

Noncatalytic and Autocatalytic Rate Constants of the Reaction of Phenyl Isocyanate with Butan-1-ol

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Abstract—The kinetics of the reaction of phenyl isocyanate with butan-1-ol have been studied in the temperature range from 30 to 60°C. The rate constants of the noncatalytic and autocatalytic reaction paths have been determined from the concentration dependences of the effective second-order rate constants. The autocatalytic reaction is characterized by lower enthalpies and entropies of activation than those of the noncatalytic reaction. The autocatalytic reaction is the major formation path of butyl phenylcarbamate.

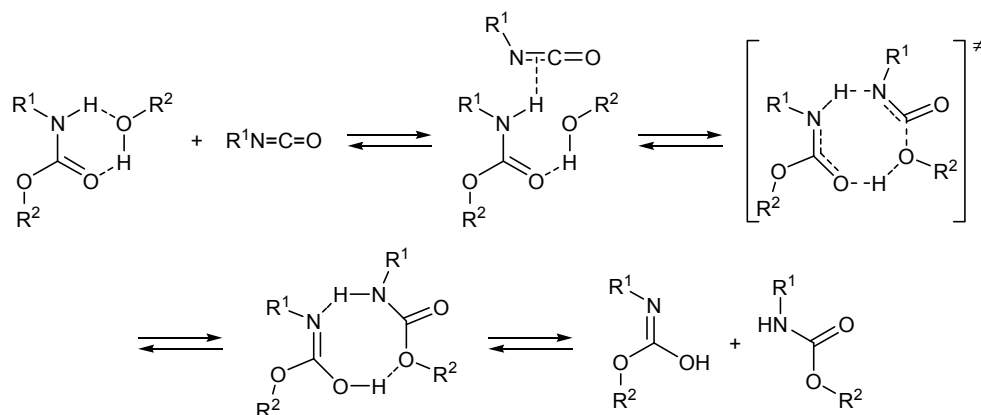
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Reactions of isocyanates with alcohols underlie the synthesis of polyurethanes that are large-scale polymers. Knowledge of kinetic parameters of these reactions is important for improving the technology of polyurethane synthesis. Even the first kinetic experiments on reactions of isocyanates with alcohols have revealed their autocatalytic character [1], and these data have been repeatedly confirmed by further studies [2–5]. However, the mechanism of autocatalytic reactions has long been unclear. It was presumed in [2, 6] that the mechanism of autocatalytic reaction involves initial formation of a complex of carbamate with isocyanate and that in the next stage this complex reacts with an alcohol molecule to give two carbamate molecules. A different mechanism was proposed in [4, 7]; it implied initial formation of a carbamate complex with alcohol and subsequent reaction with the

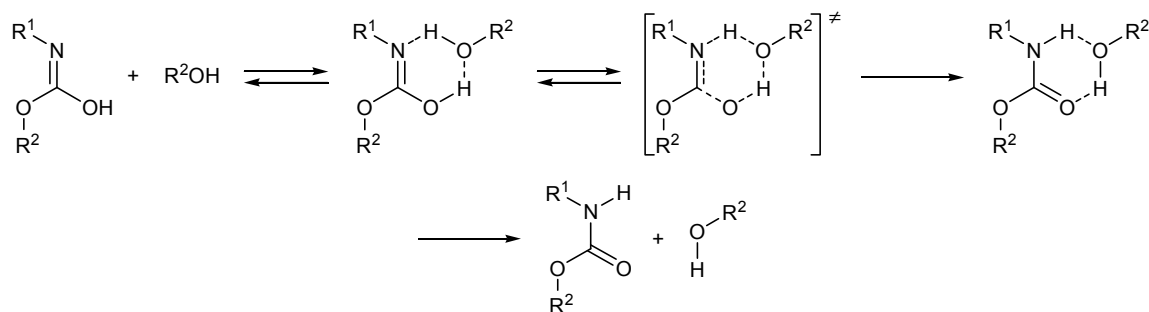
second alcohol molecule to produce two carbamate molecules. Analysis of the data given in these publications neither makes clear why carbamates catalyze the reactions of isocyanates with alcohols nor elucidates the real mechanism of autocatalysis.

