

Kinetics of the Reaction of *N,N'*-Diocetylurea with *n*-Octanol in the Presence of Tin Dibutyldilaurinate

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Received April 14, 2006

Abstract—The kinetic study of the reaction of symmetrical dioctylurea with *n*-octanol in the presence of tin dibutyldilaurinate has shown that the dependence of the reaction rate on the catalyst concentration is nonlinear. The apparent rate constants of the “associative” pathway of alcoholysis and dissociation of *N,N'*-dioctylurea at a constant catalyst concentration in various solvents are determined. The reaction proceeds via two parallel routes. The quantitative description of the effect of the solvent nature on the rates of urea alcoholysis and dissociation is proposed for this reaction series.

DOI: 10.1134/S002315840705014X

INTRODUCTION

Ethers of *N*-substituted carbamic acid find wide use in the chemical industry [1, 2], pharmaceuticals [3], and agriculture [4].

The main method for preparing carbamates involves phosgene in one of its steps. The associated environmental problems require new, safe technologies that rule out the use of toxic materials. One promising method for urethane production is the alcoholysis of substituted ureas. The yield of the desired *N*-aryl-*O*-alkyl carbamates in this method is 70–90% [5]. However, the synthesis of aliphatic urethanes according to this scheme is applicable only when a catalyst is used [6]. This is confirmed by earlier data for the noncatalytic reaction of symmetrical dioctylurea with *n*-octanol [7]. According to these data, the initial specific rate of the reaction at 170°C is $\sim 10^{-6} \text{ s}^{-1}$, limiting the applicability of the method on an industrial scale. Therefore, the reactions of ureas with alcohols in the presence of catalysts are of greatest interest. The formation of carbamates is accelerated by organotin compounds [8, 9], tertiary amines [8, 9], metal β -diketonates [10, 11], and carboxylic acids [12]. Dialkyltin carboxylates have found wide industrial use. Many kinetic studies [8, 9, 13] have been devoted to reactions of isocyanates with alcohols in the presence of these compounds.

The synthesis of carbamates by the alcoholysis of substituted ureas has been known for more than 80 years [14]. However, this method is rarely used in industry and kinetics and mechanistic data for this reaction are almost lacking. Since, in our opinion, the method is promising for commercial applications, we

studied the kinetics of a model reaction, namely, the alcoholysis of symmetrical dioctylurea with *n*-octyl alcohol in the presence of tin dibutyldilaurinate, and the kinetics of *N,N'*-dioctylurea dissociation.

EXPERIMENTAL

The kinetics of both reactions was studied in terms of the accumulation of *n*-octylamine, one of the reaction products. Its amount in a sample was determined from the absorbance of the colored solutions formed upon the interaction of amine with chloranil [15] at $\lambda = 540 \text{ nm}$. The molar absorption coefficients for the *n*-octylamine–chloranil adduct in decane, nitrobenzene, *ortho*-dichlorobenzene, benzonitrile, and phenetole have been determined previously [7]. The molar absorption coefficient in *ortho*-xylene, diglyme, and DMF is $\epsilon = 0.65 \pm 0.01 \text{ l mmol}^{-1} \text{ cm}^{-1}$ ($r = 0.997$).

The initial *N,N'*-dioctylurea was synthesized by the transamination of carbamide. The structure and individual character of the product were proved by ^1H NMR spectroscopy [7]. Solvents were purified and dried using known procedures [16], and *n*-octanol was distilled prior to use. The physicochemical constants of the solvents and alcohols are close to or coincide with reference data. The absorption of solutions was measured on a Specord M-40 spectrometer (Germany) in a 10-mm quartz cell at $\lambda = 540 \text{ nm}$.

