KINETICS AND MECHANISM OF CATALYTIC URETHANE FORMATION BY REACTION OF FLUORINATED OLIGOETHER DIOLS AND MODEL ALCOHOLS WITH CYCLOALIPHATIC AND AROMATIC ISOCYANATES

St. Petersburg State Institute of Technology (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia

Abstract—The kinetics of the dibutyltin dilaurate (DBTDL) – catalyzed urethane formation reactions of cyclohexyl isocyanate (CHI) with model monofunctional fluorinated alcohols and fluoropolyether diol Z-DOL H-1000 of various molecular weights (100 – 1084 g·mol⁻¹) in different solvents were studied. IR spectroscopy and chemical titration methods were used for measuring the rate of the total NCO disappearance at 30-60°C. The effect of the reagents and DBTDL catalyst concentrations, the solvent and hydroxyl-containing compound nature, and the temperature on the reaction rate and mechanism were investigated. Depending on the initial reagent concentration and solvent, the reactions could be well described by zero-order, first-order, second-order, or more complex equations. The reaction mechanism, including the formation of intermediate ternary or binary complexes of reagents with the tin catalyst, could vary with the concentration and solvent and even during the reaction. The results were treated with a rate expression analogous to those used for enzymatic reactions. Under the explored conditions, the rate of the uncatalyzed reaction of fluorinated alcohols with CHI was negligible. Moreover, there was no allophanate formation, nor were there other side reactions, catalysis by urethane in the absence of DBTDL, or a synergetic effect in the presence of the tin catalyst.

Keywords: macromonomers; catalyst; structure-property relations.

Polyurethanes (PU) are high-molecular weight compounds containing carbamate (–NHCOO–) units [1]. Urethanes have long been studied, and they are now widely used in almost all branches of industry for the manufacture of rigid or elastic (including foamed) materials, plastics, elastomers, coatings, etc. In particular, PU materials are used for coating of aircrafts and railcars, anticorrosion coating of chemical industry equipment, etc. Pigmented PU coatings are especially valuable for protection of ferrous and nonferrous metals, wood, leather, rubber, fabrics, and paper due to their good adhesion to various substrates, excellent water, air, oil, solvent, and abrasive resistance, perfect insulating properties, high glitter, and wear resistance upon long-term usage [1–5]. The properties of PU can be improved via chemical modification, e.g., by introduction of silicon, halogen (especially fluorine), and other atoms into molecules of initial diols and poly- or macroisocyanates [6, 7]. Fluorine-containing polymers attract specific interest from the viewpoint of their large-scale application due to their very high heat resistance, chemical stability, and other unique properties [8]. They are generally synthesized by radical polymerization of fluorinated monomers such as tetrafluoroethylene, vinylidene or vinyl fluoride, hexafluoropropylene, and chlorotrifluoroethylene. Recent advances in the field of photopolymerization enabled large-scale manufacture of various difunctional derivatives of perfluorinated polyethers (PFPEs) [9] which may be used as macromers for the preparation of segmented polymers. The presence of PFPE segments in macromolecules essentially changes their physicochemical properties, in particular enhances their thermal and chemical stability, reduces the surface energy, changes the refractive index, and reduces the glass transition temperature [10, 11].

Perfluorinated polyether macromolecules with terminal functional groups consist of three segments RₚRₚRHW, where Rₚ is a statistical copolymer composed of CF₂CF₂O and CF₂O constitutional repeating units, and RH is a hydrogenated segment with the corresponding functional groups. The most interesting are PFPEs having terminal hydroxy groups; their structure may be represented as follows [10, 11]:

\[
\begin{align*}
\text{HOCH₂CF₂O(CF₂CF₂O)ₚ(CF₂O)ₚCF₂CH₂O(OCH₂CH₂)ₙH} & \quad \text{Z-DOL TX},
\end{align*}
\]

Rₚ = 1–2; Mₚ = 700 – 4000.
Z-DOL TX is obtained from Z-DOL by reaction with ethylene oxide in the presence of alkali as catalysts. Molecules of such fluorinated diols contain chemically bound segments which strongly differ in nature. Therefore, their physicochemical properties largely depend on the length of the internal segment; in particular, their hydrophobicity is proportional to the length of R₂. Diols Z-DOL TX possessing longer terminal hydrogenated segments are better compatible with hydrogenated solvents and co-monomers, and their reactivity is similar to the reactivity of non-fluorinated diols, whereas the reactivity of Z-DOL in nucleophilic addition reactions is strongly affected by the electron-withdrawing R₃ segment.

