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Infrared Kinetic Study of the Catalyzed and Uncatalyzed Reaction of Butanol-1 with α-Naphthylisocyanate in Various Solvents

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ABSTRACT

The condensation reaction of α-naphthylisocyanate with n-butanol has been studied in toluene and in bis(2-methoxyethyl) ether (diglyme) by IR spectroscopy at different temperatures (20-60°C). A kinetic study shows that it is first order with respect to each reactant even when the reaction is catalyzed by tin octoate. A general mathematical treatment indicates that secondary reactions may occur in some conditions of temperature, solvent and catalyst, but do not take place in our system. The activation enthalpy and entropy have been determined.

Formation of polyurethane by polyaddition of diisocyanate and diols has been widely reported in the literature. It appears as a very complex reaction in all cases. Due to this fact, many authors [1-6] have studied model reactions such as the catalyzed and uncatalyzed addition of a monoalcohol with a monoisocyanate in various solvents. However, many controversies exist both for kinetics and mechanism. Thus Baker et al. [1], who studied an uncatalyzed reaction, suggest a mechanism that begins with the formation of a complex between isocyanate and alcohol and is followed by the reaction of this complex with a second molecule of alcohol, resulting in a carbamate, the kinetic order being between 2 and 3. On the other hand, Ephraim [3] suggests complexation of the alcohol either with itself or with the solvent or the carbamate formed during the addition reaction. The reaction of these complexes with isocyanate is first order with respect to isocyanate and between first and second order with respect to alcohol. Sato [4] proposed a combination of these two mechanisms. When the reaction is catalyzed, its order is not simple and two mechanisms have been suggested: (1) Baker's mechanism [1] where the catalyst forms a complex with the isocyanate before reacting with the alcohol, and (2) Farkas's mechanism [6] where the catalyst forms a double complex, first with the alcohol and then with the isocyanate to give a carbamate.

In the present work we intend to examine the behavior of the α-naphthylisocyanate-n-butanol system before and after the conversion where secondary reactions may appear. Such a complete study is rarely found in the literature.

EXPERIMENTAL

Commercial α-naphthylisocyanate (Aldrich) was distilled under vacuum before use.

Toluene (Prolabo) was first distilled and then purified according to Vogel [7] and sodium dried.

Bis(2-methoxyethyl) ether (diglyme) was refluxed for 1 day over copper sulfate in order to destroy peroxides, then distilled and dried several times with sodium wire.

n-Butanol was purified according to Vogel [7] by fractionating after drying with potassium carbonate.

Kinetic study was performed in a Pyrex reactor placed in a thermostated bath. At determined times, samples are removed and immediately analyzed by IR spectroscopy (Perkins Elmer 577). Isocyanate exhibits a characteristic vibration at 2260 cm^{-1} and the hydroxyl group of n-butanol a vibration at 3380 cm^{-1}. The Beer-Lambert law was checked for these two bands, and molar absorption coefficients were determined ($\epsilon_{NCO} = 1570$, $\epsilon_{OH} = 37.7$). The conversion is determined by the decrease of the intensity of the band at 2260 cm^{-1} with respect to time. This titration method cannot be used for conversions above 95%.

RESULTS AND DISCUSSION

All experiments were performed in conditions where n-butanol (nBu) was always in excess with respect to α-naphthylisocyanate (αNI). From conversion plots it appears that when conversion is below 80%, the order of the reaction is one with respect to each reactant.