Alcoholysis was carried out in a 50-ml three-necked temperature-controlled reactor equipped with a reflux condenser, a calcium chloride tube, a thermometer, and a magnetic stirrer. A weighed sample of *N,N'*-dioctylurea (0.8–1.0) was loaded into the reactor, a solvent (30 ml) was added, and the temperature of the system was maintained at 130°C with an accuracy of $\pm 0.5 \text{ K}$. Then a solution of tin dibutyldilaurinate in *n*-octanol,

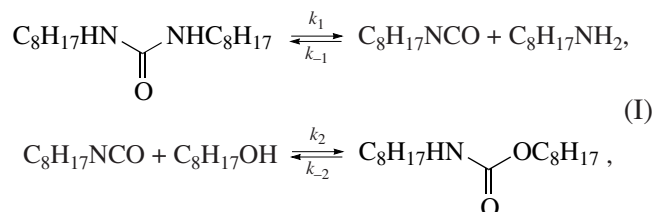
brought to the same temperature, was added to the reactor. The amounts of the alcohol and catalyst were determined from the difference between the weights of the tube before and after sampling of a certain volume of the solution for the reaction. The moment of addition of the alcohol-catalyst mixture was considered to be the reaction onset time. Samples (1 ml) were taken at certain intervals and analyzed by photocolormetry [15].

The dissociation of *N,N'*-dioctylurea was carried out in the reactor described above. Before maintaining a constant temperature, a weighed sample of *N,N'*-dioctylurea (1.8–2.0 g) was placed in the flask and a solvent (27 ml) was added. The reactor was heated to a preset temperature, and then a solution (3 ml) of tin dibutyldilaurinate in the same solvent was added to the reaction mixture. The amount of the catalyst added was 3 mol % of the *N,N'*-dioctylurea weight. It was determined as described above. Then the experiment was carried out in the same way as the alcoholysis procedure.

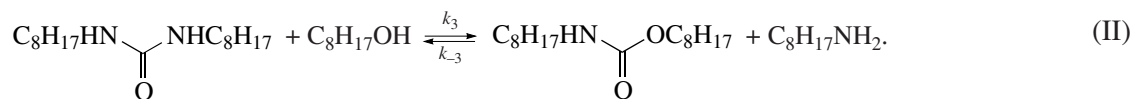
RESULTS AND DISCUSSION

When choosing a kinetic model for the reaction examined, we relied on the mechanism of the noncatalytic conversion of ureas to carbamates, which was studied earlier in greater detail [7].

The noncatalytic reaction proceeds via both the dissociation of the starting urea, i.e., the so-called “dissociative” pathway [17],



and the “associative” pathway, which can be presented as follows [17]:



The rate-determining step of the “dissociative” mechanism of alcoholysis is the decomposition of urea [5].

It should be mentioned that reactions (I) and (II) can take place both with and without a catalyst. However, a comparison of the reaction rates in the presence and absence of tin dibutyldilaurinate allows us to neglect the noncatalytic route in further discussion and processing of the experimental data. The study of *N,N'*-dioctylurea alcoholysis at 170°C in decane showed that the catalytic reaction occurs 10^2 times more rapidly than the noncatalytic reaction. Thus, in this case, the rate constants of the reactions shown in schemes (I) and (II) refer only to the catalytic route of alcoholysis.

To determine the kinetic parameters of the reaction, we earlier proposed [7] processing experimental data in terms of the initial specific reaction rate $W_{0, \text{sp}}^{\text{cat}}$, which can be defined as

$$W_0 = -\frac{dC_u}{dt}(t=0),$$

$$W_{0, \text{sp}}^{\text{cat}} = \frac{W_0}{C_{u, 0}},$$

where $C_{u, 0}$ is the initial urea concentration and W_0 is the alcoholysis rate at the initial time moment.

It should be mentioned that, as a rule, the rate of a catalytic reaction is a function of the catalyst concentration. To reveal this dependence, we carried out a series of experiments on the alcoholysis of *N,N'*-dioctylurea with *n*-octanol in various solvents at 130°C. The studies

were carried out at a constant alcohol concentration of $C_{\text{alc}} = 0.3647 \pm 0.0050$ mol/l. The tin dibutyldilaurinate concentration was varied between 10^{-4} and 10^{-2} mol/l.