We showed previously that fluorinated oligoether diols (FOE) react with aromatic and cycloaliphatic diisocyanates in polar and less polar solvents at an NCO-to-OH ratio of 2 : 1 in the presence of dibutyltin dilaurate (DBTDL) to form oligoether dicarbamates with terminal isocyanate groups, fluorinated macrodiamocyanates [12–14].

It was found that these reactions sometimes conformed well to commonly used second-order kinetic equation up to a high conversion (90–100%, calculated on the reacted hydroxy groups). However, considerable disagreement between the experimental and calculated kinetic curves was often observed at a conversion of 40–60%. The observed differences depended on a number of factors, including solvent properties, temperature, and catalyst [12, 13]. Moreover, the apparent rate constants (k_{app}) formally calculated by the second-order kinetic equation at different conversions depended on the reactant concentrations, and the dependence was described by a curve with maxima [13], which was difficult to rationalize.

Therefore, in the present work we performed a more detailed study on the kinetics of catalytic urethane formation reactions with the use of model fluorinated alcohols with different molecular weights and diol Z-DOL H-1000 (Table 1). As the second reactant we used cyclohexyl isocyanate (CHI) possessing only one NCO group, in contrast to diisocyanates studied previously, which contained chemically nonequivalent NCO groups. The reaction kinetics were studied in solution at an NCO-to-OH ratio of 1 in the presence of DBTDL as catalyst. The effects of reactant concentration, solvent nature, and catalyst concentration on the reaction rate were examined.

The structures and properties of model fluorinated alcohols and Z-DOL H-1000 are given in Table 1. 2,2,2-Trifluoroethanol (TFE, Fluka) was distilled just before use; all other alcohols and Z-DOL H-1000 (Solvay Solexis) were dried for 2 h at 60°C under reduced pressure. Cyclohexyl isocyanate (Aldrich) and dibutyltin dilaurate (M&T Chemicals) were used without additional purification. Ethyl acetate (EA), hexafluoroxylene (HFX), tetrahydrofuran (THF), and methyl isobutyl ketone (MIBK) were purified as described in [12, 13]. The reaction kinetics were studied by IR spectroscopy, as well as by direct determination of the concentration of unreacted NCO groups by chemical titration [12, 13]. The kinetic curves obtained by these independent methods usually coincided, as shown in Fig. 1.

The second-order rate constants at NCO : OH = 1 were calculated by the equation

$$\frac{1}{a} = k \cdot \frac{[\text{Cat}]}{c} \cdot \tau + \frac{1}{a}$$  \hspace{1cm} (1)

where a and c are, respectively, the initial and current concentrations of NCO (mol/l), [Cat] is the catalyst concentration (mol/l), and τ is the reaction time (h). The catalytic rate constant $k_{cat}$ (mol⁻¹ h⁻¹) was calculated as $k_{cat} = k \cdot [\text{Cat}]$, where k is the apparent rate constant expressed in l mol⁻¹ h⁻¹ units.

The first-order rate constants were calculated by the equation

$$\ln \frac{a}{c} = k \cdot [\text{Cat}] \cdot \tau$$  \hspace{1cm} (2)

The catalytic first-order rate constant $k_{cat}$ (s⁻¹ or h⁻¹) was determined from the equation $k_{cat} = k \cdot [\text{Cat}]$, where k is given in l mol⁻¹ s⁻¹ or l mol⁻¹ h⁻¹.

