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ON THE MECHANISM OF THE CATALYTIC ACTION OF Co^{2+} COMPOUNDS IN THE REACTION OF URETHANE FORMATION

Questions concerning the preparation of urethanes with the use, as catalysts, of metal compounds possessing variable valence have been investigated by a number of authors ([1]-[6]). In some of these works the catalytic role of metal ions was explained by their complex formation with the isocyanate, causing an increase in the electrophilicity of the carbonyl carbon ([4]-[6]). Such an interpretation appears quite plausible; however, the mechanism of catalysis has been little studied.

In the present work, kinetic and spectrophotometric methods of investigation were used to study the mechanism of the catalytic effect of Co^{2+} salts on the urethane-formation reaction.

As starting components for the study of the indicated reaction, phenyl isocyanate (I) and *n*-butyl alcohol (Sp) were taken; the catalyst was caprylic-acid Co^{2+}. The reaction rate was determined by the dilatometric method. The apparatus for dosing the starting components and catalyst made it possible to carry out the investigation under vacuum. Electronic absorption spectra (e.a.s.) were recorded on an SF-4 spectrophotometer in all-welded quartz cuvettes, allowing all determinations also to be carried out under vacuum.

The starting substances were subjected to careful purification: 1) phenyl isocyanate was distilled twice under vacuum over freshly ignited calcium oxide; 2) absolute *n*-butyl alcohol, preliminarily purified from impurities, was dried over CaO, distilled in the presence of metallic magnesium, and stored over calcium hydride; 3) toluene was purified from impurities, distilled over metallic sodium, and stored as a solution with lithium ethyl; 4) caprylic-acid Co^{2+} was obtained by the exchange reaction of the sodium salt of caprylic acid and acetic-acid Co^{2+}, washed with water to remove impurities, and dried under vacuum at 100°. According to analysis data ([7]), the compound obtained corresponds to the formula $Co(C_7H_{13}COO)_2$. The resulting salt was dissolved in toluene and stored as a 0.1 mol/l solution under vacuum.

The kinetics of the process was studied at various ratios of the reacting compo-

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Fig. 2. Dependence of the reaction rate of urethane formation on the depth of reaction for different methods of mixing the components.

Figure 2: Fig. 2. Dependence of the reaction rate of urethane formation on the depth of reaction for different methods of mixing the components.

nents and at a temperature of 12°. The catalyst concentration was varied from 0.002 to 0.012 mol/l.

It was established that, upon simultaneous mixing of all components, the reaction rate increases with the extent of the process (Fig. 1, *I*). (The reaction rate was estimated from the kinetic curves shown in Fig. 1.) In this connection, the influence of the order of mixing of the reaction components on the catalytic activity of Co^{2+} caprylate was studied. It was found that, when the catalyst was preliminarily dissolved in a mixture of phenyl isocyanate with toluene (at a ratio of 1 : 1), the catalytic activity of cobalt increases strongly (Fig. 1, *II*), and an even sharper increase in the reaction rate is observed with increasing degree of conversion (Fig. 2, *III*).

Preliminary mixing of the catalyst with a solution containing *n*-butyl alcohol and toluene (1 : 1) showed a decrease in the rate of the urethane-formation reaction (Fig. 1, *III*); in this case, with a fourfold excess of alcohol relative to isocyanate, the catalytic action of Co^{2+} caprylate was not detected (Fig. 1, *IV* and *V*). In the case of an excess of phenyl isocyanate, however, the catalytic action of Co^{2+} does not disappear.

Fig. 1. Kinetic curves of the reaction of formation of *n*-butyl phenylurethane in the presence of Co^{2+}.
I –all components mixed at once, $C = 2$ mol/liter, $C_0 = 0.004$ mol/liter; **II** –Co^{2+} caprylate preliminarily dissolved in a mixture of phenyl isocyanate with toluene (1 : 1), $C = 2$ mol/liter, $C_0 = 0.004$ mol/liter; **III** –Co^{2+} caprylate preliminarily dissolved in a mixture of alcohol with toluene (1 : 1), $C = 2$ mol/liter, $C_0 = 0.004$ mol/liter; **IV** –Co^{2+} caprylate preliminarily dissolved in a mixture of alcohol with toluene (1 : 1), [Al] = 2 mol/liter, [I] = 0.5 mol/liter, $C_0 = 0.004$ mol/liter; **V** –without catalyst, $C = 2$ mol/liter; **VI** –all components mixed at once, $C = 0.5$ mol/liter, $C_0 = 0.003$ mol/liter, $C_{\mathrm{BFU}} = 1$ mol/liter; **VII** –all components mixed at once, $C = 0.5$ mol/liter, $C_0 = 0.003$ mol/liter. Curves **I-III**, **V-VII** are for an equimolecular ratio. **IV** is for a nonequimolecular ratio. (C is the total concentration of the components in mol/liter, $M_0 = C/2$, C_0 is the catalyst concentration in mol/liter; temperature 12°.)

Fig. 3. Dependence of the rate of the urethane-formation reaction on catalyst concentration, C—mole/liter, temperature 12°. I—all components were mixed at once; II—Co^{2+} caprylate was preliminarily dissolved in a mixture of phenyl isocyanate with toluene. The designations are the same as in Fig. 1.

Figure 3: Fig. 3. Dependence of the rate of the urethane-formation reaction on catalyst concentration, C—mole/liter, temperature 12°. I—all components were mixed at once; II—Co^{2+} caprylate was preliminarily dissolved in a mixture of phenyl isocyanate with toluene. The designations are the same as in Fig. 1.

