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The Reaction of Aliphatic Isocyanates with Some Compounds Which Contain an Active-Hydrogen

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The Reaction of Aliphatic Isocyanates with Some Compounds Which Contain an Active-Hydrogen

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ABSTRACT

A study has been made of the kinetics and mechanism of the reactions of aliphatic isocyanates with several active-hydrogen compounds. The effect of hydrogen chloride on the reaction of aliphatic isocyanates with alcohols, water, ureas, and urethanes has been investigated. The significance of these results to the application of aliphatic isocyanate-terminated prepolymers to wool is discussed.

INTRODUCTION

Isocyanate-terminated prepolymers which have been used extensively in the production of polyurethane foams, adhesives,

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elastomers, and coatings are generally prepared from aromatic rather than aliphatic diisocyanates. The reasons for this include:

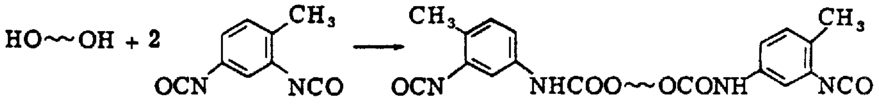
(1) The lower cost of aromatic diisocyanates.

(2) The lower toxicity of aromatic isocyanates, especially those of higher molecular weight.

(3) The greater reactivity of aromatic isocyanates with alcohols and polyols.

(4) The greater control of the capping reactions afforded by unsymmetrical aromatic diisocyanates.

The difference in reactivity of the isocyanate groups in unsymmetrical diisocyanates is shown in 2,4-tolylene diisocyanate (TDI) where the group in the 4 position is about 10 times more reactive than that in the 2 position. In contrast, the isocyanate groups of hexamethylene diisocyanate (HMDI) have equal reactivity (only recently have unsymmetrical aliphatic diisocyanates become readily available [1]). Therefore, the reaction of 2 moles of TDI with 1 mole of a diol gives a predominately isocyanate-terminated product as the result of preferential reaction of the 4-isocyanate group (Eq. 1). On the other hand, when 2 moles of HMDI are reacted with 1 mole of a diol, chain extension may become a problem (Eq. 3).



(1)

$$HO\sim\sim OH + 2\ ONC(CH_2)_6NCO \rightarrow OCN(CH_2)_6NHCOO\sim\sim OCONH(CH_2)_6NCO \qquad (2)$$

$$HO\sim\sim OH + 2\ OCN(CH_2)_6{-}NHCOO\sim\sim OCONH(CH_2)_6{-}NCO \rightarrow$$

$$OCN\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim NCO,\ \text{etc.} \qquad (3)$$

The literature on the kinetics of isocyanate reactions is largely devoted to the aromatic rather than aliphatic systems. However, it is generally believed that the prepolymers used in the manufacture of nonyellowing coatings and in the production of permanent-press all-wool garments contain aliphatic isocyanates [2, 3].

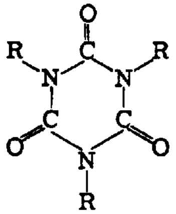
The free isocyanate groups of these prepolymers may undergo a number of reactions during curing. These include the reaction with water to form a urea via an amine intermediate (Eq. 4), reaction with a urea to form a biuret (Eq. 5), reaction with urethanes to form

$$\sim NCO + H_2O \rightarrow \sim NH_2 + CO_2;\ \sim NCO + NH_2\sim \rightarrow \sim NHCONH\sim \quad \text{(urea)} \qquad (4)$$

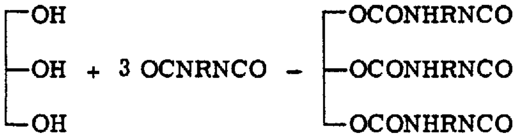
$$\sim NCO + \sim NHCONH\sim \rightarrow \sim NHCO\overset{\wr}{N}CONH\sim \quad \text{(biuret)} \qquad (5)$$

$$\sim NCO + \sim NHCO_2R \rightarrow \sim NHCO\overset{\wr}{N}CO_2R \quad \text{(allophanate)} \qquad (6)$$

$3\ RNCO \rightarrow$



(7)



$$\left[\begin{array}{l} -OH \\ -OH \\ -OH \end{array}\right. + 3\ OCNRNCO \rightarrow \left[\begin{array}{l} -OCONHRNCO \\ -OCONHRNCO \\ -OCONHRNCO \end{array}\right. \qquad (8)$$

allophanates (Eq. 6), and trimerization of the isocyanates (Eq. 7). Similarly, during the synthesis of the prepolymer from a polyol and a diisocyanate, a number of other reactions may also occur (Eq. 8), and each particular reaction is often complex and is subject to catalysis by a variety of compounds.