The zero-order reactions (with respect to both isocyanate and alcohol) were described by the kinetic equation

$$W = \frac{dc}{dt} = k \cdot [\text{Cat}]$$  \hspace{1cm} (3)

In this case, $W = k_{cat} = k \cdot [\text{Cat}]$, where $k_{cat}$ is expressed in mol l⁻¹ h⁻¹, and $k$ in s⁻¹ (or h⁻¹). The value of $W = k_{cat}$ for a definite catalyst concentration was determined from the linear relation

$$a - c = k \cdot [\text{Cat}] \cdot \tau$$  \hspace{1cm} (4)

The values of $k$ were determined from the equation $W = k_{cat} = k \cdot [\text{Cat}]$ for different initial catalyst concentrations.

The catalytic rate constants $k_{cat}$ were determined from two or three parallel runs; the relative error in their determination was usually within ± 5 %.

---

**Experimental**

The structures and properties of model fluorinated alcohols and Z-DOL H-1000 are given in Table 1. 2,2,2-Trifluoroethanol (TFE, Fluka) was distilled just before use; all other alcohols and Z-DOL H-1000 (Solvay Solexis) were dried for 2 h at 60°C under reduced pressure. Cyclohexyl isocyanate (Aldrich) and dibutyltin dilaurate (M&T Chemicals) were used without additional purification. Ethyl acetate (EA), hexafluoroxylene (HFX), tetrahydrofuran (THF), and methyl isobutyl ketone (MIBK) were purified as described in [12, 13]. The reaction kinetics were studied by IR spectroscopy, as well as by direct determination of the concentration of unreacted NCO groups by chemical titration [12, 13]. The kinetic curves obtained by these independent methods usually coincided, as shown in Fig. 1.

The second-order rate constants at NCO : OH = 1 were calculated by the equation

$$\frac{1}{a} = k \cdot \frac{[\text{Cat}]}{c} \cdot \tau + \frac{1}{a}$$  \hspace{1cm} (1)

where a and c are, respectively, the initial and current concentrations of NCO (mol/l), [Cat] is the catalyst concentration (mol/l), and τ is the reaction time (h). The catalytic rate constant $k_{cat}$ (mol⁻¹ h⁻¹) was calculated as $k_{cat} = k \cdot [\text{Cat}]$, where k is the apparent rate constant expressed in l mol⁻¹ h⁻¹ units.

The first-order rate constants were calculated by the equation

$$\ln \frac{a}{c} = k \cdot [\text{Cat}] \cdot \tau$$  \hspace{1cm} (2)

The catalytic first-order rate constant $k_{cat}$ (s⁻¹ or h⁻¹) was determined from the equation $k_{cat} = k \cdot [\text{Cat}]$, where k is given in l mol⁻¹ s⁻¹ or l mol⁻¹ h⁻¹.

The zero-order reactions (with respect to both isocyanate and alcohol) were described by the kinetic equation

$$W = \frac{dc}{dt} = k \cdot [\text{Cat}]$$  \hspace{1cm} (3)

In this case, $W = k_{cat} = k \cdot [\text{Cat}]$, where $k_{cat}$ is expressed in mol l⁻¹ h⁻¹, and $k$ in s⁻¹ (or h⁻¹). The value of $W = k_{cat}$ for a definite catalyst concentration was determined from the linear relation

$$a - c = k \cdot [\text{Cat}] \cdot \tau$$  \hspace{1cm} (4)

The values of $k$ were determined from the equation $W = k_{cat} = k \cdot [\text{Cat}]$ for different initial catalyst concentrations.

The catalytic rate constants $k_{cat}$ were determined from two or three parallel runs; the relative error in their determination was usually within ± 5 %.