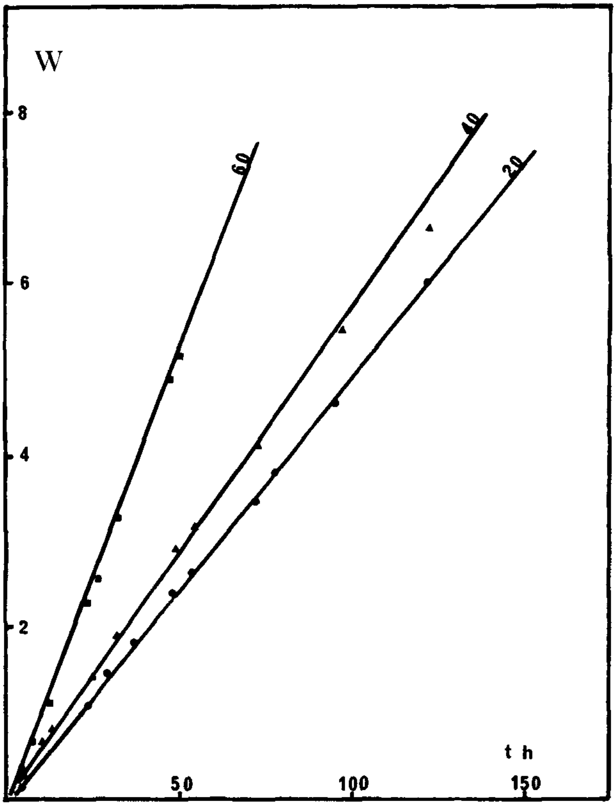


FIG. 1. Uncatalyzed reaction in toluene at various specific temperatures. Plot of W (see text) against time (h). [Butanol-1] = (25-28) × 10^{-2} mol/L. [α-Naphthylisocyanate] = 4.5 × 10^{-2} mol/L.

Let x be the concentration of α-naphthylbutyl carbamate (αNBuC) at time t, and a and b the initial concentrations of nBu and αNI. a, b, x, and t are linked by the classical relation for second-order kinetics:

$$W = \frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} = kt$$

where k is the rate constant. For different solvents and temperatures in the range 20-60°C, plots of W against time are linear (Figs. 1-4). k_{obs} values are reported in Table 1. From these values the following conclusions can be drawn.

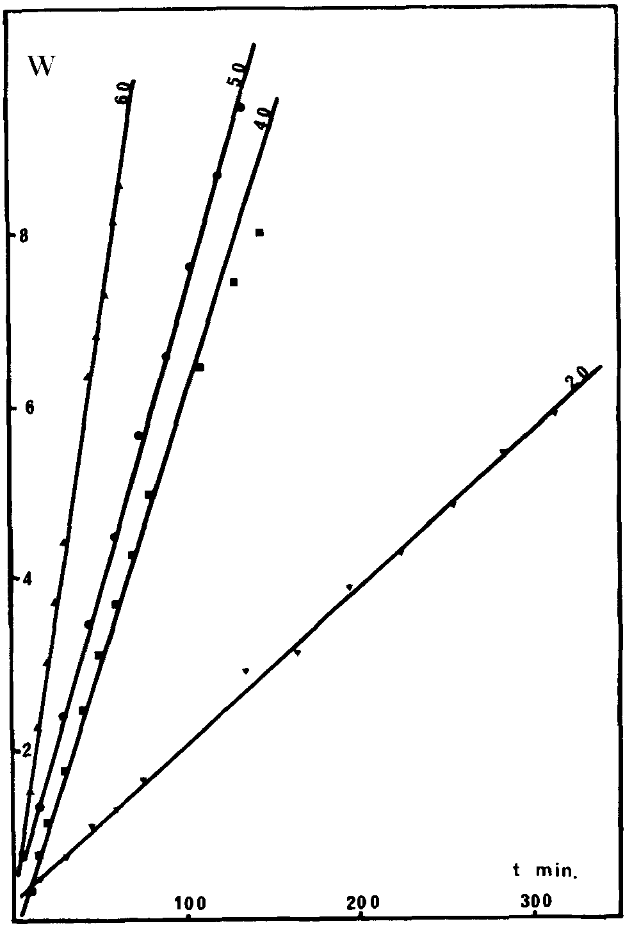


FIG. 2. Catalyzed reaction in toluene at various specific temperatures. Plot of W (see text) against time (min). [Butanol-1] = (25-28) $\times 10^{-2}$ mol/L. [α-Naphthylisocyanate] = 4×10^{-2} mol/L. [Tin octoate] = 7×10^{-4} mol/L.