We were particularly interested in the preparation of aliphatic isocyanate-terminated prepolymers for use in wool-finishing processes and in the curing of such products when applied to wool. A systematic investigation of the kinetics of the reactions between aliphatic isocyanates and some active-hydrogen compounds was therefore commenced. As model reactions those of butyl isocyanate with butanol, water, a urea, and a urethane were studied and some of the results are reported here.

EXPERIMENTAL

Materials

Spectroquality Matheson, Coleman, and Bell p-dioxane was purified immediately before use by passing it through Merck neutral alumina, activity I. The resulting dioxane was free of peroxides and contained less than 0.002% water (Karl Fischer titration).

n-Butyl isocyanate was obtained from Eastman Kodak and purified by distillation from phosphorus pentoxide, followed by refluxing over calcium oxide and finally fractionation from calcium oxide; the fraction boiling at 114.5-115°C was used in the kinetic experiments.

Analar n-butanol was purified by distillation; the fraction boiling at 117-118°C was used in the kinetic studies.

Hydrogen chloride was used as a dilute stock solution in dry dioxane.

Tri-n-butylurea was prepared by adding di-n-butylamine (6.5 g) dropwise with stirring to a solution of n-butyl isocyanate (4.9 g) in dry benzene (8 ml). After 1 hr the mixture was fractioned to give tri-n-butylurea, bp 112°C/0.03 Torr.

O,N-Di-n-butylcarbamate was prepared by the dropwise addition of n-butanol (3.7 g) to n-butyl isocyanate (4.5 g) in dry benzene (4 ml) containing 2 drops of triethylamine. The solution was left at room temperature overnight and then fractioned under reduced pressure. The urethane used in the kinetic studies had a bp 94°C/1.5 Torr (lit. bp 101°C/4 Torr [4]).

Kinetic Measurements

Solutions were prepared by adding a known volume of a solution of butyl isocyanate in dioxane to a given volume of dioxane, which in the case of the acid-catalyzed reactions contained a standardized concentration of hydrogen chloride or hydrogen bromide. The vessels were stoppered quickly and placed in a constant-temperature (± 0.1°C) water-bath. After 15 min an aliquot of the active-hydrogen compound (butanol, water, tri-n-butylurea or O,N-di-n-butylcarbamate) in dioxane was added and the solution thoroughly mixed. This time was taken as the initial time of reaction Aliquots were withdrawn at convenient times and added to an excess of a standard solution of di-n-butylamine solution. The unchanged di-n-butylamine was back-titrated with a standard solution of hydrochloric acid [5] and the concentration of the isocyanate in the reaction mixture was thereby calculated. Corrections were made for the amount of acid present in the reaction mixture.

Control experiments in the absence of an active-hydrogen compound showed that the concentration of butyl isocyanate and hydrogen chloride remained constant during the time taken for a kinetic investigation.

Experiments designed to measure the effect of added urethane were performed in an identical manner to those described above with the urethane being included in the solution to be equilibrated for 15 min.

In the reverse mixing procedure, a solution of butanol in dioxane was added to a solution of hydrogen chloride in dioxane and the stoppered flask placed in a constant temperature water-bath. After 15 min a butyl isocyanate solution in dioxane was added.

Gas chromatographic analyses were carried out using a Hewlett Packard research chromatograph, model number 7620A, and a glass column packed with a silicone gum rubber.

Infrared spectra were recorded on a Beckman IR-9 Spectrometer. An electrically heated cell was used and the temperature measured by a thermocouple placed in one of the sodium chloride windows of the cell. Equilibrium constants for the butyl isocyanate-hydrogen chloride system in dioxane were measured by observing the change in the intensity of the isocyanate peak at 2280 cm^{-1} for different hydrogen chloride concentrations. The accuracy of these measurements was reduced by reaction of the isocyanate with water to give carbon dioxide which gave a peak at 2340 cm^{-1}.

RESULTS AND DISCUSSION

The Reaction of Butyl Isocyanate with Butanol

It has long been recognized that aromatic isocyanate-alcohol reactions are complex and this fact has led to a vast number of papers on the subject (e.g., Refs. 6-8). Our studies of the reaction between butyl isocyanate and butanol in dioxane indicate that it also is a complex reaction. Initial studies using compounds purified by standard procedures indicated that a catalyst (shown to be hydrogen chloride) was present in the butyl isocyanate as an impurity. Subsequently the isocyanate was purified by refluxing over calcium oxide for several hours, and distilling from this medium.