---

**Table 1. Characteristics of the hydroxy-terminated FPEs and model fluorinated alcohols**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Formulas</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>p</th>
<th>q</th>
<th>purity %</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE</td>
<td>CF₂(OH)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>99</td>
<td>Fluka</td>
</tr>
<tr>
<td>GAL 7002 X</td>
<td>O₂[(CF₂(CF₃)O)ₚ-(CF₂CH₂O)ₚ]-CF₂CH₂OH</td>
<td>282.5</td>
<td>1</td>
<td>-</td>
<td>&gt;99</td>
<td>Ausimont</td>
</tr>
<tr>
<td>GAL 402</td>
<td>O₂[(CF₂(CF₃)O)ₚ-(CF₂CH₂O)ₚ]-CF₂CH₂OH</td>
<td>615</td>
<td>3</td>
<td>-</td>
<td>&gt;99</td>
<td>Ausimont</td>
</tr>
<tr>
<td>CF₂-Z-DOL-Oh*</td>
<td>CF₂-O-(CF₂-CF₂O)ₚ-(CF₂O)ₚ-CF₂CH₂OH</td>
<td>924</td>
<td>5.1</td>
<td>4.0</td>
<td>97.6</td>
<td>Ausimont</td>
</tr>
<tr>
<td>Z-DOL H-1000**</td>
<td>HOOC-(CF₂O)₂-(CF₂O)₂-(CF₂O)₂-CF₂CH₂OH</td>
<td>1084</td>
<td>5.0</td>
<td>5.0</td>
<td>99.7</td>
<td>Ausimont</td>
</tr>
</tbody>
</table>

* MWD = 1.19, equivalent weight = 992 g equiv⁻¹, content of end groups (mol %) = 52.8 –OH, 44.4 –OCF₂CF₂, 3.8 –OCF₃, and 0 –COOH.

** MWD = 1.19, equivalent weight = 544 g equiv⁻¹, content of end groups (mol %) = 99.7 –OH, 0.3 –OCF₃, and 0 –COOH.

---

**Fig. 1 Conversion versus time for the reaction of TFE with CHI in HFX at 40°C.** [DBTDL] = 0.75·10⁻⁴ M, NCO:OH = 1. [TFE + CHI] = 31.5 wt %, and [OH] = 1.78 equiv/L. (a) chemical titration and (c) IR spectroscopy.
Results and Discussion
Catalytic Reaction of 2,2,2-Trifluoroethanol with Cyclohexyl Isocyanate in Solution

The reaction of TFE with CHI (NCO : OH = 1) was studied in different solvents (HFX, THF, MIBK, EA) over a wide range of overall reactant concentrations (2.5 to 40.6 wt %), which corresponded to change of the concentration of OH groups from 0.148 to 2.25 M. The concentration of DBTDL was varied from 0.25·10⁻⁴ to 1.855·10⁻⁴ M.

First, it was found that TFE does not react with CHI in the absence of a catalyst or the reaction is very slow. In HFX at 40°C, [OH] = 1.18 M, the conversion of NCO in 5 h was close to zero. Therefore, the contribution of noncatalytic reaction can be neglected, and the reaction is not catalyzed by the alcohol. Second, the reaction rate does not depend on the mode of addition of DBTDL (whether it was mixed with TFE or with CHI), as well as on the time of preliminary storage of the reactants before mixing. In most cases, DBTDL was initially mixed with the alcohol in a solvent, the resulting solution and a solution of CHI were kept for 0.5 h at 40 ± 0.1°C, and the solutions were quickly mixed together; this moment was taken as reaction start.

Unexpected results were obtained while studying the kinetic of the reaction of TFE with CHI at high reactant concentrations, i.e., under the conditions used in practice for the preparation of macrodisocyanates. In HFX at 40°C, [TFE + CHI] = 31.5 wt %, [OH] = 1.78 M, NCO : OH = 1, [DBTDL] = 0.75·10⁻⁴ M, the gain in the conversion of NCO groups did not decrease with time as might be expected for second-order reaction, but conformed to a linear dependence up to a value of 65% (Fig. 1). This means that the reaction rate remains constant, i.e., it does not depend on the reactant concentrations which change during the process.

These findings could be rationalized assuming additional catalysis, or synergistic effect of the arising carbamate groups, or additional consumption of isocyanate groups due to side reactions (e.g., formation of allophanates, cyclization, or oligomerization). However, by special experiments we showed that such processes do not occur or their contribution is negligible.

Therefore, the only reason for the observed behavior of the TFE–CHI reaction system should be change of the reaction mechanism. To clarify this problem we examined the reaction kinetics in more detail.