The nature of the autocatalytic effect of carbamates on the above transformations was ascertained by quantum chemical calculations. Carbamates are capable of forming H-complexes with alcohols, which possess enhanced electron-donor properties in comparison to alcohol associates [8]. Taking into account nucleophilic character of the addition of alcohols to isocyanates, increased reactivity of carbamate–alcohol complexes compared to alcohol associates should be expected in reactions with isocyanates. Carbamate–alcohol complexes react with isocyanates to give pre-reaction complexes which are converted through a cy-

Scheme 1.



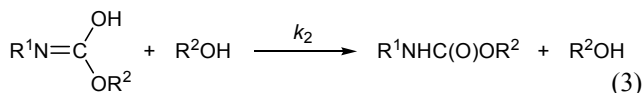
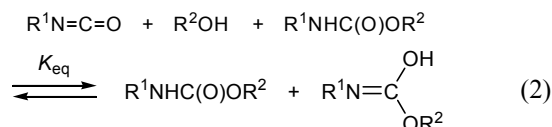
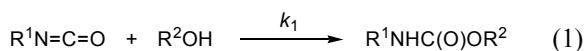
Scheme 2.



clis transition state to the complexes of carbonimidates with carbamates, which then decompose to give isolated molecules [8] (Scheme 1).

This stage is reversible and is characterized by increase of the free energy. The autocatalytic reaction becomes thermodynamically favorable at the stage of isomerization of carbonimide to carbamate [8]. This transformation is efficiently catalyzed by alcohols [8–10], and it also involves formation of pre- and post-reaction complexes (Scheme 2).

In the autocatalytic reactions of isocyanates with alcohols, molecules of the latter participate in two different stages. Knowledge of the mechanisms of non-catalytic [9, 11–13] and autocatalytic reactions [8] of isocyanates with alcohols could make it possible to infer kinetic equations describing these processes. The products of reactions of isocyanates with alcohols, i.e., carbamates, accumulate along two paths, noncatalytic and autocatalytic. In terms of formal kinetics, these paths are described by Eqs. (1)–(3), and the rate of accumulation of carbamates is given by kinetic equation (4) (k_1 , k_2 , and K_{eq} are effective quantities):



$$\frac{\partial[\text{C}]}{\partial\tau} = k_1[\text{R}^1\text{NCO}][\text{R}^2\text{OH}] + k_2[\text{E}][\text{R}^2\text{OH}]. \quad (4)$$

Here, $[\text{C}]$ is the current concentration of carbamate, $[\text{R}^1\text{NCO}]$ and $[\text{R}^2\text{OH}]$ are the current concentrations of isocyanate and alcohol, respectively, and $[\text{E}]$ is the current concentration of carbonimide. The second

step does not affect the carbamate concentration. The current concentration of isocyanate is given by Eq. (5):

$$[\text{R}^1\text{NCO}] = [\text{R}^1\text{NCO}]_0 - [\text{C}] - [\text{E}], \quad (5)$$

where $[\text{R}^1\text{NCO}]_0$ is the initial isocyanate concentration.

The rate of the transformation of carbonimidates to carbamates is very high [8–10]. Therefore, the concentration of the former can be neglected, and Eq. (5) can be simplified to Eq. (6). As follows from Eq. (6), the rate of accumulation of carbamate is equal to the rate of consumption of isocyanate [Eq. (7)]:

$$[\text{R}^1\text{NCO}] = [\text{R}^1\text{NCO}]_0 - [\text{C}]; \quad (6)$$

$$\frac{\partial[\text{R}^1\text{NCO}]}{\partial\tau} = -\frac{\partial[\text{C}]}{\partial\tau}. \quad (7)$$

In Eq. (4), the concentration of carbonimide $[\text{E}]$ is unknown. It can be determined from Eq. (8) for the equilibrium constant K_{eq} of its formation [Eq. (9)]:

$$K_{\text{eq}} = \frac{[\text{E}]}{[\text{R}^1\text{NCO}][\text{R}^2\text{OH}]}; \quad (8)$$

$$[\text{E}] = K_{\text{eq}}[\text{R}^1\text{NCO}][\text{R}^2\text{OH}]. \quad (9)$$

