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### On the Mechanism of Polyurethane Formation Catalyzed by Metal Chelates and Organotin Compounds

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## On the Mechanism of Polyurethane Formation Catalyzed by Metal Chelates and Organotin Compounds

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### SUMMARY

The mechanism of the catalyzed linear polyurethane formation in the presence of dibutyltin dilaurate, copper acetylacetonate, and similar catalysts was investigated. It was found that the central ion coordinates with the isocyanate group. The second reacting component may be coordinated by the organic substituent or ligand groups near the central ion. It was concluded that the catalytic mechanism would vary depending on such reaction conditions as temperature, solvent, and the nature of the ligands near the central ion.

### INTRODUCTION

The mechanism of linear polyurethane formation is not well understood since there is no definite opinion as to the nature of the elementary act of NCO and OH group interaction. The theories on the catalysis of isocyanate-alcohol reactions by metal compounds also appear to be contradictory[1-3].

An analysis of some data concerning the mechanism of polyurethane formation in the presence of different catalysts leads one to conclude that the most reasonable mechanism for the reaction is one involving the

formation of intermediate complexes between the catalyst and the reagents [4, 5]. Such complexes have been identified in some cases [6, 7].

The catalytic action of some p-diketonates of metals has been studied by Fisher and Weisfeld; their semi-quantitative calculations of relative activity of the acetylacetonate series have been published [8, 9]. The mechanism of urethane formation has been studied by Bruenner and Oberth [10], who have discussed the possibility that catalyst modification leads to the formation of an active  $\text{Fe}(\text{AcAc})_2\text{OR}$  compound. This compound is active as a catalyst in the reaction of urethane formation through an intermediate complex involving alcohol. These investigations [7-10] represent the available literature on the catalysis of urethane formation by metal chelates.

In contrast, the mechanism of urethane formation in the presence of organotin compounds has been investigated in more details [3]. Some authors [11] believe that the reaction proceeds through the intermediate (binary or ternary) complexation of the organotin compound with the reagents. Another mechanism proposes the reaction proceeds through consecutive stages which can be described as the coordination-anionic reaction complicated by alcohol of the formed metal carbamate [12]. Neither of these two interpretations of the catalytic mechanism have been fully proved.

The purpose of the present study is the investigation of kinetics and mechanism of linear polyurethane formation from hexamethylene diisocyanate (HMDI) and di- and triethyleneglycol (DEG; TEG) in solution in the presence of dibutyltin dilaurate (DBTDL) and copper-bis-acetylacetonate  $[\text{Cu}(\text{AcAc})_2]$ .

The choice of these compounds as catalysts is based on their high catalytic activity. The elementary act of the interaction of NCO and OH groups has been studied using as a model the system phenylisocyanate-methanol in the presence of  $\text{Cu}(\text{AcAc})_2$  and  $\text{Be}(\text{AcAc})_2$ , respectively, in which the reactant concentration approximated the concentration of reagents in the polyurethane reaction.

## RESULTS AND DISCUSSION

The kinetics of reactions of HMDI and DEG/TEG interaction has been investigated in chlorobenzene at a reagent concentration of  $10^{-1}$  mole/l and a catalyst concentration near  $10^{-5}$  mole/l. It was established that the sequence of the preliminary mixing of DBTDL with each of the components

and the time of the standing following the preliminary mixing prior to the reaction did not affect the reaction rate. When  $\text{Cu}(\text{AcAc})_2$  was used as the catalyst, the character of reaction of HMDI and TEG was dependent on the sequence of mixing catalyst and reagents (Fig. 1). At a  $\text{Cu}(\text{AcAc})_2$  concentration of  $5 \times 10^{-5}$  mole/l with a preliminary standing with TEG, an induction period was observed, its duration being dependent on catalyst concentration and temperature. The induction period was absent when  $\text{Cu}(\text{AcAc})_2$ , at a concentration of  $2.5 \times 10^{-5}$  mole/l, was preliminarily mixed with HMDI.