Effect of Reactant Concentration

The kinetics of the reaction of TFE with CHI were studied over a wider concentration range, from 2.5 to 40.6 wt %, other conditions being equal. The results are shown in Figs. 2 and 3 and Table 2. As follows from the data in Fig. 2 and Table 2, the conversion changes linearly with time in the concentration range from 10.1 to 40.6 wt % ([OH] = 0.592–2.25 M). The time dependence of the conversion remains linear up to some limiting value which increases in parallel with the overall reactant concentration; this limiting value is ~40 % at [TFE + CHI] = 10.1 wt % and ~70 % at [TFE + CHI] = 40.6 wt %.

By contrast, no linear time dependence of the conversion was observed at lower reactant concentrations (<10.1 wt %); as might be expected, the reaction rate decreased with time (Fig. 3) due to reduction of the reactant concentrations. Moreover, at [TFE + HCl] = 2.5 wt % the reaction is excellently described by second-order kinetic equation up to a high conversion (85%; Fig. 3, curve 1), and at [TFE + CHI] = 7.4 wt %, by first-order kinetic equation up to a conversion of 70% (Fig. 3, curve 2). Here, the limiting conversion, i.e., that until which the reaction follows second-order kinetics, decreases from ~85 to less than 50% as the overall reactant concentration [TFE + CHI] rises from 2.5 to 7.4 wt % (Table 2).
The data presented in Figs. 1–3 and Table 2 led us to conclude with certainty that the order of the reaction of TFE with CHI in HFX at 40°C (NCO : OH = 1) depends on the overall reactant concentration. The reaction is of overall second order at [TFE + CHI] = 2.5–5.0 wt %, first order at [TFE + CHI] > 20.6 wt %, i.e., within the above concentration ranges the reaction up to a maximal conversion is described well by equations of different orders rather than of the same order.

Taking into account that the contribution of side reactions is insignificant (see above), the difference between the experimental kinetic curves and those calculated according to the first- and second-order equations (Fig. 3, curve 2; see also Fig. 5 for the other examined reaction systems) may be rationalized by change of the urethane formation mechanism upon variation of the initial reactant concentration, which requires appropriate kinetic equations to be applied. In the zero-order reaction, the conversion should be directly proportional to the catalyst concentration [DBTDL]:

\[ W = k \cdot [\text{Cat}] \]

As shown in Fig. 4, the reaction of TFE with CHI in HFX at 40°C at a sufficiently high reactant concentration (31.5 wt %) follows zero-order kinetics up to a conversion of 55–70% (see also Fig. 8).

We also found that, apart from the reactant concentration, the order of the reaction depends on the solvent nature. In THF at 40°C, NCO : OH = 1, the reaction kinetics conform to first-order equation up to a conversion of 90% (Fig. 5). If zero- or second-order equation is used, the calculated kinetic curve matches the experimental one up to a conversion of 38 and 53%, respectively. Table 3 contains more detailed data illustrating solvent effect on the order of the reaction of fluorinated alcohols with CHI.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>[Alcohol + CHI], wt. %</th>
<th>[OH], equiv/L</th>
<th>Conversion, %</th>
<th>Reaction order</th>
<th>First-order Rate coefficient ( k_{\text{cat}}, \text{h}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFX</td>
<td>31.5</td>
<td>1.78</td>
<td>65</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>0.72</td>
</tr>
<tr>
<td>THF</td>
<td>41.6</td>
<td>1.78</td>
<td>55</td>
<td>0</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>0.46</td>
</tr>
<tr>
<td>EA</td>
<td>30.7</td>
<td>1.28</td>
<td>21</td>
<td>2</td>
<td>0.29</td>
</tr>
<tr>
<td>MIBK</td>
<td>30.7</td>
<td>1.18</td>
<td>10</td>
<td>2</td>
<td>0.30</td>
</tr>
<tr>
<td>GAL-402</td>
<td>66.3</td>
<td>1.30</td>
<td>60</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>THF</td>
<td>70.5</td>
<td>1.18</td>
<td>36</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

* Until linearity for the zero-, first-, or second-order plots.

