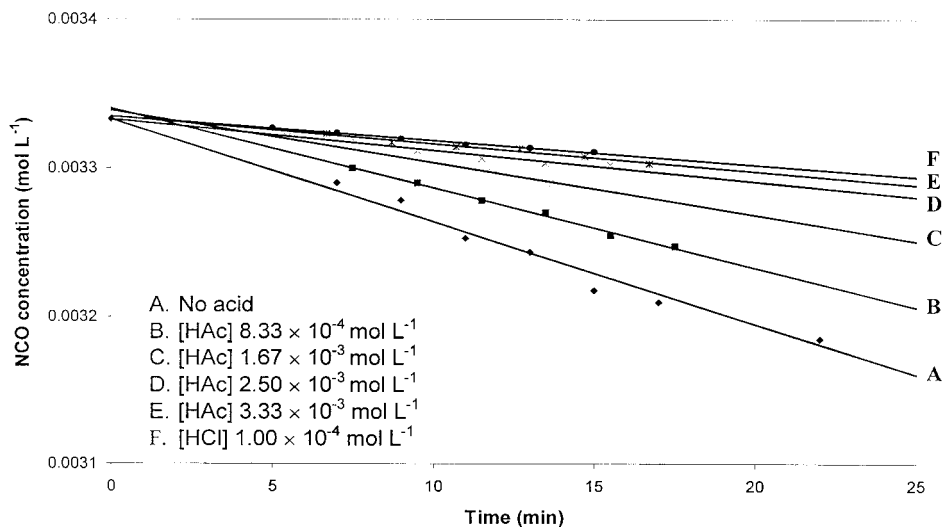
Figure 6 NCO concentration changes as a function of reaction time: the effect of acids. Reaction conditions were $[OH] = 6.67 \times 10^{-2}$ mol L^{-1}; $[DBTDL] = 2.00 \times 10^{-4}$ mol L^{-1}; solvent: XY/BA (1:1 w/w); temperature: 30 °C.

Partially because of the excess acid (**7**) over the catalyst (**1**), this equilibrium is shifted so far to the right that

$$[8] \cong [1]_0 \tag{43}$$

and then

$$[1] = (k_6/k_5)([8]/[7]) = (k_6/k_5)([1]_0/[7]) = k'/[7] \tag{44}$$

Comparing eqs. 41 and 44 results in eq. 45:

$$R = k[4][2]^{1/2}[7]^{-1/2} \tag{45}$$

where $k = (k_1^{1/2} k_3 k_6)/(k_2^{1/2} k_6)$.

Equation 45 shows that the reaction rate is inversely proportional to the square root of acetic acid concentration, which again agrees with experimental results. It is therefore indicated that when acetic acid is added to the reaction system, the moderate inhibition effect may not be caused by the dissociated protons, as in the case of strong acid, but most probably is caused by the complexation of the acid with DBTDL. On the other hand, the dissociation constant of the weak acetic acid is so small that the proton concentration resulting from its dissociation is negligible compared with that originated from the DBTDL–OH complexation.
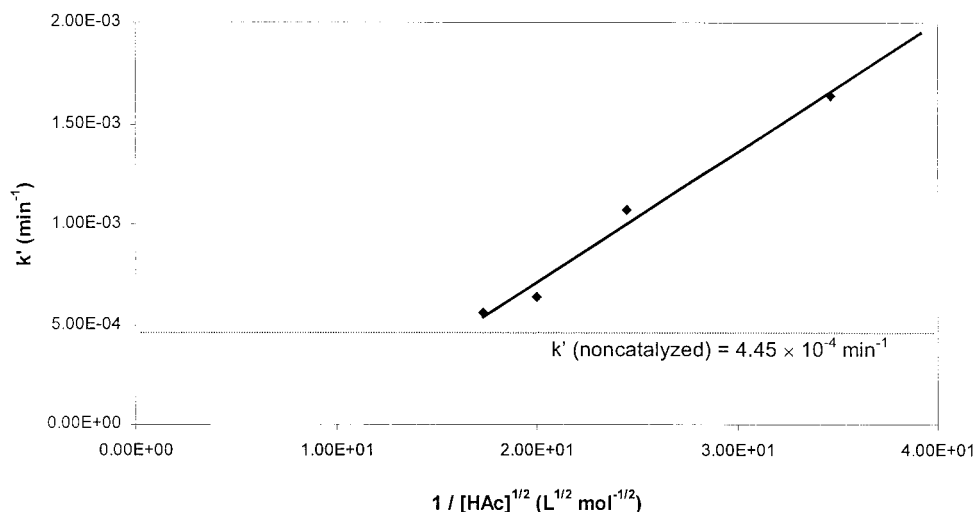

Figure 7 Reaction rate, k', plotted as a function of the inverse of the square root of acetic acid concentration. Reaction conditions were $[NCO] = 3.33 \times 10^{-4}$ mol L^{-1}; $[OH] = 6.67 \times 10^{-2}$ mol L^{-1}; $[DBTDL] = 2.00 \times 10^{-4}$ mol L^{-1}; solvent: XY/BA (1:1 w/w); temperature: 30 °C.
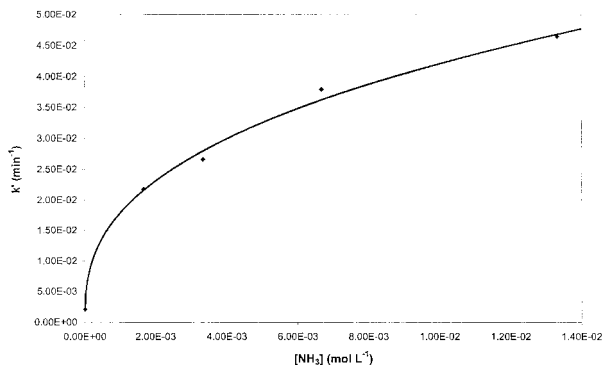
Figure 8 Reaction rate, k', plotted as a function of NH_3 concentration. Reaction conditions were $[OH] = 6.67 \times 10^{-2}$ mol L^{-1}; $[DBTDL] = 2.00 \times 10^{-4}$ mol L^{-1}; solvent: XY/BA (1:1 w/w); temperature: 30 °C.

The effect of basic environment on the reaction rate constant is another avenue for the validity of the proposed complexation process (eq. 31). When the basicity is increased, there should be an increase in the reaction rate constant because the equilibrium (eq. 31) will shift toward the right side. These results are shown in Figure 8. The addition of ammonia into the reaction system results in an increase of the rate constant. However, there is a nonlinear relationship between k' and $1/[NH_3]^{1/2}$, indicating that the function of NH_3 shifts the equilibrium (eq. 31) towards the intermediate side without being involved in interactions similar to those expressed by eq. 42.

CONCLUSIONS

For noncatalyzed acrylic polyol–HDI trimer reaction system, the reaction is second-order, first order in isocyanate and alcohol, and there is no deviation from the generally accepted kinetics derived from the Baker mechanism. However, for the catalyzed reaction system, reaction rate expressions measured experimentally do not agree with mechanism proposed for noncatalyzed systems. Our data show that the reaction rates for the catalyzed system are proportional to the concentration of isocyanate, to the square root of alcohol concentration, and to the square root of the catalyst concentration. Based on these kinetic studies, a new mechanism for the catalyzed system is postulated (eq. 42). An important step in this mechanism is an equilibrium involving alcohol and catalyst, resulting in the formation of an active anion, which is the intermediate toward the final urethane product. The presence and the function of an active anion are further confirmed by the fact that increasing acidity or basicity significantly affects the reaction kinetics.

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