The sought dependence turned out to be nonlinear. The alcoholysis rate initially increases with increasing catalyst concentration. Once a tin dibutyldilaurinate concentration of 1.5×10^{-3} – 5×10^{-3} mol/l is reached, it tends to a constant value (Table 1). Dependences of this type are observed in all the solvents studied, except for decane, in which the rate increases throughout the catalyst concentration range examined (Fig. 1). It should be mentioned that the shape of the curves was determined in a wide range of tin dibutyldilaurinate concentrations for *ortho*-xylene, phenetole, nitrobenzene, and benzonitrile. For diglyme, DMF, and *ortho*-dichlorobenzene, we determined only the region where the alcoholysis rate was constant at various catalyst concentrations (Table 1).

Thus, the interval in which the alcoholysis rate is independent of the tin dibutyldilaurinate concentration was found for each solvent and the apparent reaction rates in this C_{cat} region can be determined according to the equation proposed in [7]. This equation relates the initial specific reaction rate $W_{0, \text{sp}}^{\text{cat}}$ to the rate constants of the “associative” and “dissociative” alcoholysis pathways:

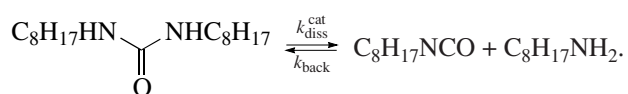
$$W_{0, \text{sp}}^{\text{cat}} = k_1 + k_3 C_{\text{alc}, 0}, \quad (1)$$

where k_1 and k_3 are the apparent rate constants of the “dissociative” and “associative” mechanisms of the catalytic reaction, respectively, and $C_{\text{alc},0}$ is the initial alcohol concentration.

Equation (1) makes it possible to determine the apparent rate constants of the catalytic process by varying the initial alcohol concentration and measuring the initial reaction rate and to determine the true route of the alcoholysis.

We carried out a series of experiments on the reaction of symmetrical dioctylurea with *n*-octanol in various solvents at a constant temperature and various alcohol concentrations. The experiments were carried out in the catalyst concentration range where the alcoholysis rate is independent of C_{cat} . By fitting the kinetic data to a polynomial function followed by differentiation, we determined the initial specific reaction rate at the corresponding initial concentrations of *n*-octanol (Table 2).

The results obtained show that the initial alcoholysis rate $W_{0,\text{sp}}^{\text{cat}}$ is a linear function of the initial alcohol concentration. Dependence (1) is valid for all the solvents studied. According to Eq. (1), the rate constants of the “associative” reaction pathway k_3 were determined (Table 3). The kinetic data were processed using the differential equation for the scheme of chemical reactions (I) and (II). The rate constants of the “dissociative” route (k_1 values) are comparable with the confidence interval and, in some cases, take negative values. Evidently, this is due to the error of the differential determination method and to the strong effect of even a slight error in the initial specific reaction rate. To estimate the rate constant of the monomolecular step of alcoholysis (k_1), we studied urea dissociation in the presence of tin dibutylidilaurinate at the same temperature:



Note that the dissociation rate constant $k_{\text{diss}}^{\text{cat}}$ can differ from the rate constant of the “dissociative” route k_1 . The process described by scheme (I) occurs in the presence of *n*-octanol. Alcohols and organotin compounds form reactive complexes [9] that can affect the reaction rate. In this case, the catalytic activities of the organotin compound and its complex with alcohol differ. However, the equilibrium constant, which is the ratio of the rate constants of the forward and reverse reactions, is the same for urea dissociation and the process described by the first equation in scheme (I) and can be determined by a special study of the dissociation reaction (Table 4):

$$K = \frac{k_{\text{diss}}^{\text{cat}}}{k_{\text{back}}} = \frac{k_1}{k_{-1}}.$$

Table 1. Dependence of the initial specific reaction rate on the tin dibutylidilaurinate concentration (C_{cat})