The observed rate constant k_{obs} depends on the nature of the solvent. The values obtained in toluene are below those obtained in diglyme. It seems that the only effect of an initial addition of αNBuC (Expt 10, 11, and 24, Fig. 5) is to increase the k_{obs} value and that the order of the reaction is not changed. αNBuC is a weak catalyst for its own formation which is generally admitted when the solvent has a low dielectric constant (toluene). In the case of diglyme, an increase of the rate constant is observed until the conversion is 50%

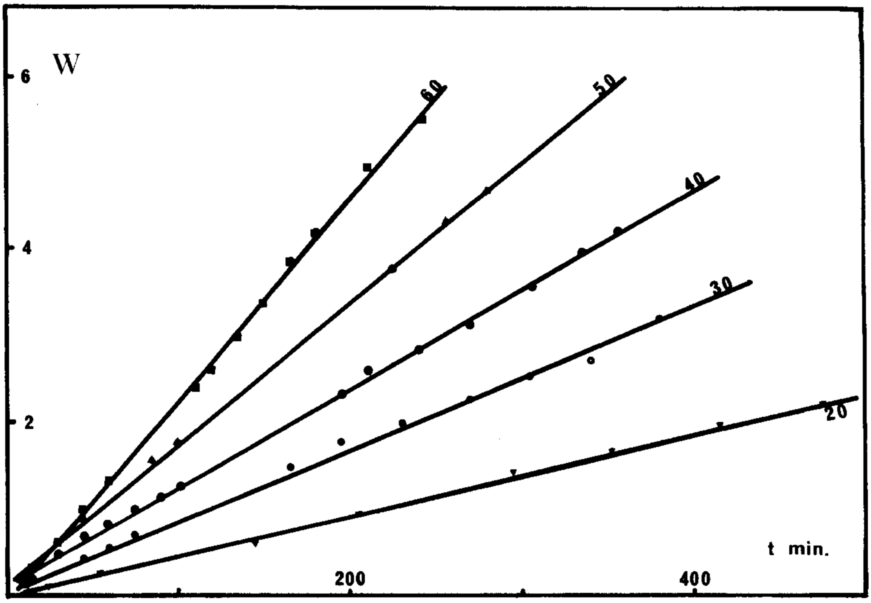


FIG. 3. Uncatalyzed reaction in diglyme at various specific temperatures. Plot of W (see text) against time (min). [Butanol-1] = $(50\text{-}85) \times 10^{-2}$ mol/L. [α-Naphthylisocyanate] = 4.5×10^{-2} mol/L.

($k_{obs} = 23.67 \times 10^{-4}$) followed by an important decrease. This shows that αNBuC reacts rapidly with αNI to give an allophanate. For this reason the reaction of αNI with nBu cannot take place immediately and appears only when half of the αNI is consumed. These two reactions are simultaneous, the kinetics being controlled by the slower one (carbamate formation with $k_{obs} = 0.74 \times 10^{-4}$ lower than $k_{obs} = 1.9 \times 10^{-4}$ in Expt 15 where no carbamate is added at the beginning). These conclusions are supported by Expt 23. No alcohol is added initially, and Fig. 6, corresponding to this experiment, shows two straight lines. The first corresponds to the formation of the allophanate with a value of k_{obs} slightly higher than in the reaction of butanol and isocyanate performed in the same conditions (Expt 24), and the second corresponds to biuret formation with a very high rate constant. On the other hand, no allophanate and no biuret are formed (Expt 12, $k_{obs} = 0$) in toluene. This may explain the two straight lines.

The presence of tin octoate does not modify the kinetic order but in this case k_{obs} depends on the solvent. In toluene, k_{obs} increases considerably but in diglyme it decreases slightly. This solvent effect