To explain these facts let us consider some data concerning the urethane formation from phenylisocyanate and methanol in the presence of  $\text{Cu}(\text{AcAc})_2$ . A study of  $\text{Cu}(\text{AcAc})_2$ , phenylisocyanate, and methanol interaction was made by means of spectroscopy in the visible and IR regions. The  $\text{Cu}(\text{AcAc})_2$  absorbance in dioxane in the visible region is connected with the electron transfer between Cu d-orbitals. For some compounds with the symmetry  $D_{2h}$ , which is inherent in  $\text{Cu}(\text{AcAc})_2$ , 4 transitions can be expected. However, there are only three bands in the spectra of crystalline  $\text{Cu}(\text{AcAc})_2$  [13]. In dioxane solution there is only one wide asymmetric band with a maximum near  $610 \text{ m}\mu$ . This shows the interaction of  $\text{Cu}^{2+}$  and the solvent which leads to the complex formation. The band analysis also shows that the field created by ligands surrounding the Cu ion in dioxane solution has the symmetry of a tetragonal bipyramid, i.e., the Cu ion has the axial bonds with dioxane molecules.

The absorbance of  $\text{Cu}(\text{AcAc})_2$  in the visible region is sensitive to the presence of phenylisocyanate in solution. By the addition of phenylisocyanate, the color of the solution changes, in the course of time, from blue to green. The increase in phenylisocyanate concentration leads to the broadening and increasing of the intensity of the absorption band of  $\text{Cu}(\text{AcAc})_2$  (Fig. 2). This is considered evidence that the interaction of phenylisocyanate with the central ion of  $\text{Cu}(\text{AcAc})_2$  results in complex formation.

By using the method of limited logarithmically, it was established that the ratio of components in the complex is 1:1. It was therefore formed by substitution of a dioxane molecule by a phenylisocyanate molecule. To demonstrate the proposition that interaction of phenylisocyanate with  $\text{Cu}(\text{AcAc})_2$  takes place without opening or clipping off the chelate ring, the IR adsorption of  $\text{Cu}(\text{AcAc})_2$  solution in chloroform in the presence of HMDI was studied since the latter does not absorb in the  $1700\text{--}1500 \text{ cm}^{-1}$  region;  $\text{Cu}(\text{AcAc})_2$  has two sharp bands at  $1580$  and  $1530 \text{ cm}^{-1}$  associated with the chelate ring [14]. Opening or clipping off one

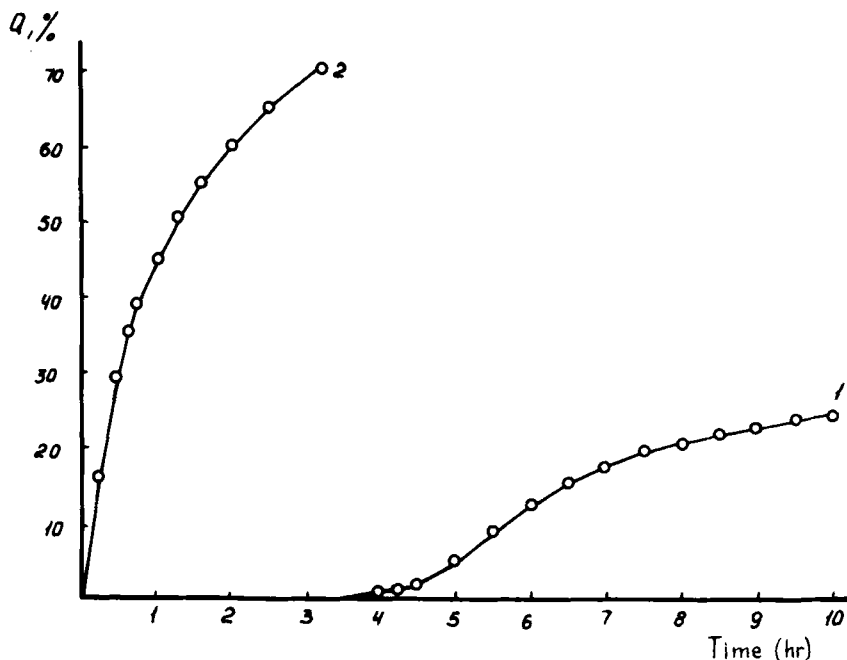


Fig. 1. The dependence of the degree of reaction completion on time for different orders of preliminary mixing of  $\text{Cu}(\text{AcAc})_2$  with reagents.

(1)  $\text{Cu}(\text{AcAc})_2$  + TEG. (2)  $\text{Cu}(\text{AcAc})_2$  + HMDI.

of two chelate rings should reduce the intensity of these bands to one-half their values; this was not observed in the presence of HMDI. The chelate catalyst stability in the presence of phenylisocyanate is confirmed by its ESR spectra (Fig. 3) for bis(3-ethylacetylacetonate) Cu 1) in a mixture of 60% toluene and 40% chloroform and 2) in phenylisocyanate, respectively, at the room temperature.