Solvent	$C_{\text{cat}} \times 10^3$, mol/l	$W_{0,\text{sp}}^{\text{cat}} \times 10^5$, s ⁻¹	r^*
Decane	0.092	1.38 ± 0.07	0.997
	0.302	2.46 ± 0.08	0.998
	1.361	4.06 ± 0.20	0.997
	4.560	6.41 ± 0.85	0.993
	6.399	8.40 ± 0.16	0.999
	9.382	10.85 ± 0.26	0.999
	11.93	12.99 ± 0.25	0.999
<i>ortho</i> -Xylene	0.102	1.98 ± 0.03	0.999
	0.558	3.48 ± 0.11	0.999
	1.590	5.70 ± 0.30	0.999
	2.430	5.40 ± 0.12	0.999
	3.850	6.86 ± 0.33	0.999
	5.090	7.81 ± 0.11	0.999
	9.898	8.37 ± 0.12	0.999
Phenetole	14.90	8.30 ± 0.13	0.999
	0.000	0	—
	0.039	1.27 ± 0.06	0.997
	0.076	1.33 ± 0.05	0.998
	0.246	2.54 ± 0.09	0.999
	0.818	3.47 ± 0.04	0.999
	4.040	5.97 ± 0.45	0.999
<i>ortho</i> -Dichlorobenzene	5.274	5.21 ± 0.05	0.999
	6.226	5.94 ± 0.16	0.999
	7.535	6.50 ± 0.13	0.999
	8.900	5.89 ± 0.11	0.999
	3.750	8.22 ± 0.14	0.999
	5.765	9.41 ± 0.43	0.997
	6.696	9.74 ± 0.51	0.998
Benzonitrile	0.100	—	—
	0.977	1.24 ± 0.07	0.997
	1.500	2.65 ± 0.08	0.999
	3.248	2.82 ± 0.10	0.998
	4.770	3.07 ± 0.06	0.999
	7.440	3.32 ± 0.16	0.997
	10.61	3.29 ± 0.10	0.999
DMF	1.850	3.27 ± 0.07	0.999
	4.230	3.46 ± 0.30	0.997
	5.950	3.33 ± 0.25	0.999
Diglyme	3.126	1.82 ± 0.13	0.998
	3.140	2.16 ± 0.11	0.999
	7.640	2.09 ± 0.10	0.999
	10.00	2.08 ± 20	0.999
Nitrobenzene	0.450	0.71 ± 0.03	0.989
	0.850	1.15 ± 0.05	0.991
	1.570	3.88 ± 0.11	0.999
	3.310	4.90 ± 0.33	0.997
	4.700	4.54 ± 0.14	0.999
	6.570	4.23 ± 0.11	0.999

Note: Reaction conditions: $C_{\text{alc}} = 0.3647 \pm 0.0050$ mol/l, $T = 130^\circ\text{C}$.
* r is the correlation coefficient.

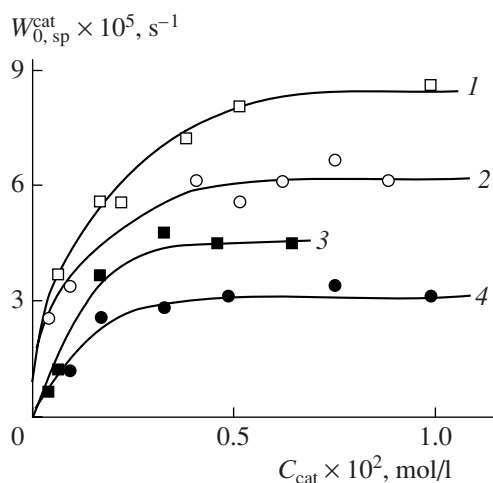


Fig. 1. Plots of $W_{0, sp}^{cat}$ versus the catalyst concentration C_{cat} at 130°C and $C_{alc} = 0.3647 \pm 0.0050$ mol/l: (1) *ortho*-xylene, (2) phenetole, (3) nitrobenzene, and (4) benzonitrile.

Thus, we have found the apparent rate constants of the decomposition of symmetrical *N,N'*-dioctylurea in various solvents at a constant catalyst concentration (Table 4). The rate constant of urea dissociation was determined by solving the kinetic equation of the reversible reaction in which the forward reaction is first-order and the reverse reaction is second-order.