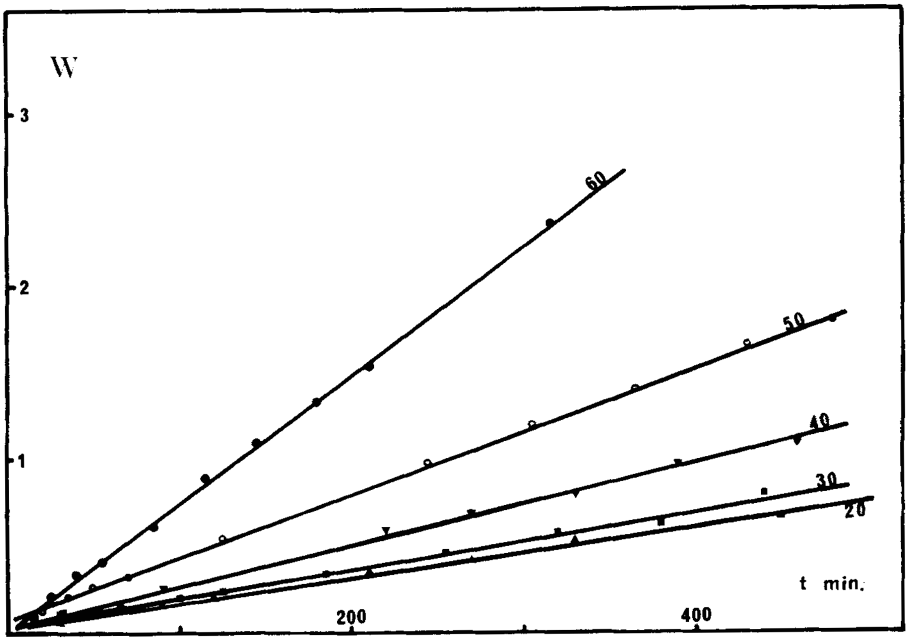


FIG. 4. Catalyzed reaction in diglyme at various specific temperatures. Plot of W (see text) against time (h). [Butanol-1] = (84-95) $\times 10^{-2}$ mol/L. [α-Naphthylisocyanate] = (4-5) $\times 10^{-2}$ mol/L. [Tin octoate] = 7×10^{-4} mol/L.

was reported by Ephraim [3] for the system phenylisocyanate-methanol in various solvents. In a first approximation, the rate constant decreases with increasing dielectric constant of the solvent and with its increasing ability to form hydrogen bonds with the alcohol. This behavior is probably the result of a complexation between the solvent and the catalyst.

It is worth recalling that the rather simple kinetic laws obtained for the addition of an alcohol to an isocyanate result, in fact, from a complicated process which is due to the possible contribution of several competitive elementary reactions:

$$\text{RNCO} + \text{R'OH} \xrightarrow{k_0} \text{carbamate (U)} \qquad (1)$$

$$(\text{R'OH})_2 \xrightarrow{k_1} 2\text{R'OH} \qquad (2)$$

$$\text{R'OH} + \text{C} \xrightleftharpoons{k_2} \text{Complex I} \qquad (3)$$

$$\text{R'OH} + \text{S} \xrightleftharpoons{k_3} \text{Complex II} \tag{4}$$

$$\text{RNCO} + \text{C} \xrightleftharpoons{k_4} \text{Complex III} \tag{5}$$

$$\text{RNCO} + \text{S} \xrightleftharpoons{k_5} \text{Complex IV} \tag{6}$$

$$\text{Complex I} + \text{RNCO} \xrightarrow{k_6} \text{carbamate} + \text{C} \tag{7}$$

$$\text{Complex II} + \text{RNCO} \xrightarrow{k_7} \text{carbamate} + \text{S} \tag{8}$$

$$\text{Complex III} + \text{R'OH} \xrightarrow{k_8} \text{carbamate} + \text{C} \tag{9}$$

$$\text{Complex IV} + \text{R'OH} \xrightarrow{k_9} \text{carbamate} + \text{S} \tag{10}$$

$$\text{Carbamate} + \text{RNCO} \xrightarrow{k_{10}} \text{allophanate} \tag{11}$$

$$2\text{RNCO} \xrightarrow{k_{11}} \text{dimere (uretidione)} \tag{12}$$

$$3\text{RNCO} \xrightarrow{k_{12}} \text{trimere (isocyanurate)} \tag{13}$$

where S is the solvent, C is the catalyst and U is the carbamate.