The values of  $g$ -factor and splitting "a" calculated from the spectra are equal, corresponding to 2.119 and  $77.16 \times 10^{-4} \text{ cm}^{-1}$  and 2.123 and  $76.78 \times 10^{-4} \text{ cm}^{-1}$ , respectively. These data establish the chelate-catalyst stability as well as complex formation in the phenylisocyanate solution. Thus, the interaction of  $\text{Cu}(\text{AcAc})_2$  and phenylisocyanate leads to the complex formation of type  $\text{C}_6\text{H}_5\text{NCO} \cdot \text{Cu}(\text{AcAc})_2$ . Owing to the tetrahedral symmetry of  $\text{Be}(\text{AcAc})_2$ , the  $\text{Be}^{2+}$  ion cannot coordinate the isocyanate and therefore  $\text{Be}(\text{AcAc})_2$  does not catalyze the interaction of  $\text{PhNCO}$  and methanol.

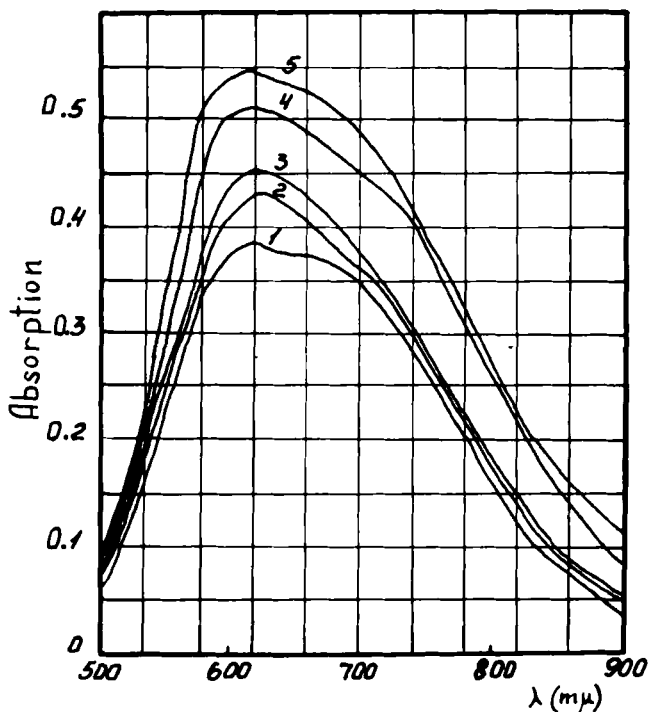
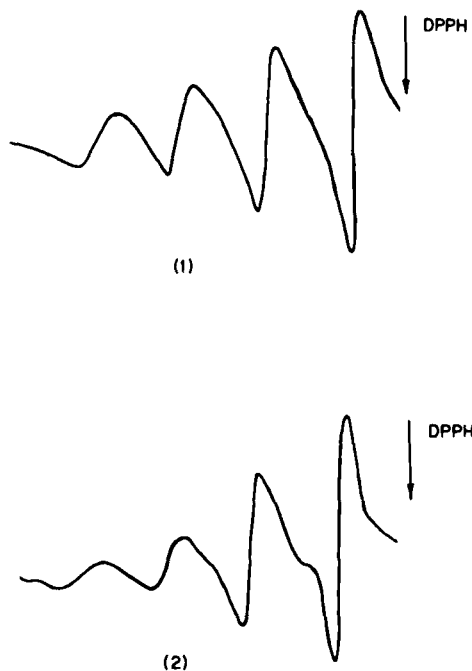


Fig. 2.  $\text{Cu}(\text{AcAc})_2$  absorption with growing concentrations of phenylisocyanate in dioxane (in mole liter<sup>-1</sup>). (1)  $1 \times 10^{-3}$ ; (2)  $0.96 \times 10^{-3} - 0.56$ ; (3)  $0.95 \times 10^{-3} - 0.82$ ; (4)  $1.04 \times 10^{-3} - 1.54$ ; (5)  $1.07 \times 10^{-3} - 1.95$ .