The catalytic effect of hydrogen chloride can be seen from the second-order plots shown in Fig. 1. Although third-order kinetics have been suggested [9] for some isocyanate-alcohol reactions, it is usually satisfactory to analyze the results as a pseudo-second-order reaction. This procedure appears to be satisfactory for the butyl isocyanate-butanol reaction. The observed second-order rate constant (k_{ob}) was related to the hydrogen chloride concentration by the expression of Eq. (9), with a catalytic rate constant (k_{cat}) of

$$10^4\ k_{ob} = 430[\mathrm{HCl}]\ \text{liter mole}^{-1}\ \text{sec}^{-1} \qquad (9)$$

430×10^{-4} $liter^2$ $mole^{-2}$ sec^{-1}. References to acid-catalysis of

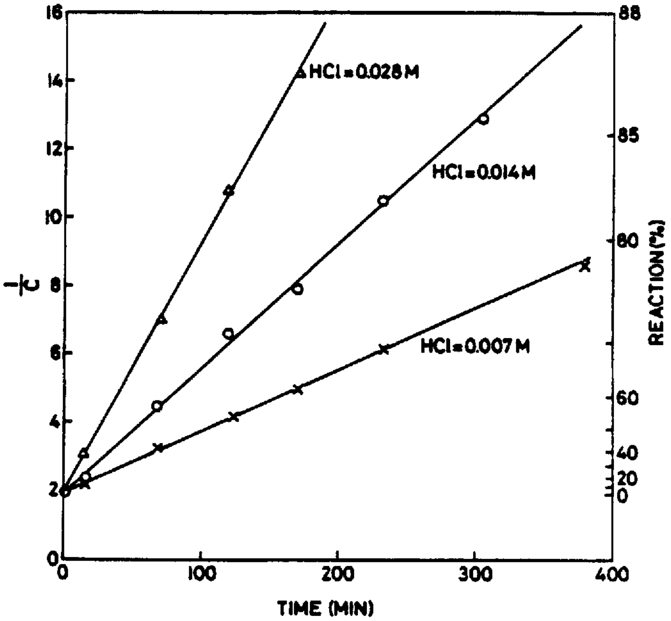


FIG. 1. The HCl-catalyzed reaction of BuNCO with BuOH in dioxane at 65° C. $[\mathrm{BuNCO}]_0 = [\mathrm{BuOH}]_0 = 0.523$ M. C is the concentration of butyl isocyanate at a given time.

reactions of aromatic isocyanates are very few [7, 10]. In some cases it has been claimed that acids are inhibitors [10].

On the other hand, tertiary amines are reported to be good catalysts for aromatic isocyanate-alcohol reactions [e.g., Refs. 6 and 10]. Triethylamine is also a catalyst for the butyl isocyanate-butanol reaction (Fig. 2). The catalytic rate constant here is 9.1×10^{-4} liter^2 mole^{-2} sec^{-1}; about fifty times less than that of the hydrogen chloride-catalyzed reaction under similar conditions. Hydrogen bromide had a similar catalytic effect to hydrogen chloride on the butyl isocyanate-butanol reaction.

In making these comparisons it is very important to specify the conditions used. This is exemplified by the data in Table 1. It can be seen that as the initial concentration of the reactants decreases k_{cat} increases. The catalytic rate constant is defined as

$$k_{cat} = \frac{k_{ob} - k_o}{[\text{catalyst}]} \simeq \frac{k_{ob}}{[\text{catalyst}]}$$

where k_{ob} is the experimentally determined second-order rate constant and k_o the corresponding second-order rate constant in the absence of a catalyst. If the catalytic effect is large then $k_{ob} \gg k_o$.