This general scheme has not been given by the authors [1-6] who studied the condensation of an alcohol with an isocyanate. Let x, y, z, and v be the concentrations of carbamate, allophanate, isocyanurate, and uretidione, respectively. Let a and b have the same definition as before. Relations (14) to (16) can be obtained from Eqs. (1) to (13):

$$\frac{dx}{dt} = k_0[\text{RNCO}][\text{R'OH}] + k_6[\text{Complex I}][\text{RNCO}] + k_7[\text{Complex II}][\text{RNCO}]$$
$$+ k_8[\text{Complex III}][\text{R'OH}] + k_9[\text{Complex IV}][\text{R'OH}] - k_{10}[\text{U}][\text{RNCO}] \tag{14}$$

$$\frac{dv}{dt} = -k_{11}[\text{RNCO}]^2 \tag{15}$$

$$\frac{dz}{dt} = -k_{12}[\text{RNCO}]^3 \tag{16}$$

TABLE 1. Kinetic Values Relative to the Reaction of n-Butanol (nBu) with Naphthylisocyanate (αNI)[a]

Expt no.	T (°C)	nBu[b] $\times 10^{-2}$ (mol/L)	αNI[a] $\times 10^{-2}$ (mol/L)	[αNBuC] $\times 10^{-2}$ (mol/L)	[Oct.Sn] $\times 10^{-4}$ (mol/L)	Solvent	K_{obs} $\times 10^{-4}$ (mol/L/s)	ΔH^* (kcal/mol)	ΔS^* (cal/mol)
1	20	25.70	4.30	0	7	Toluene	2.50		
2	30	26.80	4.50	0	7	"	3.17		
3	40	24.00	4.42	0	7	"	10.17	11.80	23.20
4	50	27.80	4.10	0	7	"	11.33		
5	60	28.45	4.60	0	7	"	25.00		
6	20	27.76	4.38	0	0	"	0.137		
7	30	27.90	4.63	0	0	"	0.145	3.10	11.9
8	40	24.00	4.40	0	0	"	0.158		
9	60	26.90	4.70	0	0	"	0.250		
10	40	40.70	3.77	2.47	0	"	0.75		
11	40	32.60	6.19	1.15	0	"	0.58		
12	40	0	6.45	2.02	0	"	0		
13	20	75.30	4.00	0	0	Diglyme	0.78		
14	30	85.30	4.21	0	0	"	1.48		
15	40	55.10	4.48	0	0	"	1.9	7.50	6.80
16	50	57.90	4.48	0	0	"	2.87		
17	60	59.80	4.40	0	0	"	3.63		

18	20	95.70	2.84	0	0	"	0.25		
19	30	84.50	4.20	0	7	"	0.28		
20	40	84.90	4.78	0	7	"	0.45	7.9	5.4
21	50	87.20	4.63	0	7	"	0.60		
22	60	84.70	4.05	0	7	"	1.25		
23	40	0	4.19	1.64	0	"	26.7 100		
24	40	78.45	4.07	1.15	0	"	23.34 0.7		
25	20	74.60	5.62	0	75	"	1.38 1.10		
26	20	79.20	5.81	0	45	"	1.2 0.7		
27	20	78.10	6.15	0	23	"	0.75 0.45		

$^{a}\alpha NB_{u}$ is naphthylcarbamate, and Oct.Sn is tin octoate. a and b are the initial concentrations of αNI and nBu.