For the reaction in dioxane, the character of kinetic curves depends also on the sequence of mixing the catalyst and reagents. If methanol is the first to be introduced into the reaction, a distinct induction period is observed; the reaction rate is less than in the case in which isocyanate and catalyst are allowed to interact first. Thus, one may conclude that the isocyanate  $\text{Cu}(\text{AcAc})_2$  complex is responsible for the catalytic action and that its formation is time-dependent, which explains the appearance of an induction period.

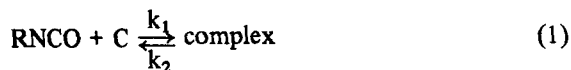
The reaction of HMDI and TEG was studied for two monomer concentrations, 0.1 and 0.2 mole/l at  $\text{NCO}/\text{OH} = 1$ . The  $\text{Cu}(\text{AcAc})_2$  concentration was changed in the range of  $3\text{--}12 \times 10^{-5}$  mole/l. The catalyst was allowed to remain in preliminary contact with the isocyanate for a period of 45-50 min.



**Fig. 3** EPR spectra of bis(3-ethylacetylacetonate)Cu in a mixture of chloroform 40%—toluene 60% (1) and in phenylisocyanate (2) at room temperature.

The experimental data concerning the kinetics of the reaction of HMDI and TEG were evaluated according to the following suggestion mechanism:

- 1) The catalyst (C) and diisocyanate (RNCO) form a complex



Equilibrium constant:  $K = k_1/k_2$

- 2) The reaction rate limiting step is a slow bimolecular interaction of the intermediate complex and glycol (R'OH):



The following conclusions refer to the case where catalyst concentration is much less than the concentration of the initial compounds and the complex concentration is balanced instantaneously.

From Eq. (1) it follows that complex concentration is

$$[\text{complex}] = K[\text{RNCO}][\text{C}]$$

where  $[\text{RNCO}]$  and  $[\text{C}]$  are equilibrium concentrations. The initial concentration in terms of equilibrium concentrations is expressed as

$$[\text{complex}] = \frac{K[\text{RNCO}]_0[\text{C}]_0}{1 + K[\text{RNCO}]_0} \quad (3)$$

Then, the urethane formation rate then will be:

$$W = k_3 [\text{complex}] [\text{R}'\text{OH}]$$

$$W = \frac{k_3 K [\text{RNCO}]_0 [\text{R}'\text{OH}]_0 [\text{C}]_0}{1 + K [\text{RNCO}]_0}$$

or

$$\frac{dx}{d\tau} = \frac{k_3 K (a - x)(b - x)(C)}{1 + K(a - x)} \quad (4)$$

If the Vant' Hoff principle [1] is applied to the given system, the more general expression (5) is obtained for the reaction rate in which  $[\text{RNCO}] = [\text{R}'\text{OH}]$ .

$$\frac{dx}{d\tau} = \frac{k_3 k_1 (a - x)(b - x)(C)}{k_2 + k_3(b - x)} \quad \text{or}$$

or

$$\frac{dx}{d\tau} = \frac{k_3 K (a - x)^2 C_0}{1 + K(a - x)} \quad (5)$$

From the above differential equation for the reaction rate, it is clear that the reaction order will be determined by the value of the stability constant for complex  $\text{Cu}^{2+}$  and isocyanate or by the absolute values of  $k_2$  and  $k_3$ . For two limiting cases  $K(a - x) \gg 1$  or  $k_3(b - x) \gg k_2$ , the reaction is of the first order. If  $K(a - x) \ll 1$  or  $k_3(b - x) \ll k_2$ , the reaction can be described as a reaction of second-order.

The rate constants for reactions of HMDI and TEG do not remain constant during the course of the reaction under the conditions investigated and were calculated as first- or second-order accordingly. We have, therefore, calculated the rate constants from Eq. (4) in its integral form.



The integration of Eq. (5) leads to the expressions,

$$\tau = \frac{1}{k_3 KC} \frac{x}{a(a-x)} + \frac{1}{KC} \ln \frac{a}{a-x}$$

or

$$k_3 = \frac{1}{KC} \frac{x}{a(a-x)\tau} + \frac{1}{C\tau} \ln \frac{a}{a-x} \quad (6)$$

By substitutions of

$$\frac{1}{\tau} \ln \frac{a}{a-x} = W^I \quad \text{and} \quad \frac{x}{a(a-x)\tau} = W^{II}$$

Eq. (6) becomes:

$$k_3 = \frac{1}{KC} W^{II} + \frac{1}{C} W^I \quad (7)$$

in which  $W^I$  and  $W^{II}$  are the rate coefficients calculated for the first- and second-orders, respectively.