The rates of the “dissociative” and “associative” routes of the reaction under study are comparable at 170°C without a catalyst [7]. The data obtained at 130°C in the presence of tin dibutyldilaurinate also indicate that the rates of the mono- and bimolecular pathways are comparable. This follows from an analysis of Eq. (1). As mentioned above, the rate constant of the “dissociative” route (k_1) can be estimated from the apparent rate constant of urea decomposition at a fixed catalyst concentration. The data in Table 4 show that this value ranges from 1.5×10^{-6} to $6.0 \times 10^{-6} \text{ s}^{-1}$ in different solvents at a tin dibutyldilaurinate concentration of $\sim 6.5 \times 10^{-3} \text{ mol/l}$. The apparent rate constant of the “associative” route at the same catalyst concentration is $10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$. Since the alcohol concentration is 0.1–0.8 mol/l, one of the terms in Eq. (1) is about $\sim 10^{-6}$ (k_1) and the second term has an order of $\sim 10^{-5}$ ($k_3 C_{alc, 0}$). Therefore, the alcoholysis routes are comparable and the reaction can proceed via both urea dissociation and bimolecular conversion.

For quantitative estimation of the effect of the properties of the medium on the alcoholysis rate, we used the Palm–Koppel equation, which takes into account the main types of interactions between the solvent and the solutes [18]:

$$\log k = \log k_0 + yY + pP + eE + bB,$$

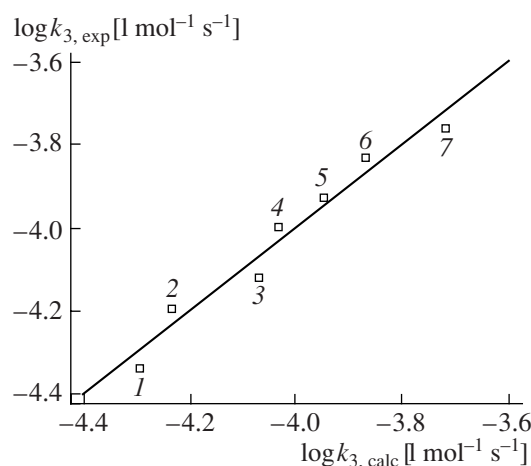


Fig. 2. Experimental k_3 data fitted to the Palm–Koppel equation at 130°C for various solvents: (1) DMF, (2) diglyme, (3) benzonitrile, (4) nitrobenzene, (5) *ortho*-dichlorobenzene, (6) phenetole, and (7) *ortho*-xylene.

where Y , P , E , and B are the polarity, polarizability, acidity, and basicity of the solvent (Table 5); y , p , e , and b are the sensitivity of the reaction to change of the respective parameters of the medium; k_0 is the rate constant in the gas phase.

The acidity (E) and basicity (B) exert no substantial effect on the apparent rate constant of the “associative” alcoholysis route.

In the case of a bimolecular process characterized by the apparent rate constant k_3 , the above dependence is described by the following equation ($r = 0.957$):

$$\log k_3 = -(4.63 \pm 0.24) + (3.58 \pm 0.58)P - (1.84 \pm 0.25)Y. \quad (2)$$

The correlation between the apparent rate constant of urea dissociation at a fixed catalyst concentration and the solvent properties at 130°C according to the Palm–Koppel equation has the form ($r = 0.975$)

$$\log k_{diss}^{cat} = -(8.21 \pm 0.25) + (7.16 \pm 0.66)P + (0.0012 \pm 0.0002)B. \quad (3)$$

Equation (3) is valid for all solvents studied but benzonitrile and nitrobenzene. The agreement between the experimental rate constants k_3 and k_{diss}^{cat} and the same quantities calculated using the Palm–Koppel equation is illustrated in Figs. 2 and 3.

To explain the dependence of the alcoholysis rate on the catalyst concentration and correlations (2) and (3), we will consider the mechanism of the reaction.