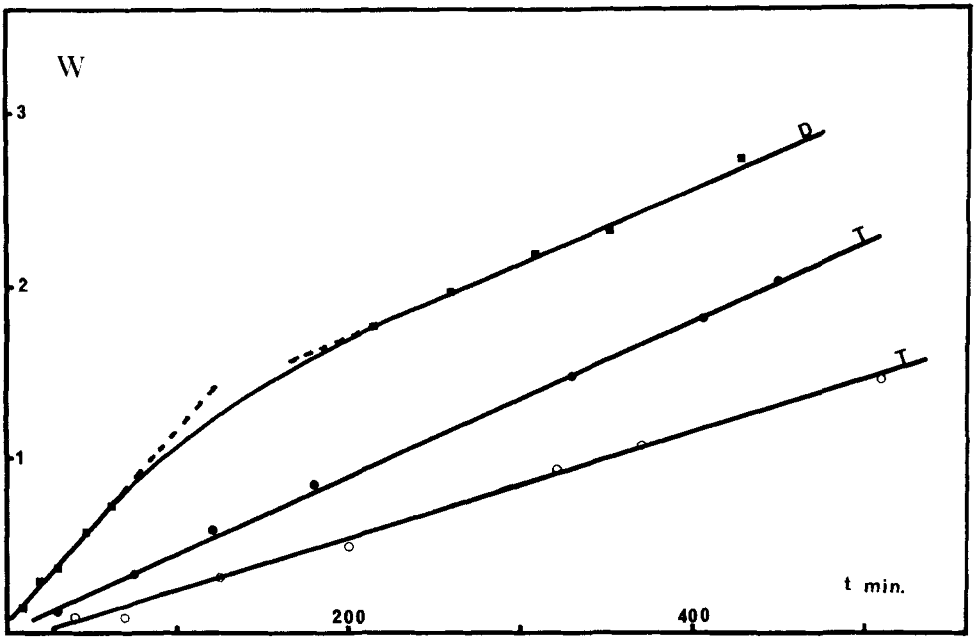


FIG. 5. Effect of initially added naphthylbutylcarbamate on the kinetics of the reaction. Plot of W (see text) against time (min). Temperature = 40°C, D = diglyme, T = toluene. [Naphthylbutylcarbamate]: (■) 1.15×10^{-4}, (●) 2.47×10^{-4}, (○) 1.15×10^{-4} mol/L.

If the existence of a quasistationary state is accepted, the concentrations of the various complex can be obtained from Relations (3) to (6):

$$[\text{Complex I}] = k_2[\text{R'OH}][\text{C}]$$

$$[\text{Complex II}] = k_3[\text{R'OH}][\text{S}] = k_3'[\text{R'OH}]$$

$$[\text{Complex III}] = k_4[\text{RNCO}][\text{C}]$$

$$[\text{Complex IV}] = k_5[\text{RNCO}][\text{S}] = k_5'[\text{RNCO}]$$

The following equations can be developed:

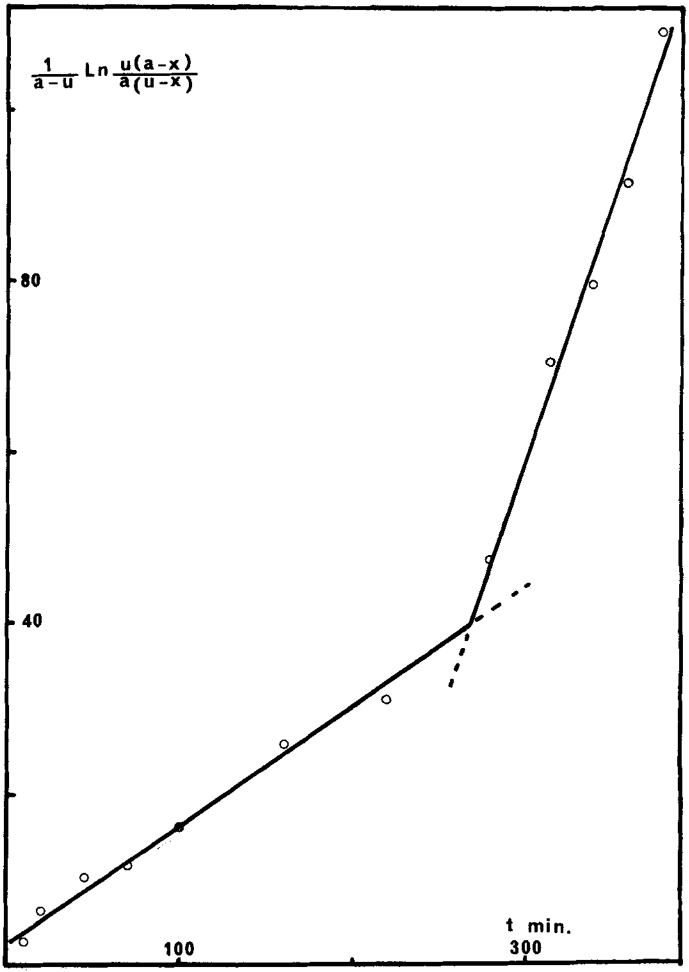


FIG. 6. Allophanate and biuret formation in diglyme. u, a, and x: see text. Temperature = 40°C. [α-Naphthylisocyanate] = 4.2×10^{-3} mol/L. [Naphthylbutylcarbamate] = 1.64×10^{-3} mol/L.