Our results indicate inconsistency of the assumption that the reaction is catalyzed by the arising carbamate groups or it involves other side processes with participation of NCO groups, which is often encountered in the literature to rationalize deviation of the experimental kinetic curves for urethane formation from those calculated according to second-order equation. In fact, it is necessary to take into account reactant concentration and describe the reaction kinetics with the use of zero-, first-, and second-order equations or sometimes more complex expressions (Table 4).
Reactions of Higher Molecular Fluorinated Alcohols and Diols with Cyclohexyl Isocyanate

Analogous kinetic studies were performed with fluorinated alcohols with higher molecular weights (M = 282–1084), as well as with oligoether diol Z-DOL H-1000 (Table 1). In most cases the reactions were carried out in HFX at an NCO : OH ratio of 1 : 1. As an example, Fig. 6 shows the experimental kinetic curves and those calculated according to first- and second-order equations for the reaction of Z-DOL H-1000 with CHI in HFX at 40°C (NCO : OH = 1) at different reactant concentrations. It is seen that, as in the reaction with TFE, the order of the reaction changes from second to first with rise in the reactant concentration. Further increase of the overall reactant concentration to 55 wt % leads to zero-order kinetics (Fig. 7). Similar results were obtained for all fluorinated alcohols; they are summarized in Table 2.

Analysis of the data given in Table 2 allowed us to draw the following conclusions:

1. The order of the reactions of cyclohexyl isocyanate in hexafluoroxylene with the examined fluorinated alcohols and diol having different molecular weights changes depending on the initial reactant concentration from zero in concentrated solution (40.3–66.3 wt %; the concentration range is determined by molecular weight of the alcohol) to first (25–50 wt %) and second (dilute solution, 5.1–20.3 wt %).

2. Regardless of the molecular weight and functionality of alcohols, the urethane formation reaction at [OH] > 1.18 M follows zero-order kinetics up to a conversion of 50–70%, at 0.30 M < [OH] < 1.18 M, first-order kinetics up to a conversion of 70–85%, and at [OH] < 0.30 M, second-order kinetics up to a conversion of 70–80%.

By analogy with the TFE–CHI system, the rates of the zero-order reactions of heavier fluorinated alcohols and diol Z-DOL H-1000 with CHI remain constant up to a conversion of 50–60% at different catalyst (DBTDL) concentrations (Fig. 7) and are directly proportional to the initial catalyst concentration, \( W = k \cdot [\text{Cat}] \). These results are summarized in Table 4 and Fig. 8.
Mechanism of Urethane Formation Catalyzed by DBTDL

Mechanisms of catalytic urethane formation reactions were the subject of numerous studies, but the results were often contradictory [15–24]. Analysis of the available data shows that catalysis by metal-containing catalysts generally involves formation of various intermediate complexes, e.g., between organocatalyst and reactants, including ternary complexes. Britain and Gemeinhardt [25] were among the first who studied metal-catalyzed urethane formation, namely the kinetics of the reaction of 2,4-tolylene disiocyanate (TDI) with polyoxypropylene triol.

The authors proposed a mechanism which implies initial formation of a catalyst–isocyanate complex (RN=C=O•MX₂, where M is a metal ion) which then reacts with alcohol to give a ternary complex. Mutual arrangement of the hydroxy and isocyanate groups in that complex is most favorable for their subsequent interaction. The ternary complex can also be formed in a different order, i.e., via initial formation of a complex catalyst–alcohol. This mechanism was subjected to criticism by Smith [26], for it assumed attack by one electron-deficient center on another. He proposed a mechanism which also implied formation of a ternary complex, but the alcohol molecule therein coordinated to metal ion at the ether oxygen atom rather than at the hydroxy group. Robins [27] also presumed formation of a ternary complex consisting of isocyanate, metal ion, and alcohol to interpret the results obtained by studying organometallic catalysis of urethane formation. The catalytic effect due to the presence of metal ion in the complex is determined by two factors. The first of these is enhancement of electrophilicity of the isocyanato group as a result of its coordination to metal ion at the oxygen or nitrogen atom (not shown in Scheme 1), and the second is favorable orientation of the reacting groups.