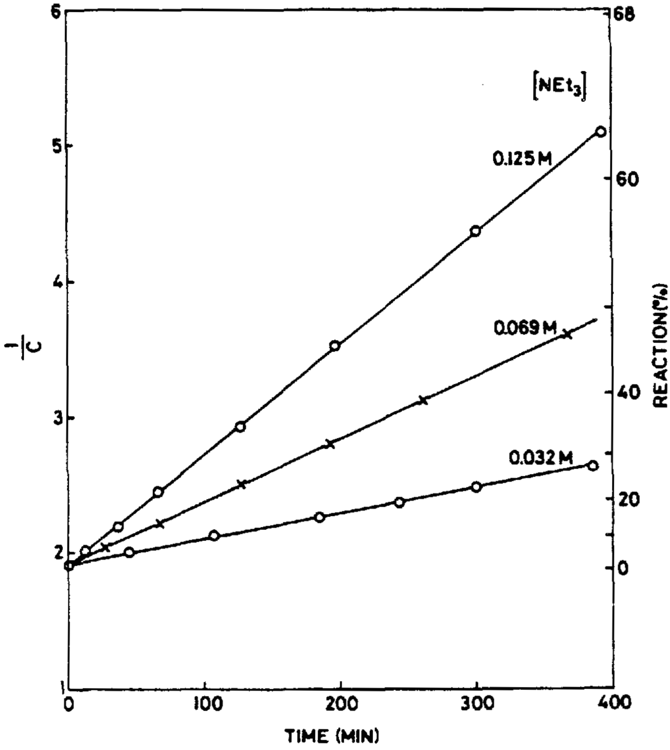


FIG. 2. The NEt_3-catalyzed reaction of BuNCO with BuOH in dioxane at 65°C. $[BuNCO]_0 = [BuOH]_0 = 0.535$ M. $10^4 k_{ob} = 0.2 + 9.1 [NEt_3]$ liter $mole^{-1}$ sec^{-1}. C is the concentration of butyl isocyanate at a given time.

By analogy with the mechanism proposed by Baker [11-13] for the amine-catalyzed reaction of aromatic isocyanates with alcohols, a mechanism involving protonation of the butyl isocyanate (Eq. 10) followed by the reaction of the complex with butanol may be written.

TABLE 1. The HCl-Catalyzed Reaction of BuNCO and BuOH in Dioxane at 65°C. $[\mathrm{BuNCO}]_0 = [\mathrm{BuOH}]_0$; $[\mathrm{HCl}]_0 = 0.014$ M

[BuOH] (M)	$10^4 k_{ob}$ (liter mole^{-1} sec^{-1})	$10^4 k_{cat}$ (liter^2 mole^{-2} sec^{-1})[a]
0.523	6.0 ± 0.4	430
0.418	7.7 ± 0.4	550
0.209	14 ± 0.6	1000
0.105	28 ± 1	2000
0.0523	44 ± 4	3100

[a] $k_{cat} = k_{ob}/[\mathrm{HCl}]_0$.

An alternative mechanism in which the alcohol is initially protonated appears less likely because this would reduce the likelihood of nucleophilic attack of the alcohol entity on the isocyanate group.

$$\mathrm{BuNCO} + \mathrm{H}^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\mathrm{BuNCOH}]^+ \qquad (10)$$

$$[\mathrm{BuNCOH}]^+ + \mathrm{BuOH} \xrightarrow{k_3} \mathrm{BuNHCO_2Bu} + \mathrm{H}^+ \qquad (11)$$

A steady-state treatment for the mechanistic scheme depicted in Eqs. (10) and (11) yields the rate expression (12). For the system

$$\text{rate} = \frac{k_1 k_3 [\mathrm{HCl}]_0 [\mathrm{BuNCO}][\mathrm{BuOH}]}{k_1 [\mathrm{BuNCO}] + k_2 + k_3 [\mathrm{BuOH}]} \qquad (12)$$

shown in Eq. (10) at equilibrium, $k_2 \gg k_3$ [BuOH], and Eq. (12) then takes the form of Eq. (13) where $K_1 = k_1/k_2$. Alternatively, if $k_2 \gg k_1$

$$\text{rate} = \frac{K_1 k_3 [\mathrm{HCl}]_0 [\mathrm{BuNCO}][\mathrm{BuOH}]}{1 + K_1 [\mathrm{BuNCO}]} \qquad (13)$$

[BuNCO], Eq. (12) may be written in the form of Eq. (14) which corresponds to Baker's equation. Irrespective of whether we consider Eq. (12), (13), or (14), it is clear that the observed

$$\text{rate} = \frac{k_1 k_3 [\text{HCl}]_0 [\text{BuNCO}][\text{BuOH}]}{k_2 + k_3 [\text{BuOH}]} \qquad (14)$$

second-order rate constant, defined as

$$k_{ob} = \text{rate}/([\text{BuNCO}][\text{BuOH}])$$

will be directly proportional to the catalyst concentration but will, in general, not be a constant but will change as the reaction proceeds. As shown in Fig. 1, k_{ob} is proportional to $[\text{HCl}]_0$. Figure 1 also shows that k_{ob} is constant under a given set of conditions. Such an observation requires that the denominator in Eqs. (12), (13), and (14) is constant. From Eq. (13), if $K_1[\text{BuNCO}] \ll 1$, then k_{ob} should be constant over most of the reaction. On the other hand, if $K_1[\text{BuNCO}] \gg 1$, pseudo-first-order kinetics would be expected. Since k_{ob} is constant and $[\text{BuNCO}] \leq 0.5$, K_1 should be much less than 2. We have found that an equilibrium is rapidly established between butyl isocyanate and HCl by observing the change in absorbance of the isocyanate group at 2280 cm^{-1} in the ir spectrum. Our preliminary studies suggest a value for K_1 at 65°C of about 0.2 liter mole^{-1}.