$$\frac{dx}{dt} = [k_0 + k_3'k_7 + k_5'k_9 + (k_2k_6 + k_4k_8)[C]](a - x)(b - x)$$

$$- k_{10}(x - y)(a - x - y)$$

$$= [K + K_c[C]] (a - x)(b - x) - k_{10}(x - y)(a - x - y) \qquad (17)$$

with

$$K = k_0 + k_3'k_7 + k_5'k_9$$

$$K_c = k_2k_6 + k_4k_8$$

$$\frac{dv}{dt} = - k_{11}(a - x - y - 2v)^2 \qquad (18)$$

$$\frac{dz}{dt} = -k_{12}(a - x - y - 2v - 3z)^3 \qquad (19)$$

If n is the overall concentration of the reacted isocyanate, the general kinetics of the process is given by

$$\frac{dn}{dt} = [K + K_c[C]] (a - x)(b - x) - k_{10}(x - y)(a - x - y)$$

$$- k_{11}(a - x - y - 2v)^2 - k_{12}(a - x - y - 2v - 3z)^3 \qquad (20)$$

Arnold, Nelson, and Verbanc [3] analyzed the dimerization of isocyanate resulting in an uretidione. This reaction takes place only under certain conditions of temperature and in the presence of basic catalysts such as pyridine, amines, and phosphines. Since our system has an acidic character, we can consider that this reaction does not take place. On the other hand, we verified that in the presence of tin octoate, the isocyanate alone (i.e., without added alcohol) does not dimerize or trimerize even after contact times beyond the duration of the kinetic study. Nawata, Krista, and Frisch [9] have determined the conditions of isocyanurate formation, and they are quite different from our experimental choice. Moreover, the literature [9] mentions that tin octoate does not lead to the formation of allophanate or isocyanurate. The only case where allophanate formation was observed corresponds to Expt 23 where diglyme is the solvent. Two reactions take place successively:

$$\text{isocyanate} + \text{carbamate} \longrightarrow \text{allophanate}$$

$$\text{allophanate} + \text{isocyanate} \longrightarrow \text{biuret}$$

Their rate constants (26.7×10^{-4} for the first and 0.01 for the second) are much higher than those obtained for the reaction isocyanate-alcohol. Consequently these reactions do not control the overall kinetics. Moreover, in our system the allophanate formation is strongly handicapped since the alcohol concentrations are higher than those of the isocyanate. For this reason Relation (20) is reduced to

$$-\frac{dx}{dt} = [K + K_c[C]](a - x)(b - x) \tag{21}$$

corresponding to experimental results if

$$k_{obs} = K + K_c[C]$$

The value of k_{obs} depends on temperature, solvent, and catalyst. In the case of an uncatalyzed reaction, K_c is zero. In toluene, k_{obs} represents the true constant k_0 of the direct reaction of carbamate formation since Reactions (4) and (6) do not take place in this solvent. On the other hand, when the solvent is diglyme, Reactions (4) and (7) must be taken into consideration and their contribution appears in the activation enthalpy:

$-\Delta H_0^* = 3.1$ kcal/mol (toluene)

$-\Delta H^* = 7.5$ kcal/mol (diglyme)

From these two values the activation enthalpy of complexation $-\Delta H_c^* = 4.4$ kcal/mol can be obtained. However, this association is not really a complexation but rather a destruction by diglyme of the hydrogen bond association between the molecules of alcohol and a solvation of the molecules of alcohol by the diglyme. The solvated molecules are more reactive than associated molecules toward isocyanate. This is the reason for $(k_{obs})_{diglyme} > (k_{obs})_{toluene}$.