Table 2. Initial specific rates of the reaction of *N,N'*-dioctylurea with *n*-octanol in the presence of tin dibutyldilaurinate for various initial alcohol concentrations

Solvent	C_{alc} , mol/l	$C_{\text{cat}} \times 10^3$, mol/l	$W_{0, \text{sp}}^{\text{cat}} \times 10^5$, s ⁻¹	r^*
<i>ortho</i> -Xylene	0.3598	—	8.16**	—
	0.5377	8.871	10.94 ± 0.42	0.999
	0.6802	6.907	13.80 ± 0.34	0.999
Phenetole	0.1322	2.230	2.02 ± 0.02	0.999
	0.1821	1.900	3.09 ± 0.03	0.999
	0.3599	—	5.90**	—
<i>ortho</i> -Dichlorobenzene	0.5467	2.760	8.20 ± 0.37	0.999
	0.3616	—	9.12**	—
	0.5302	2.690	11.05 ± 0.23	0.999
	0.5453	8.459	11.90 ± 0.44	0.999
Benzonitrile	0.8517	3.650	15.02 ± 0.9	0.999
	0.1848	2.100	1.68 ± 0.03	0.999
	0.3597	—	3.03**	—
	0.5574	2.500	4.51 ± 0.10	0.999
Nitrobenzene	0.0932	2.260	1.65 ± 0.02	0.999
	0.1800	2.110	2.69 ± 0.04	0.999
	0.3668	—	4.39**	—
	0.4719	2.930	5.54 ± 0.10	0.999
DMF	0.0935	1.400	2.06 ± 0.14	0.999
	0.1807	2.180	2.41 ± 0.06	0.999
	0.3677	—	3.35**	—
	0.7100	2.600	4.88 ± 0.18	0.998
Diglym	0.3599	—	2.11**	—
	0.4457	4.360	2.96 ± 0.06	0.999
	0.4700	4.140	3.02 ± 0.17	0.999
	0.7255	3.248	4.48 ± 0.23	0.999

Note: Reaction conditions: $T = 130^\circ\text{C}$.* r is the correlation coefficient.** Averaged $W_{0, \text{sp}}^{\text{cat}}$ value in the C_{cat} range where the reaction rate is independent of C_{cat} (Table 1).

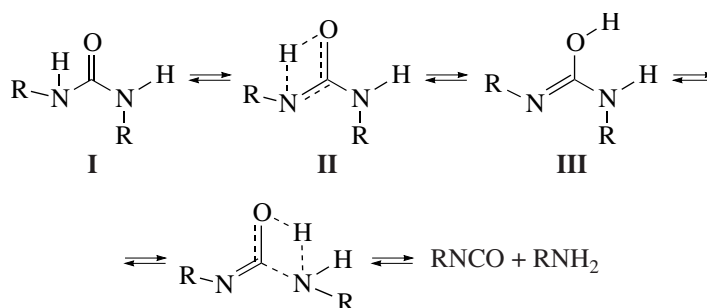
The literature contains no data on the decomposition of dialkylureas under the action of organotin compounds. Studies on the mechanism of the catalytic interaction of ureas with alcohols are also scarce. For this reason, in order to interpret the results, we assume that ureas can be converted into carbamates through both dissociation and bimolecular interactions. Our assumption is based on the known mechanism of the noncatalytic transamination of ureas, a process that is chemically similar to alcoholysis and also has a two-pathway route [19].

The decomposition of ureas was found to proceed via isomerization (Scheme 1).

Table 3. Apparent rate constants of the “associative” route of the reaction of *N,N'*-dioctylurea with *n*-octanol in the presence of tin dibutyldilaurinate

Solvent	$k_3 \times 10^5$, l mol ⁻¹ s ⁻¹	r^*
<i>ortho</i> -Xylene	17.42 ± 1.28	0.995
Phenetole	14.78 ± 0.93	0.992
<i>ortho</i> -Dichlorobenzene	11.85 ± 1.31	0.988
Benzonitrile	7.59 ± 0.09	0.999
Nitrobenzene	10.04 ± 0.34	0.998
DMF	4.60 ± 0.09	0.999
Diglyme	6.42 ± 0.58	0.985

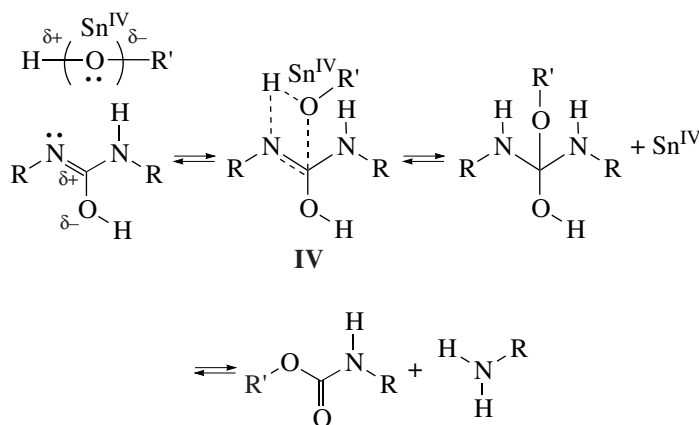
Note: Reaction conditions: $T = 130^\circ\text{C}$.* r is the correlation coefficient.