To obtain values for  $K$  and  $k_3$ , Eq. (7) is written as:

$$\left. \begin{aligned} k_3 &= \frac{1}{KC_1} W_1^{II} + \frac{1}{C} W_1^I \\ k_3 &= \frac{1}{KC_2} W_2^{II} + \frac{1}{C_2} W_2^I \end{aligned} \right\} \quad (8)$$

It is much easier to calculate the complex equilibrium constant from one experiment having calculated  $W_1^{II}$  and  $W_1^I$  for different values of  $\tau$ . The values for  $k_3$  and  $K$  found in such a way remain constant during the course of the reaction. The experimental data of a set of experiments adapted to a given scheme are presented in Table 1. The reaction of HMDI and DEG in the presence of dibutyltin dilaurate proceeds quite differently.

The dependence of the conversion degree on time at a catalyst concentration within the range of  $2.6 \times 10^{-5}$  mole/l is linear, irrespective of the sequence of the mixing of the catalyst with reagents. It shows that the reaction rate in such conditions is constant, i.e., independent of the concentration of the reagents. The experimental data for the dependence of

**Table 1.** Values of  $k_3$  and  $K$  Calculated in Conformity with Proposed Scheme for Reaction of GMDI and TEG, Catalyzed by BDTDL

$C_m$ (mole/l)	$C_c \times 10^5$ (mole/l)	Q (%)	$k_3$ , ( $l \text{ mole}^{-1} \text{ sec}^{-1}$ )	$K$ ( $l \text{ mole}^{-1}$ )
0.1	6.6	85	3.34	33.9
0.1	11.8	65	3.37	34.1
0.1	2.9	75	3.38	30.9
0.2	3.1	60	3.29	32.6

Q on  $\tau$  are presented in Fig. 4. The data can be interpreted as due to an acceleration of the process. Such an acceleration is due either to the synergetic action of the urethane formed, or to the additional isocyanate consumption during the secondary reaction due to allophanate formation. In fact, the reaction of model diurethane from ethyleneglycolmonomethyl ether with HMDI in the presence of DBTDL (concn,  $3 \times 10^{-5}$  mole/l) does not take place.

The infrared spectra of the polyurethanes obtained in uncatalyzed reaction and in the reaction catalyzed by TDBDL are identical as shown in Fig. 5. These data exclude the allophanate formation; the same conclusion was drawn by Frisch and his co-workers [15].

In order to find out the synergetic effect of urethanes in the presence of DBTDL, the dependence of the reaction rate on the addition of the diurethanes of HMDI-alcohol was also studied and a synergetic effect was not observed. The addition of diurethanes based on HMDI and ethyleneglycol monomethyl ether, as well as of low molecular polyurethane fraction formed in the reaction, slow down the process to a great extent. The experimental data concerning the effect of the addition of diurethanes on the reaction rate are presented in Table 2. On the basis of the above results, a reaction mechanism can be proposed which includes a ternary complex of the catalyst with the diisocyanate and the glycol. The rate limiting stage is apparently the interaction of OH and NCO groups in the catalyst coordination sphere. The high activity of the organotin compounds in the urethane formation is probably associated with the ability of the central Sn ion to coordinate easily with the NCO group having free 4f and 5d orbitals. Besides, organotin compounds which bonds such Sn-Cl or Sn-O can form H bonds with the OH groups of glycol similar to metal