Since a value of $K_1 \lesssim 0.1$ results in a system which gives second-order kinetics, it follows that k_{ob} should be independent of initial concentrations. However, such is not the case (Table 1). The dependence of k_{ob} on initial concentrations has been used as evidence of a mechanism analogous to that shown in Eqs. (10) and (11). Rearrangement of Eq. (14) yields Eq. (15). Although a plot of the reciprocal of the observed rate constant against the initial alcohol concentration for various alcohol concentrations is approximately linear, it is clearly invalid to adopt such a procedure in this case.

$$\frac{[\text{HCl}]_0}{k_{ob}} = \frac{k_2}{k_1 k_3} + \frac{[\text{ROH}]}{k_1} \qquad (15)$$

As expected, the values of k_1 and k_2/k_3 (or K_1) so obtained are inconsistent. The changes in k_{ob} with the initial concentrations cannot be a specific kinetic effect but must be due to other factors. These may include changes in the dielectric constant, changes in the solvation of some or all of the species in solution by dioxane and butanol, and hydrogen bonding phenomena. Because kinetics which are internally of the second-order are observed, whichever factor or factors are changed when the initial concentrations of the reactants are varied must then remain substantially unchanged, or, at least, be mutually compensating, for the duration of the reaction.

A possible explanation for the greater catalytic effect of hydrogen chloride on the aliphatic isocyanates [7, 10] may be that there is a preferential protonation on the oxygen atom of the NCO group for aromatic isocyanates and on the nitrogen atom of the NCO group for aliphatic ones. These modes of protonation are consistent with the electronic structure of aromatic and aliphatic isocyanates [7, 15]. If the nitrogen-protonated species is more reactive with nucleophiles than the unprotonated or oxygen-protonated species, a satisfactory explanation is provided for the observed results. These predictions are supported by semi-empirical molecular orbital calculations in the INDO approximation [21] and indicate that the oxygen atom of the aromatic isocyanate is more negatively charged relative to the nitrogen atom than is the oxygen atom of the aliphatic compound.

A second-order plot for the "uncatalyzed" butyl isocyanate-butanol reaction was nonlinear with the slope increasing as the reaction proceeded and this was shown to be the result of catalysis by the urethane product. Under conditions where the catalytic rate constant for the hydrogen chloride-catalyzed reaction was 430 × 10^{-4} liter^2 mole^{-2} sec^{-1}, the catalytic rate constant for urethane-catalysis was found to be 5.8 × 10^{-4} liter^2 mole^{-2} sec^{-1}. Thus the effect of urethane catalysis was usually swamped in the presence of hydrogen chloride. This was confirmed by the constancy of the observed second-order rate constant for sufficiently high concentrations of hydrogen chloride when various amounts of urethane were added to the reaction mixture (Table 2).

The observed rates were independent of the order of mixing the reagents but were very sensitive to small amounts of water with increasing

TABLE 2. The Effect of Added Urethane on the HCl-Catalyzed Reaction of BuNCO and BuOH in Dioxane at 65°C. $[\mathrm{HCl}]_0$ = 0.014 M. $[\mathrm{BuNCO}]_0 = [\mathrm{BuOH}]_0$ = 0.105 M

$[\mathrm{Urethane}]_0$	0.023 M	0.046 M	0.085 M
$10^4 k_{ob}$ (liter mole^{-1} sec^{-1})	27.8	28.5	28.2

concentrations of water decreasing the rate. Therefore special care is necessary in purifying all reagents.

The energies of activation (E_a) for the uncatalyzed and catalyzed butyl isocyanate-butanol reaction were found to be 69.0 ± 2.1 kJ/mole (from initial rates) and 57.3 ± 4.2 kJ/mole, respectively (Table 3). A value of about 42 kJ/mole is an average value for the E_a for the uncatalyzed phenyl isocyanate-butanol reaction and 21-34 kJ/mole for the corresponding triethylamine catalyzed reaction [6]. Values for E_a of 67 and 92 kJ/mole have been reported for the reaction between tert-octyl isocyanate and ethanol and 2-butanol, respectively [6].