Scheme 1. Monomolecular decomposition of urea.

According to the literature, it is precisely isourea **III** that is attacked by the nucleophile during the bimolecular interaction [19]. Thus, for both the bimolecular and

monomolecular routes of carbamate formation, isourea is the major intermediate involved in the reaction (Scheme 2).



Scheme 2. Reaction of urea with alcohol in the presence of a catalyst (bimolecular interaction).

As can be seen from experimental data, the alcoholysis rate is a nonlinear function of the catalyst concentration and tends to a limit as the catalyst concentration is increased.

This influence on the apparent rate constant of the catalytic reaction is well known. It is usually observed when the catalyst concentration substantially exceeds the concentration of one of the reactants. This phenomenon is explained by the fact that all of the reactant in the system is converted into its active form and, therefore, a further increase in the catalyst concentration cannot affect the reaction rate. One would infer that, in our case, urea should be responsible for the reaction rate reaching a constant value. However, its concentration was higher than the catalyst concentration throughout the experimental series. This indicates that even if a urea-catalyst complex forms in the reaction, it is not responsible for the nonlinear relationship between the alcoholysis rate and the tin dibutyldilaurinate concentration.

It should be mentioned that, for the catalytic reactions of isocyanates with alcohols, the dependence of

the apparent rate constant on the tin dibutyldilaurinate concentration is also nonlinear [20, 21]. The results obtained are explained from the standpoint of the mechanism of the noncatalytic reaction of isocyanate with alcohol, according to which the reaction occurs in steps to form an intermediate four-membered alcohol-isocyanate complex [22], which is subsequently transformed rapidly into urethane. The effect of the catalyst is to increase the concentration of the alcohol-isocyanate complex. Therefore, the dependence of the reaction rate on the organotin compound concentration is nonlinear because, even at very high catalyst concentrations, the reaction rate cannot exceed the value determined by the expression $W = k[X]$, where $[X]$ is the equilibrium concentration of the alcohol-isocyanate complex.

An analysis of Scheme 2, which describes the bimolecular reaction of urea with alcohol, provides a similar explanation for the nonlinear dependence of the alcoholysis rate on the tin dibutyldilaurinate concentration. By analogy with the transamination of ureas, we assume that an alcohol molecule interacts directly with

Table 4. Apparent rate constant of the dissociation of *N,N'*-dioctylurea in the presence of tin dibutyldilaurinate*

Solvent	C_{cat} , mol/l	$K \times 10^3$, mol/l	$k_{\text{back}} \times 10^2$, l mol ⁻¹ s ⁻¹	$k_{\text{diss}}^{\text{cat}} \times 10^6$, s ⁻¹
Decane	0.0069	0.0058	26.00	1.50
<i>ortho</i> -Xylene	0.0067	0.0900	5.50	4.94
Phenetole	0.0063	0.1200	4.60	5.52
<i>ortho</i> -Dichlorobenzene	0.0064	0.0740	7.84	5.80
Benzonitrile	0.0068	0.0054	37.00	2.00
Nitrobenzene	0.0065	0.1200	4.10	4.97
DMF	0.0071	0.1200	3.60	4.32
Diglyme	0.0053	0.0260	8.07	2.10

* $T = 130^\circ\text{C}$.**Table 5.** Parameters of the Palm–Koppel equation for the solvents studied