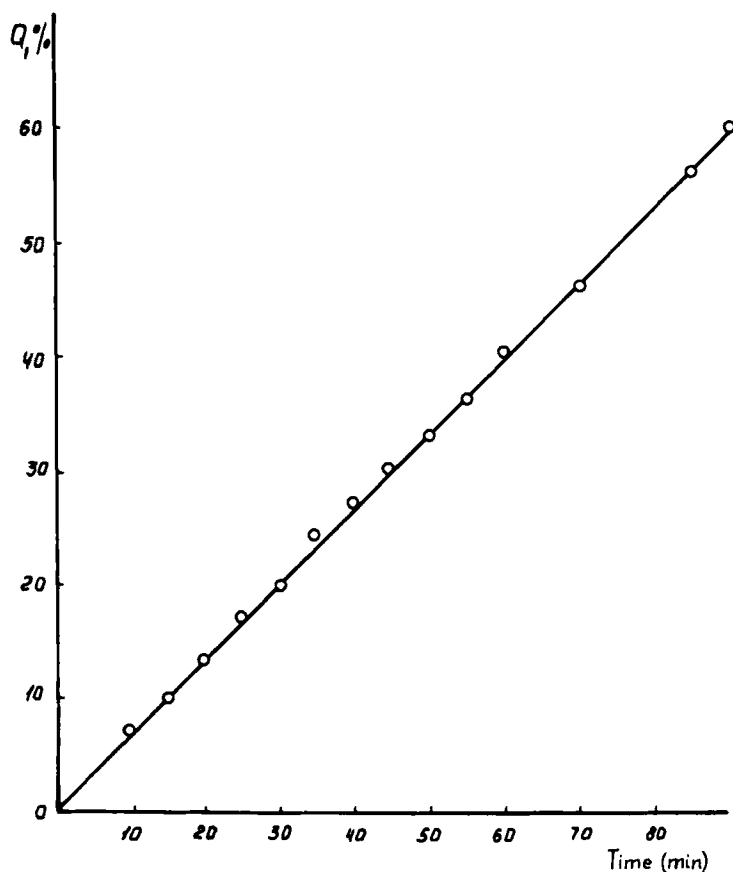
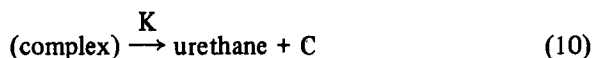
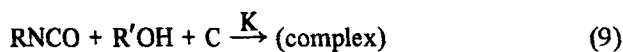


Fig. 4. The dependence of  $Q$  on  $\tau$  of the HMDI reaction with DEG, catalyzed by BDTD ( $C_m = 0.2$  mole/l;  $C_c = 2 \times 10$  mole/l;  $t = 50^\circ\text{C}$ ).

chelates [6]. Thus, the central ion as well as the haloid atom or the oxygen of acid residue may take part in the complex formation. In such a case, the reaction mechanism scheme is presented as follows:



If the ternary complex concentration is constant and is equal to the equilibrium concentration, then

$$(\text{complex}) = K (\text{RNCO})(\text{ROH})(\text{C}) \quad (11)$$

Expressing the equilibrium diisocyanate, glycol, and catalyst concentrations through initial ones, and, taking into consideration the fact that the catalyst concentration is 4 orders less than that of reagents, there is obtained the expression

$$(\text{complex}) = \frac{K[\text{RNCO}]_0[\text{R}'\text{OH}]_0[\text{C}]_0}{1 + K[\text{RNCO}]_0[\text{R}'\text{OH}]_0} \quad (12)$$

Then, for the reaction rate determined by the Eq. (10) at  $\text{RNCO} = \text{ROH}$ ,

$$\frac{dx}{d\tau} = \frac{kK(a-x)(b-x)[\text{C}]_0}{1 + K(a-x)(b-x)}$$

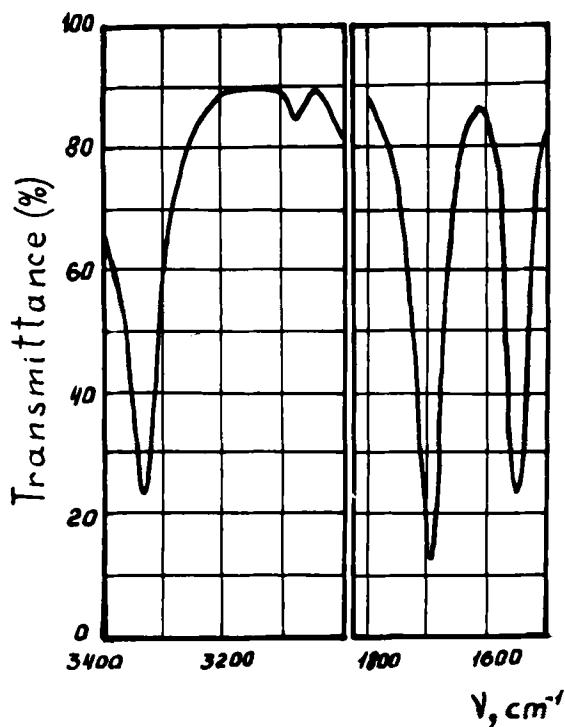


Fig. 5. Infrared spectrum of polyurethane from DEG and HMDI.