With account taken of Eq. (9), the differential kinetic equation for the rate of consumption of isocyanato groups and accumulation of carbamate groups appears as Eq. (10).

$$-\frac{\partial[\text{R}^1\text{NCO}]}{\partial\tau} = \frac{\partial[\text{C}]}{\partial\tau} = k_1[\text{R}^1\text{NCO}][\text{R}^2\text{OH}] + K_{\text{eq}}k_2[\text{R}^1\text{NCO}][\text{R}^2\text{OH}]^2. \quad (10)$$

The quantity $K_{\text{eq}}k_2$ is the effective rate constant of the autocatalytic reaction. A peculiar feature of differential Eq. (10) is that it includes the current alcohol concentration to both the first and the second power. If

the reaction of isocyanate with alcohol is carried out in large excess of the latter, i.e., $[R^2OH]_0 \gg [R^1NCO]_0$, integral kinetic equation (11) can be derived from Eq. (10):

$$\ln \frac{[R^1NCO]_0}{[R^1NCO]} = [R^2OH]_0(k_1 + K_{eq}k_2[R^2OH]_0)\tau. \quad (11)$$

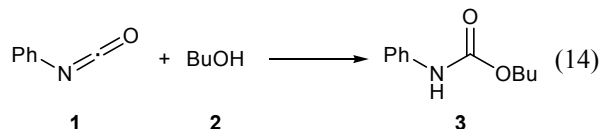
Using Eq. (11), we can determine the rate constants of the noncatalytic and autocatalytic reactions in a series of experiments differing by excess alcohol concentration. Up to now, the autocatalytic path was commonly ignored in kinetic studies of reactions of isocyanates with alcohols, and the rate constants under excess alcohol were calculated by integral pseudo-first-order equation:

$$\ln \frac{[R^1NCO]_0}{[R^1NCO]} = [R^2OH]_0 k_{ef}\tau. \quad (12)$$

Comparison of Eqs. (11) and (12) shows that the effective rate constants calculated by the latter should inevitably depend on the initial alcohol concentration [Eq. (13)], which in fact was observed experimentally [4, 14–16].

$$k_{ef} = k_1 + K_{eq}k_2[R^2OH]_0. \quad (13)$$

We studied the kinetics of the reaction of phenyl isocyanate (**1**) with butan-1-ol (**2**) [reaction (14)] with the goal of determining the rate constants for the noncatalytic and autocatalytic paths and the corresponding thermodynamic activation parameters. The kinetics of reaction (14) were the subject of numerous studies [17–20]. However, the kinetic data obtained therein were treated either without considering or considering improperly the autocatalytic character of this reaction.



The kinetics of reaction (14) were studied in the temperature range 30–60°C. The activation parameters of the noncatalytic and autocatalytic paths of the reaction of isocyanate **1** with alcohol **2** were calculated by the least-squares method from the temperature dependences of the rate constants.

Table 1 contains the effective, noncatalytic, and autocatalytic rate constants of reaction (14). It is seen that the effective rate constants are concentration-

Table 1. Effective (k_{ef}), noncatalytic (k_1), and autocatalytic ($K_{eq}k_2$) rate constants for the reaction of phenyl isocyanate (**1**) with butan-1-ol (**2**) in chlorobenzene at different temperatures