Fig. 2. Dependence of the rate of the reaction of urethane formation $\bar{v} = v/[\mathrm{Sp}][\mathrm{I}]$ on the depth of reaction for different methods of mixing the components. Temperature 12°. **I** —all components mixed at once; $C = 2$ mol/liter, $C_0 = 0.004$ mol/liter; **II** —all components mixed at once, $C = 2$ mol/liter, $C_0 = 0.008$ mol/liter; **III** —Co^{2+} caprylate preliminarily dissolved in phenyl isocyanate, $C = 2$ mol/liter, $C_0 = 0.004$ mol/liter; **IV** —Co^{2+} caprylate preliminarily dissolved in a mixture of phenyl isocyanate with toluene $(1:1)$; $C = 0.5$ mol/liter, $C_0 = 0.004$ mol/liter, $C_{\mathrm{BFU}} = 1$ mol/liter; **V** —Co^{2+} caprylate preliminarily dissolved in a mixture of phenyl isocyanate with toluene $(1:1)$; $C = 0.5$ mol/liter, $C_0 = 0.004$ mol/liter.

The course of the curves in Figs. 1 and 2 shows that, in the case of simultaneous mixing of all reaction components and when the catalyst has been preliminarily dissolved in the alcohol, up to a reaction depth of ∼ 60–70% the process has a stationary character. The increase in rate as the reaction proceeds indicates the catalytic effect of the urethane being formed. The activating role of urethane was confirmed by carrying out the catalytic reaction in the presence of butylphenylurethane (BPU), taken in an amount exceeding the initial concentrations of the reacting components (Fig. 1, *VI*, *VII*; Fig. 2, *IV*, *V*).

Fig. 3. Dependence of the rate of the urethane-formation reaction on catalyst concentration, C—mole/liter, temperature 12°. I—all components were mixed at once; II—Co^{2+} caprylate was preliminarily dissolved in a mixture of phenyl isocyanate with toluene. The designations are the same as in Fig. 1.

The dependence of the reaction rate on catalyst concentration was also investigated for different methods of mixing the reaction components. As is seen from Fig. 3, *II*, in the case of preliminary dissolution of Co^{2+} caprylate in a mixture of phenyl isocyanate with toluene, under comparable conditions (for a reaction depth of ∼ 80–85%) the reaction rate is proportional to the catalyst concentration. When all components of the system were mixed simultaneously, in the region of stationary course of the process the reaction rate increased more slowly than the catalyst concentration (Fig. 3, *I*).

To elucidate the nature of the interaction of the catalyst with the medium, electronic absorption spectra (EAS) were recorded for $0.015\,M$ solutions of Co^{2+}

caprylate with the components of the system (Table 1 and Fig. 4).

The data presented indicate the formation of Co^{2+} caprylate complexes of different composition. Comparison of the results of kinetic and spectrophotometric measurements makes it possible to conclude that, upon interaction of the catalyst with the components of the system, the order and method of their mixing determine the type of complex formed and its catalytic activity. Thus, when Co^{2+} caprylate interacts with the alcohol (Fig. 4, *III*), the electrons of the ligand molecules completely screen the Co^{2+} field and exclude activation of the isocyanate molecules.

Table 1

Electronic absorption spectra of $0.015\,M$ solutions of Co^{2+} caprylate

System investigated	λ_1	λ_2	λ_3	$I_{\lambda_1}/I_{\lambda_{2(3)}}$
Co^{2+} caprylate + toluene	570	1150		1.17
Co^{2+} caprylate + toluene + phenyl isocyanate *	545	1150		1.43
Co^{2+} caprylate + toluene + phenyl isocyanate **	520	1150		1.6
Co^{2+} caprylate + alcohol + toluene	570 ± 5	1150	1200	0.805
Co^{2+} caprylate + butylphenylurethane + toluene	560	1150		1.3

Fig. 4

Figure 4: Fig. 4

System investigated	λ_1	λ_2	λ_3	$I_{\lambda_1}/I_{\lambda_{2(3)}}$
Co^{2+} caprylate + tetrahydrofuran	535	1175		1.0
Co^{2+} caprylate + tetrahydrofuran + phenyl isocyanate	530		1200	1.17

* 30 min after mixing the components.
** The isocyanate was heated with Co^{2+}.

In the presence of phenyl isocyanate, Co^{2+} salts apparently form two types of complexes: (a) with a smaller number of isocyanate molecules (probably 1 : 1), having reduced solubility in a mixture of isocyanate with toluene; (b) with a larger number of isocyanate molecules (possibly 1 : 2), having better solubility in the indicated mixtures. The Co^{2+} complexes with isocyanate, (a) and especially (b), possess considerable catalytic activity in this reaction.

Fig. 4. Electronic absorption spectra of 0.015 mole/liter Co^{2+} caprylate in various media.
I –toluene + Co^{2+} caprylate; **II** –phenyl isocyanate + toluene + Co^{2+} caprylate; **III** –*n*-butyl alcohol + toluene + Co^{2+} caprylate; **IV** –*n*-butylphenylurethane + toluene + Co^{2+} caprylate.

The results obtained make it possible to conclude that, under conditions of preliminary dissolution of the catalyst in the isocyanate, catalytically active complexes of nonequilibrium composition are formed. The observed acceleration of the process with increasing extent of reaction (Fig. 2, **I** and **II**) indicates a change in the composition of the Co^{2+} complexes with the components of the system and an increase in their catalytic activity.

Comparison of the kinetic data obtained with Co^{2+} caprylate at low concentrations of the initial components in the presence of *n*-butylphenylurethane and without it (Fig. 1, **VI** and **VII**, and Fig. 2, **IV**, **V**) shows that the increase in rate observed at high degrees of conversion is due to participation of the reaction product (urethane) in the formation of catalytically active Co^{2+} complexes with ligands.

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