TABLE 3. The Energy of Activation (E_a) for the HCl-Catalyzed Reaction of BuNCO and BuOH in Dioxane. $[HCl]_0 = 0.014$ M. $[BuNCO]_0 = [BuOH]_0$

Temp. (°C)	$[BuNCO]_0$ (M)	$10^4 k_{ob}$ (liter mole^{-1} sec^{-1})	E_a (kJ/mole)
45	0.212	3.6 ± 0.2	61.1
65	0.209	14 ± 0.6	
45	0.106	7.9 ± 0.4	54.0
65	0.105	28 ± 1	

The Reaction of Butyl Isocyanate with Water

The butyl isocyanate-water reaction in dioxane was also found to be catalyzed by hydrogen chloride. When the data were plotted assuming a second-order reaction, the plot was nonlinear with the slope gradually increasing as the reaction proceeded. This effect was shown by gas chromatographic analysis of the products to be due, in part, to further reaction of the di-n-butylurea with butyl isocyanate to form a biuret. The di-n-butylurea product also was found to be a catalyst for this reaction. For an initial water concentration of about 0.5 M the initial catalytic rate constant for hydrogen chloride catalysis was found to be 8.8×10^{-4} liter^2 mole^{-2} sec^{-1}. The energy of activation for this reaction was found to be about 62.3 kJ/mole. An E_a of 38.5 kJ/mole has been reported for the reaction between HMDI and water but the experimental conditions were not given [14], and a value for E_a of 58.5 ± 4.2 kJ/mole for the perchloric acid-catalyzed hydrolysis of methyl isocyanate in 40% aqueous dioxane has been published recently [15, 16].

The Reaction of Butyl Isocyanate with a Urea and a Urethane

A summary of some results for the reaction of water, butanol, a urea, and a urethane with butyl isocyanate is given in Table 4. It can be seen that hydrogen chloride catalyzes the urea reaction but not the urethane reaction. Although the errors in the rate constants for the urea and urethane reactions with butyl isocyanate are somewhat greater than for the butanol reaction, it appears that the urea and urethane react at similar rates. This is in contrast to the corresponding reactions with aromatic isocyanates where ureas are reported to react about 100 times faster than urethanes [6]. Because ureas and urethanes may dissociate via several alternative routes [6] and the products from the reaction of ureas and urethanes with butyl isocyanate are likely to be as reactive with the latter as the ureas and urethanes themselves, further kinetic studies were not attempted.

TABLE 4. Reaction of BuNCO with Active-Hydrogen Compounds in Dioxane at 65°C. $[BuNCO]_0 = [\text{Active-H Compound}]_0 \approx 0.5$ M

Active-H compound (AH)	Catalyst	$10^4 k_0$	$10^4 k_{cat}$[a] (liter^2 mole^{-2} sec^{-1})
H_2O	HCl	~0.1	8.8
	$(BuNH)_2CO$	~0.1	1.5
$BuNHCONBu_2$	HCl	0.05	8
$BuNHCO_2Bu$	HCl	0.025	0
BuOH	HCl	0.2	430
	NEt_3	0.2	9.1
	$BuNHCO_2Bu$.	0.2	5.8

[a] $k_{cat} = (k_{ob} - k_0)/[\text{catalyst}]$.

Conclusions

These results enable certain conclusions to be drawn about the nature of the cured isocyanate prepolymers on wool and of the possible wool-polymer and polymer-polymer interactions. The choice of reactive prepolymers such as Zeset TP (Du Pont) [17], with free acid chloride groups, and Synthappret LKF (Bayer), with free isocyanate groups, as products for the treatment of wool, was originally made in anticipation that the reactive groups would react with the amino and hydroxyl groups of wool to form a three-dimensional polymer on the surface. However, it now appears that at least with isocyanate prepolymers surface grafting is unlikely [3, 18]. It has been suggested that a three-dimensional polymer network is necessary to shrinkproof wool [19]. Because the reactions of aliphatic isocyanate groups are slow in the absence of added catalysts, the curing of the isocyanate prepolymers most likely results from reaction with water, the only active-hydrogen compound present in large amounts. The reaction of a difunctional isocyanate-terminated prepolymer with water would then result in a chain-extended linear molecule and not a three-dimensional polymer-wool network; it follows that to form a three-dimensional network the prepolymer must have a functionality greater than 2, e.g., Synthappret LKF which has a functionality of 3 [3].