Table 2. Influence of the Addition of Diurethanes on the Reaction Rate of HMDI with DEG in Chlorobenzene at 50°C

Experi- ment No.	$C_m$ (mole/l)	$C_c \times 10^5$ (mole/l)	Cureth (mole/l)	$\tau$ (min)	Mixing order
20	0.19	2.82	—	30	DBTDL + DEG
21	0.18	2.73	—	30	DBTDL + HMDI
35	0.19	2.80	0.1	38	DBTDL + DEG + $[C_4H_9OCNH]_2(CH_2)_6$
36	0.18	2.81	0.1	32	DBTDL + GMDI + $[C_4H_9OCNH]_2(CH_2)_6$
43	0.22	2.15	—	70	DBTDL + DEG
41	0.19	1.85	30% wt	400	DBTDL + DEG + $[CH_3OCH_2CH_2OCNH](CH_2)_6$
42	0.19	1.93	30% wt	430	DBTDL + DEG + polyurethane fraction

Then, choosing the initial reagents concentration in such a way that

$$K(a - x)(b - x) \gg 1$$

there is obtained

$$dx/d\tau = kC_0$$

In this case, the reaction rate is proportional to the catalyst concentration; its order approaches zero. It is possible to describe the kinetic curve by the equation of zero-reagent-order in the conditions under investigation. The observed dependence allows us to calculate the rate constant of the limiting stage of the urethane formation. The data of the typical experiment with monomer concentration at  $0.4 \times 10^{-5}$  mole/l and DBTDL concentration  $4 \times 10^{-5}$  mole/l are presented in Table 3. The rate constant is calculated for the zero-order reaction. The reaction rate is proportional to the catalyst concentration; its reagent order being equal to a zero-order.

For homogeneous systems, all schemes of mechanisms including the formation of the catalyst and reagents intermediate complexes, a zero-reaction-order is possible only in one case; namely, when a ternary complex is responsible for the catalysis, the catalyst is practically combined in complexes, and the reaction rate limiting stage is the OH and NCO interaction in the catalyst coordination sphere. The experimental data

**Table 3.** Reaction of HMDI with DEG, Catalyzed by DBTDL  
( $C_m = 0.44$  mole/l;  $C_c = 4.4 \times 10^{-5}$  mole/l;  $t = 50^\circ\text{C}$  in Chlorobenzene)

$\tau$ (min)	Q (%)	$x \times 10^2$ (mole/l)	$\frac{x}{\tau} \times 10^2$ (mole l min)	$K_0$ ( $\text{min}^{-1}$ )
10	8.2	3.6	0.36	82
20	14.9	6.6	0.33	77
30	23.2	10.2	0.34	77
43	33.1	14.6	0.34	77
55	43.1	18.9	0.32	73
60	46.1	20.3	0.34	77
70	54.0	23.8	0.34	74

of the reaction of HMDI with DEG in the presence of DBTDL are satisfactorily described by Eq. (10) derived for the reaction rate. The reaction rate has linear dependence on the catalyst (DBTDL) concentration for two sequences of mixing it with reagents. Figure 6 shows the logarithmic reaction rate dependence on the logarithmic catalyst concentration. The rate constants for both cases are nearly equal:  $K_I = 50.12 \text{ min}^{-1}$  and  $K_{II} = 60.26 \text{ min}^{-1}$ .

## EXPERIMENTAL

### Preparation of the Initial Reagents

Hexamethylenediisocyanate was purified by double vacuum distillation; bp, 75-75.5°/1 mm;  $n_D^{20}$  1.4520; product content, 98.5%

Diethyleneglycol was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , distilled in vacuo, and then dried once again over the molecular sieves of  $\text{Na}_2\text{AM}$  and redistilled; bp, 99.5°C/1.5 mm;  $n_D^{20}$  1.4465; moisture content according to Fischer, 0.01%.

Phenylisocyanate was distilled in vacuo bp 56°C/14 mm;  $n_D^{20}$  1.5370; pure product content, 98.8%.

All solvents were purified by the known methods [16].