Initial concentration of butan-1-ol (2), M	$k_{ef} \times 10^4$, L mol ⁻¹ s ⁻¹	$k_1 \times 10^5$, L mol ⁻¹ s ⁻¹	$K_{eq}k_2 \times 10^4$, L ² mol ⁻² s ⁻¹
30°C			
0.137	1.51	2.32	9.18
0.183	1.87		
0.220	2.26		
0.256	2.59		
40°C			
0.326	4.41	3.99	12.3
0.434	5.69		
0.488	6.43		
50°C			
0.272	4.75	6.04	15.6
0.360	6.49		
0.434	7.39		
0.508	8.45		
60°C			
0.275	5.44	6.23	16.8
0.367	6.70		
0.376	7.08		
0.501	8.17		

dependent at all the examined temperatures. The activation parameters of the noncatalytic and autocatalytic reaction paths are given in Table 2. These data show that the energy of activation of the autocatalytic reaction is considerably lower than the energy of activation of the noncatalytic process. This is consistent with the assumption that intermolecular donor-acceptor interactions play an important role in the reaction under study, namely transformations of the more electron-donor complex of carbamate **3** with alcohol **2**

Table 2. Activation parameters of the noncatalytic and autocatalytic paths of the reaction of phenyl isocyanate (**1**) with butan-1-ol (**2**) in chlorobenzene

Parameter	Noncatalytic reaction	Autocatalytic reaction
E_A , kJ/mol	31	19
ΔH^\ddagger , kJ/mol	28	15
$\log A$	0.90	0.92
$-\Delta S^\ddagger$, J K ⁻¹ mol ⁻¹	239	251

are faster than those involving less electron-donor associates of **2**.

The autocatalytic reaction is characterized by a lower entropy of activation than the noncatalytic one. This is consistent with the results of quantum chemical calculations [8]. The isokinetic temperature for the examined reaction was estimated at 1083 K.

The concentration dependences of the effective second-order rate constants of the reaction of isocyanate **1** with cyclopentanol in toluene, dibutyl ether, and acetonitrile at 25°C were given in [15]. Treatment of these data according to Eq. (13) gave the following values: $k_1 = 1.37 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$, $K_{\text{eq}} k_2 = 1.45 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ (dibutyl ether); $k_1 = 0.44 \times 10^{-5} \text{ L} \times \text{mol}^{-1} \text{ s}^{-1}$, $K_{\text{eq}} k_2 = 0.10 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ (acetonitrile). The data for toluene were strongly dispersed, so that we were unable to reliably determine the rate constants of noncatalytic and autocatalytic reactions in this solvent. The rate constants for both reaction paths, noncatalytic and autocatalytic, decrease as the solvent polarity increases [21]. The reasons for the observed solvent effect on the reactions of isocyanates with alcohols were analyzed in [22].

The effective rate constants of the noncatalytic and autocatalytic reactions have different dimensions. Therefore, it is impossible to infer which path is pre-

ferred by direct comparison of these constants. However, the obtained data can be used to calculate the conversion of isocyanate to carbamate assuming that only the noncatalytic path is operative and that both noncatalytic and autocatalytic processes occur simultaneously. Under pseudo-first-order conditions, the current concentration of isocyanate is described by Eq. (15) provided that the reaction follows the noncatalytic path alone. If both paths are operative, the current concentration of isocyanate is described by Eq. (16).

$$[\text{R}^1\text{NCO}] = [\text{R}^1\text{NCO}]_0 \exp(-k_1[\text{R}^2\text{OH}]_0 \tau); \quad (15)$$

$$[\text{R}^1\text{NCO}] = [\text{R}^1\text{NCO}]_0 \exp(-k_1[\text{R}^2\text{OH}]_0 + K_{\text{eq}} k_2 [\text{R}^2\text{OH}]_0^2) \tau. \quad (16)$$

Figure 1 shows how the concentration of isocyanate **1** changes in the reaction with butan-1-ol (**2**) via the noncatalytic path alone and via concurrent noncatalytic and autocatalytic paths. If the reaction of **1** with **2** followed only the noncatalytic path, the conversion of **1** in 20 h would be 28.4%, whereas the experimental conversion in that time was 92.9%. Thus, the major path for the formation of carbamate in the reaction of isocyanate **1** with alcohol **2** is autocatalytic. Its contribution should increase when carbamate is added to the initial reaction mixture.