Organometallic catalyst should meet the following requirements: (1) their complexing power should be sufficient to create a required concentration of ternary complex [equilibrium (1) and (2) in Scheme 1]; (2) they should not reduce the nucleophilicity of the alcohol oxygen atom so strongly that step (3) be improbable; and (3) they should not form strong complexes with the resulting urethane; otherwise the catalyst would be forced out from the reaction zone.

The possibility for catalytic reactions of alcohols with isocyanates to proceed through intermediate ternary complex was also considered in later publications [21, 24, 28].

Our experimental data showed that under the examined conditions (1) noncatalytic reactions of fluorinated alcohols with CHI can be neglected, for their rates are insignificant; (2) the process is not accompanied by side reactions such as formation of aliphilanes and other reactions; (3) there is no additional catalysis by urethane groups being formed. By contrast, addition of model carbamate-containing compounds sometimes inhibited urethane formation.

Therefore, we propose the following mechanism to rationalize our kinetic data on the reactions of fluorinated alcohols and diols with CHI in solution. In the first step, catalyst C, isocyanate B, and alcohol A produce ternary complex ABC:

\[
A + B + C \xrightarrow{k_1} \text{ABC} \quad \text{Step 1}
\]

The rate-determining step is slow decomposition of intermediate complex ABC into urethane X and catalyst C:

\[
\text{ABC} \xrightarrow{k_2} \text{urethane(X)} + C \quad \text{Step 2}
\]

The rate of formation of urethane is given by Eq. (5):

\[
W = \frac{dx}{dt} = k_3 \cdot [\text{ABC}] \quad (5)
\]

In terms of the quasi-stationary state approximation, taking into account that the concentration of DBTDL (catalyst) is much lower (by about four orders of magnitude) than the reactant concentration and that the equilibrium concentration of ternary complex is attained rapidly, we obtain the following expression for the initial concentrations of isocyanate, alcohol, and catalyst:

\[
[\text{ABC}] = \frac{[A]_0 \cdot [B]_0 \cdot [C]_0}{k_3 + k_1 + [A]_0 \cdot [B]_0} \quad (6)
\]

Here, \(k_3 + k_1\)/k_1 is the Michaelis constant \(K_M\) for enzyme-catalyzed reactions.

If \(k_3 << k_1\), then Eq. (6) simplifies to:

\[
W = \frac{dx}{dt} = k_3 \cdot [A]_0 \cdot [B]_0 \cdot [C]_0 \quad (7)
\]

or more general equation

\[
\frac{dx}{dt} = k_3 (a-x) \cdot (b-x) \cdot [C]_0 \quad (8)
\]

It follows from Eq. (6) that the concentration of ABC complex \([\text{ABC}]\) increases with rise in the initial reactant concentrations \([A]_0\) and \([B]_0\). If \([A]_0\) and \([B]_0\) are sufficiently high \(([A]_0 \cdot [B]_0 \gg K_M)\), Eq. (6) is transformed into \([\text{ABC}] = [C]_0\).

In other words, at high concentration of the reactants the entire amount of the initial catalyst will be bound to ternary complex ABC, and concentration of the latter will be the maximum possible.

By substituting the expression \([\text{ABC}] = [C]_0\) into Eq. (5) we obtain the maximum possible (limiting) reaction rate \(W_{\text{max}} = k_3 [C]_0\). Then Eq. (7) can be rewritten as the known Michaelis equation:

\[
W = \frac{W_{\text{max}} \cdot [A]_0 \cdot [B]_0 \cdot [C]_0}{K_M + [A]_0 \cdot [B]_0} \quad (9)
\]

Analysis of Eqs. (7) and (9) shows that the overall order of the reaction depends on \(K_M\) (i.e., on \(k_1\), \(k_2\), and \(k_3\)) and reactant concentration. When \([A]_0 \cdot [B]_0 \gg K_M\), we arrive at \(W = W_{\text{max}} = k_3 [C]_0\) (10) i.e., the reaction rate is the maximal, and the reaction is of zero order in both alcohol and isocyanate. In this case, \(k_3\) is the true rate constant for urethane formation. If \([A]_0 \cdot [B]_0 \ll K_M\), Eq. (7) is converted into

\[
W = \frac{k_3 \cdot [A]_0 \cdot [B]_0 \cdot [C]_0}{k_3 + K_M} \quad (11)
\]
which is a second-order equation (first order with respect to alcohol and isocyanate), and the rate constant is equal to the apparent one, $k_{app} = k_1 [C]_0 / (k_2 + [C]_0)$.