The results of these kinetic studies suggested the choice of suitable conditions for the preparation of a variety of isocyanate prepolymers (by the capping of polyols) and their blocked derivatives. Such polymers are presently being evaluated as agents for wool-finishing processes. The capping of diols or triols from one particular source with a diisocyanate consistently gave prepolymers with a functionality greater than 2 or 3, respectively (Table 5 [20]). This was shown to result from catalysis of the urethane-isocyanate reaction by sodium

TABLE 5. The Functionality of Some Prepolymers by Gel Point Determination [20]

Prepolymer	Nature of end groups	Cross-linker	Functionality
Diol, MW ~ 400	OH	HMDI	2.0
Triol, MW ~ 1100	OH	HMDI	3.0
Diol, MW ~ 400, capped with HMDI	NCO	Butane-1,4-diol	2.3
Triol, MW ~ 1100, capped with HMDI	NCO	Butane-1,4-diol	3.5

acetate which was present as an impurity in these polyols. It therefore seems likely that earlier claims of successful shrinkproofing with isocyanate prepolymers prepared from diols may, in fact, have been the result of using a polymer whose functionality was slightly greater than 2.

ACKNOWLEDGMENT

We wish to thank Dr. S. D. Hamann for many valuable discussions during the course of this work and also for the mathematical calculations of the appendix. We also thank Dr. T. H. Spurling for the calculations of the charge distribution on the aliphatic and aromatic isocyanates.

APPENDIX

by S. D. Hamann

Exact Kinetic Equations

The kinetic equations in the text were based on the steady-state approximation, which is not obviously valid in the present case. However, it is possible to draw the following conclusions independently of that approximation.

(a) If the equilibrium

$$\mathrm{BuNCO} + \mathrm{H}^+ \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{BuNCOH}^+$$

(where H^+ denotes a solvated proton, probably BuOH_2^+) is established very rapidly, as most protonation equilibria are, then

$$[\mathrm{BuNCOH}^+] \simeq \frac{[\mathrm{BuNCO}][\mathrm{H}^+]_0 K_1}{1 + [\mathrm{BuNCO}]K_1}$$

where $K_1 = k_1/k_2$, and Eq. (13) follows.

(b) On the other hand, if the equilibrium is established slowly in comparison with the rate of the subsequent reaction 3:

$$\mathrm{BuNCOH}^+ + \mathrm{BuOH} \xrightarrow{3} \mathrm{BuNHCO_2Bu} + \mathrm{H}^+$$

(i.e., $k_1[\mathrm{BuNCO}][\mathrm{H}^+]$, $k_2[\mathrm{BuNCOH}^+] \ll k_3[\mathrm{BuNCOH}^+][\mathrm{BuOH}]$) then Step 1 becomes rate-determining and

$$\text{rate} \simeq k_1[\mathrm{BuNCO}][\mathrm{H}^+] \simeq k_1[\mathrm{BuNCO}][\mathrm{H}^+]_0$$

(c) In the general case where the rates of all three steps are comparable, it is necessary to solve the following set of nonlinear differential equations:

$$d[\mathrm{BuNCO}]/dt = k_2[\mathrm{BuNCOH}^+] - k_1[\mathrm{BuNCO}][\mathrm{H}^+]$$

$$d[\mathrm{H}^+]/dt = k_3[\mathrm{BuNCOH}^+][\mathrm{BuOH}] + k_2/\mathrm{BuNCOH}^+] - k_1[\mathrm{BuNCO}][\mathrm{H}^+]$$

$$d[\mathrm{BuNCOH}^+]/dt = -d[\mathrm{H}^+]/dt$$

$$d[\mathrm{BuOH}]/dt = -k_3[\mathrm{BuOH}][\mathrm{BuNCOH}^+]$$

$$d[\mathrm{BuNHCO_2Bu}]/dt = -d[\mathrm{BuOH}]/dt$$

These can readily be integrated by numerical methods and some results are shown in Fig. 3 for the particular parameters given in Appendix Table 1. Throughout, $[\mathrm{BuNCO}]_0 = [\mathrm{BuOH}]_0 = 0.523$ mole l^{-1}, $[\mathrm{H}^+]_0 =$ 0.014 mole l^{-1}, and the value of k_3 has been adjusted to make the initial slope of a pseudo-second-order plot correspond with the rate constant $k_{ob} = 6.0 \times 10^{-4}$ liter mole^{-1} sec^{-1} (Table 1).