$\text{Cu}(\text{AcAc})_2$  was synthesized by mixing the distilled acetyl-acetone with freshly precipitated  $\text{Cu}(\text{OH})_2$  in water suspension. The isolated  $\text{Cu}(\text{AcAc})_2$  was then filtered, washed with water, dried in air, recrystallized from hot dioxane and, finally, purified by sublimation in vacuum,  $6 \times 10^{-3}$  mm at 115°C. Analysis: Cu found 24.0%; calculated, Cu 24.3%. Dibutyltin dilaurate; calculated,  $\text{Sn}^{\text{IV}}$  18.73%; found 18.48%.

### Method

The absorbance spectra of the solvents were recorded on a SF-4A spectrophotometer; and the IR spectra on a UR-10 spectrophotometer.

The reaction kinetics of HMDI with DEG was studied with the aid of dilatometric method. The dilatometers were filled in vacuo at  $10^{-3}$  mm Hg, and then placed into a ultrathermostat where the temperature was maintained precisely  $\pm 0.02^\circ\text{C}$ . By means of a CM-6 cathetometer, the position of the meniscus in the capillary was registered. After making measurements, the dilatometer was opened and its content poured out into a measuring flask containing the titrated solution of dibutylamine. The quantity of the reacted diisocyanate was determined by 0.1 N HCl titration of the mixture in the presence of bromphenol blue.

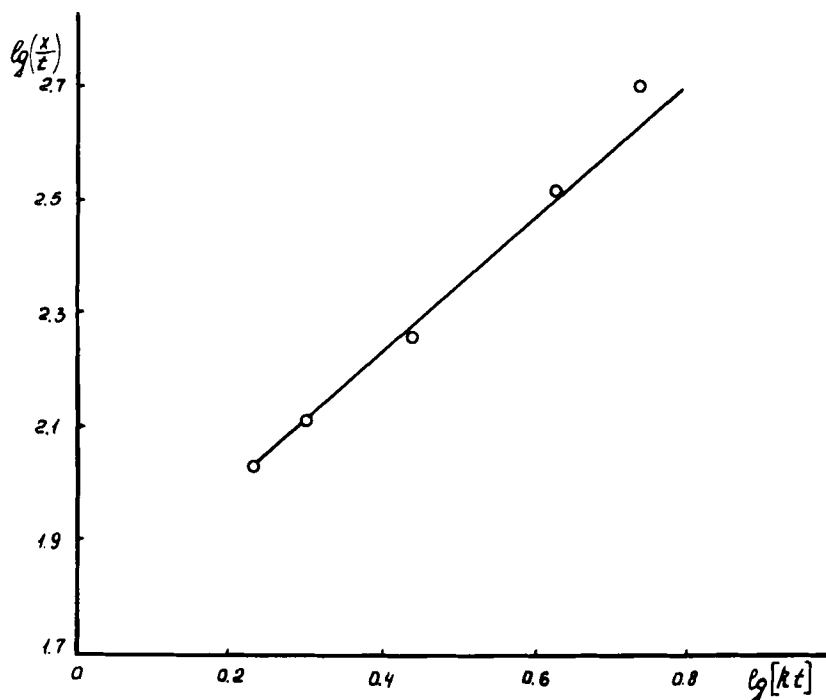


Fig. 6. The dependence of the reaction rate on BDTDL concentration ( $C_m = 0.2$  mole/l;  $NCO/OH = 1$ ;  $t = 50^\circ\text{C}$ ).

### CONCLUSIONS

The above-mentioned results make it possible to draw some conclusions concerning the catalytic mechanism of urethane formation in the presence of DBTDL,  $\text{Cu}(\text{AcAc})_2$ , and the like. The central ion coordinates the NCO group. The process is time-dependent, as was observed for  $\text{Cu}(\text{AcAc})_2$ . The second reagent (glycol) can be coordinate by the organic substituting group (or ligand) at the central ion. The reaction takes place in a coordination catalyst sphere, from which follows Eq. (10). There can also be a reaction between the catalyst complex with the NCO group and uncoordinated alcohol; the reaction can then be first- or second-order. It is also possible that the degree of participation of different stages of mechanism are involved measurably, in which case the reaction is described by a more complicated equation. The catalytic mechanism is dependent on the reaction conditions



such as temperature, solvent, and type of ligand at the catalyst central ion. A single scheme cannot be proposed for the catalysis mechanism of urethane formation by metal compounds because the mechanism for even one and the same catalyst will be changed with changing complex formation conditions. Nonetheless, taking into consideration the results obtained in this study, it is possible to propose reasonably what kind of mechanism will dominate the reaction.

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