Finally, if the product of $[A]_p$ and $[B]_0$ is comparable to $K_m$, Eq. (7) becomes more complex, and the order of the reaction is intermediate between 0 and 2. Furthermore, Eq. (8) can be represented as

$$\frac{dx}{dt} = k_2 \cdot [A]_p \cdot [B]_0 \cdot [C]_m \cdot (a-x) \cdot (b-x) \cdot (c-x) \cdot (d-x)$$

(12)

As follows from Eq. (12), in the initial period, when $(a-x) \cdot (b-x) \cdot (c-x) \cdot (d-x) > K_m$, the reaction rate is the maximal and constant, i.e., independent of the reactant concentration. As the reaction progresses, the concentration of the reactants decreases, and the product $(a-x) \cdot (b-x)$ may approach a value comparable to $K_m$. Starting from this moment, further decrease of the reactant concentration should lead to reduction of the reaction rate and hence to deviation of the conversion toward lower values from linear dependence upon time. In fact, this was observed in our experiments. When a conversion of ~60% was reached, the reaction rate decreased in all the examined systems (Figs. 1, 2, 4, 7).

In keeping with Eq. (10), the rate of zero-order reaction should be proportional to the initial catalyst concentration, and the slope of the linear dependence $W = k_3 \cdot [C]_0$ is the true rate constant $k_3$ of unimolecular decomposition of the ternary complex ABC as a result of interaction between OH and NCO groups in the coordination sphere of DBTDL. As follows from Fig. 8, this relation persists for all the examined reactions over the range of DBTDL concentrations from 0.5 - 10$^{-4}$ to 5.0 - 10$^{-3}$ M. The zero-order rate constants $k_3$ for the reactions of fluorinated alcohols and diol in HFX at 40°C (NCO : OH = 1) are given in Table 4. Under the conditions ensuring zero-order reactions of fluorinated alcohols with CHI, their reactivity increases in parallel with their molecular weights ($k = 2.3 \text{ s}^{-1}$ at 100 and $k = 3.8 \text{ s}^{-1}$ at 615).

Thus, our results led us to draw some conclusions concerning the mechanism of DBTDL-catalyzed formation of urethanes from fluorinated alcohols of different molecular weights and cyclohexyl isocyanate. The central tin ion in DBTDL readily coordinates NCO group. The second reagent (alcohol) is involved in coordination to either tin ion or the ligand, generating intermediate ternary complex; i.e., both metal ion and oxygen atom in the acid fragment (ligand) are capable of participating in complex formation. Almost the entire amount of the catalyst is complexed, and the rate-determining step is the reaction between OH and NCO groups in the coordination sphere of the catalyst. Depending on the initial reactant concentration and solvent nature, the reaction kinetics may conform to zero, first, second, or more complex order and are well described by the general kinetic equation for enzyme-catalyzed reactions.

Depending on the conditions (reactant concentration and ratio, the nature of DBTDL, etc.), the first- and second-order reactions may involve interaction of a binary RNCO · · · DBTDL complex with uncoordinated alcohol or of a binary ROH · · · DBTDL complex with uncoordinated isocyanate. The reaction mechanism may also change during the process. However, the results obtained in the present work make it possible to select conditions ensuring domination of a desired mechanism, which is important from the practical viewpoint for the preparation of polyurethane materials.

Particular attention should be given to the revealed dependence of the kinetic order of catalytic urethane formation reaction on the concentration of reactants. This is important, for comparison of the reactivity of oligoether diols on the basis of kinetic measurements performed at a low reactant concentration may be inappropriate as applied to more concentrated systems. To obtain more reliable results, it is necessary to examine the kinetics of urethane formation over a sufficiently wide range of reactant concentrations (rather than at a single concentration, as it is often used) with account taken of possible change of the reaction mechanism.

References