APPENDIX TABLE 1

Curve No.	k_1 (liter mole^{-1} sec^{-1})	k_2 (sec^{-1})	k_3 (liter mole^{-1} sec^{-1})	$K_1 = k_1/k_2$ (liter mole^{-1})
1	0.1	10	5.5	0.01
2	0.1	1	0.58	0.1
3	0.1	0.1	0.086	1
4	1	0.01	0.023	100

It is apparent that the plots approach those for second-order reactions when $K_1 < 0.1$ liter mole^{-1}, but progressively deviate at higher values. There is always a small initial upward curvature caused by the finite time of formation of the species BuNCOH^+.

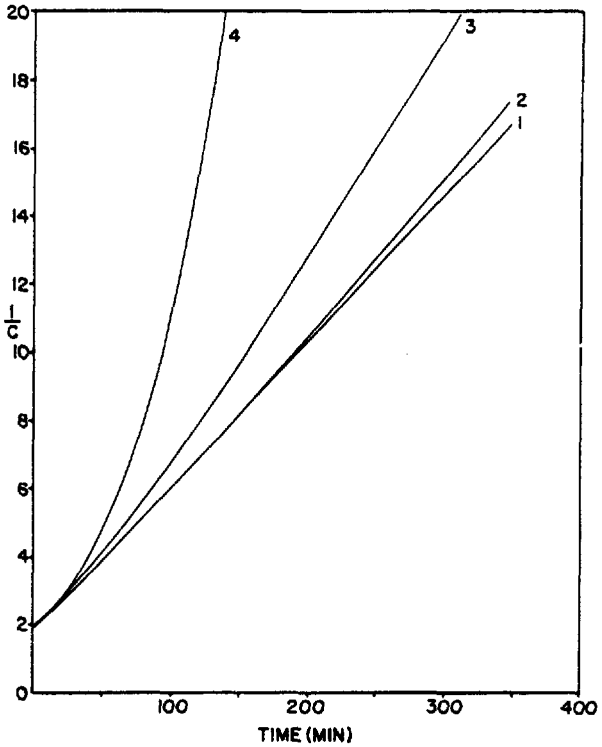


FIG. 3. Pseudo-second-order plots for the conditions listed in the Appendix. C denotes the instantaneous concentration of BuNCO.

REFERENCES

[1] K. Schmitt, Chem. Ind. Int., 3, 90 (1966); Veba-Chemie AG, Product information 22-E-269-1-1.
[2] E.g., British Patent 1,062,564; Australian Patent 288,116.
[3] R. O. Rutley, J. Soc. Dyers Colourists, 86, 337 (1970).
[4] H. Okada and Y. Iwakura, Makromol. Chem., 66, 91 (1963).
[5] ASTM D1638-61T, ASTM Standards, (1961), p. 176.
[6] J. H. Saunders and K. C. Frisch, Polyurethanes: Chemistry and Technology, Pt. 1, Wiley (Interscience), New York, 1962, Chap. IV.
[7] S. G. Entelis and O. V. Nesterov, Russ. Chem. Rev., 35, 917 (1966).

[8] K. C. Frisch and L. P. Rumao, J. Macromol. Sci.—Rev. Macromol. Chem., C5(1), 103 (1970).

[9] M. Sato, J. Org. Chem., 27, 819 (1962).

[10] A. Farkas and G. A. Mills, Advan. Catal., 13, Chap. 6 (1962).

[11] J. W. Baker, M. M. Davies, and J. Gaunt, J. Chem. Soc., 1949, 24.

[12] J. W. Baker and J. B. Holdsworth, J. Chem. Soc., 1947, 713.

[13] J. W. Baker and J. Gaunt, J. Chem. Soc., 1949, 9, 19, 27.

[14] W. Cooper, R. W. Pearson, and S. Darke, Ind. Chem., 36, 121 (1960).

[15] R. P. Tiger, L. S. Bekhli, and S. G. Entelis, Kinet. Katal., 11, 1347 (1970).

[16] R. P. Tiger, L. S. Bekhli, and S. G. Entelis, Kinet. Katal., 12, 318 (1971).

[17] R. E. Whitfield, D. E. Remy, A. G. Pittman, and W. L. Wasley, Textile Res. J., 36, 401 (1966).

[18] A. B. Kriegler, J. Textile Inst., In Press (1971).

[19] H. D. Feldtman, J. R. McPhee, and A. J. Pratt, Textile Res. J., 37, 46 (1967).

[20] M. B. Jackson and D. H. Solomon, Anal. Chem., 44, 1074 (1972).

[21] T. H. Spurling, unpublished calculations. The calculations were made with a CD6600 Fortran version of the program of J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970, using standard molecular geometrics and parameters.

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