EXPERIMENTAL

Freshly distilled phenyl isothiocyanate (**1**) (Sigma-Aldrich) was used in kinetic experiments. Butan-1-ol (**2**) was purified by refluxing over magnesium shavings in an argon atmosphere, followed by fractional distillation under atmospheric pressure. Chlorobenzene (Sigma-Aldrich) was dried by refluxing over calcium hydride under argon and was distilled under atmospheric pressure. The purity of compounds was checked by gas chromatography on a Kristall-4000M chromatograph (Russia) equipped with a flame ionization detector and a Petrocol DH capillary column, 100 m × 0.25 mm.

The concentration of isocyanate **1** in kinetic experiments was monitored by IR spectroscopy, following the absorbance at 2260 cm^{-1} (νNCO) on an InfraLYuM FT-08 spectrometer with Fourier transform (Russia). Calibration experiments showed that the concentration of isocyanate **1** is related to the optical density at 2260 cm^{-1} according to Eq. (17):

$$[\text{RNCO}] = 0.02081A - 0.01998A^2 + 0.02582A^3 - 0.00838A^4; \quad r = 0.9999. \quad (17)$$

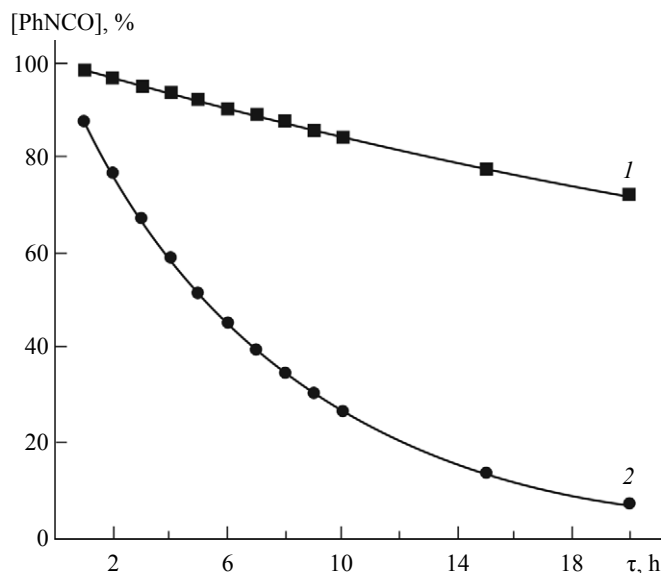


Fig. 1. Change of the concentration of phenyl isocyanate (**1**) [PhNCO] in the reaction with butan-1-ol (**2**) provided that (1) the reaction hypothetically follows only the noncatalytic path and (2) both noncatalytic and autocatalytic paths operate simultaneously. Initial concentrations of **1** and **2** 0.01 and 0.2 M, respectively; solvent chlorobenzene, temperature 30°C; $k_1 = 2.32 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$; $K_{\text{eq}} k_2 = 9.18 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$.

Here, A is the optical density at 2260 cm^{-1} , and $[\text{RNCO}]$ is the concentration of **1**, M. In the calibration experiments, the concentration of **1** was varied from 1×10^{-2} to 3×10^{-2} M. The kinetic measurements were performed under pseudo-first-order conditions. The initial concentration of isocyanate **1** was 1×10^{-2} – 3×10^{-2} M, and of butan-1-ol (**2**), 0.1–0.6 M. The reaction temperature was maintained with an accuracy of $\pm 0.1^\circ\text{C}$ using a U-2 thermostat (Germany). Samples of the reaction mixture were withdrawn and analyzed by IR spectroscopy to determine the concentration of isocyanate **1**. The effective rate constants k_{ef} were calculated by Eq. (12) from the slopes of the straight lines in the coordinates $\ln([\text{RNCO}]_0/[\text{RNCO}])-\tau$. Each run was repeated 2–4 times, and average values of the rate constants were calculated from the obtained data with an accuracy of $\pm 5\%$. The rate constants of the noncatalytic (k_1) and autocatalytic paths ($K_{\text{eq}} k_2$) were calculated from the dependences of the effective rate constant on the initial concentration of alcohol **2** using Eq. (13). In all kinetic and calibration experiments, the same cell with NaCl windows and a cell path length of 0.422 mm was used.

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