In the case of the reaction catalyzed by tin octoate, the effect of solvent is very important. With toluene, the rate constant is increased.

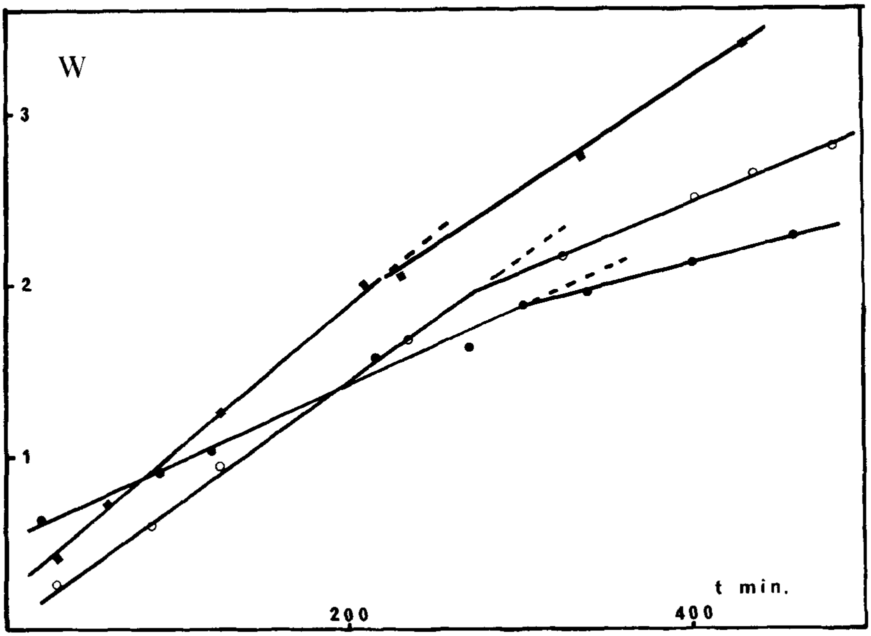
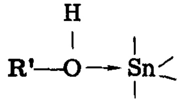


FIG. 7. Effect of tin octoate concentration. Plot of W (see text) against time (min). Solvent = diglyme. Temperature = 20°C. [Tin octoate]: (■) 7.5 × 10^{-3}, (○) 4.5 × 10^{-3}, (●) 2.3 × 10^{-3} mol/L.

This has an effect on the activation enthalpy of the reaction: $\Delta H^* = 11.8$ kcal/mol. This fact may be explained by a destruction of the aggregates of alcohol molecules followed by the formation of a complex of the type



$$\mathrm{R'{-}\overset{\displaystyle H}{\overset{|}{O}}\rightarrow \overset{|}{\underset{|}{Sn}}\!<}$$

which is more reactive toward isocyanate molecules. We studied this type of complexation by ^{1}H NMR for a series of alcohols in the presence of tin octoate in benzene and we observed a complex formation [10]. This mechanism is in good agreement with Farkas [5]. When diglyme is used as a solvent, there is no effect of catalyst except at high concentrations (Expt 25, 26, and 27). Figure 7 shows this effect. For a chosen concentration of tin octoate, two straight lines have been obtained. The first corresponds to the catalytic effect (tin octoate is a weak catalyst). When more than 50% of isocyanate is consumed, the viscosity of the solution is greater and a decrease of rate is observed. We did not take into consideration the contribution of the reaction of allophanate since, if this reaction takes place, the rate constant should increase. A possible explanation is to suppose that diglyme solvates the alcohol and hinders its complexation with tin octoate. Only a very small variation of enthalpy (7.9 instead of 7.5 kcal/mol) is observed. This solvent has, in fact, a double influence on the alcohol and the catalyst. It appears that the overall effect is controlled by the activation entropy (6.8 in the case of the uncatalyzed reaction and 5.4 in the case of the reaction catalyzed by tin octoate).

In conclusion, the condensation of n-butanol with α-naphthylisocyanate follows simple second-order kinetics. However, various secondary reactions may take place under certain experimental conditions depending on temperature, solvent, and catalyst.

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