Solvent	$-\log k_3$ [l mol ⁻¹ s ⁻¹]	$-\log k_{\text{diss}}^{\text{cat}}$ [s ⁻¹]	Parameters of solvent* [18]			
			Y	P	E	B
Decane	—	5.8239	0.1989	0.3319	0	0
<i>ortho</i> -Xylene	3.7590	5.3063	0.2555	0.3877	0	68
Phenetole	3.8303	5.2581	0.3411	0.3888	0.8	158
<i>ortho</i> -Dichlorobenzene	3.9263	5.2366	0.4286	0.4129	0	28
Benzonitrile	4.1198	5.6990	0.4708	0.4004	0	155
Nitrobenzene	3.9983	5.3063	0.4788	0.4147	0	67
DMF	4.3372	5.3645	0.4798	0.3414	2.6	291
Diglyme	4.1925	5.6779	0.4032	0.3197	0	238

* Y is polarity, P is polarizability, E is acidity, and B is basicity.

a molecule of isourea **III** through four-centered transition state **IV**, which further decomposes to form urethane. Thus, the catalyst introduced into the system accelerates the steps of formation and decomposition of alcohol–isourea complex **IV** without changing the constant of its monomolecular conversion to urethane. Indeed, if the rate-determining step of the catalytic reaction is the rearrangement of this complex to carbamate, then the dependence of the reaction rate on the catalyst concentration will be nonlinear and, even at high tin dibutyldilaurinate concentrations, the reaction rate will not exceed the value determined by the decomposition rate of the alcohol–isourea complex.

Note that the assumption that the catalyst forms, with one of the reactants, an intermediate responsible for the acceleration of the process is common for all catalytic studies. The complexes of organotin catalysts with alcohols are well known. A linear dependence of the reaction rate of urethane formation on the alcohol–Sn(IV) complex concentration was observed [23]. This finding suggests that it is possibly the alcohol compounds with organotin catalysts that are responsible for catalysis in the urethane formation reactions. This assumption is illustrated in Scheme 2. However, special physicochemical experiments on complex formation

are needed to determine what complexes are responsible for catalysis in the reaction examined.

Correlations (2) and (3) also agree well with Schemes 1 and 2.

Expressions (2) and (3) show that the polarizability of the solvent favors both alcoholysis routes. This indicates some similarity between the alcoholysis routes, which is due to urea isomerization. Obviously, the electron densities are redistributed during the isomerization reaction. As shown in Scheme 1, this process involves proton transfer from the nitrogen atom to oxygen in the case of urea **I** turning into isourea **III** and from the oxygen atom to another nitrogen atom in the case of the decomposition of isourea **III**. Thus, this interaction is facilitated when the solvents containing labile π bonds are involved. This is the reason why the polarizability of the solvent has a favorable effect on the reaction rate.

The adverse effect of the solvent polarity on the rate of the bimolecular route (see Eq. (2)) can be explained by considering Scheme 2. Transition state **IV** is less polarized than the starting isourea, and, hence, the stabilization of isourea due to its interaction with polar solvent molecules is higher than the stabilization of the transition state.

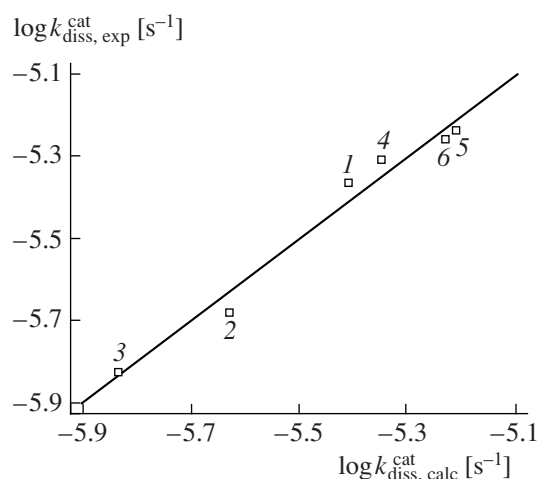
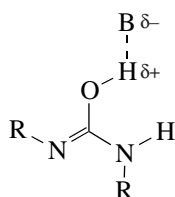


Fig. 3. Experimental $k_{\text{diss}}^{\text{cat}}$ data fitted to the Palm–Koppel equation at 130°C for various solvents: (1) DMF, (2) diglyme, (3) decane, (4) *ortho*-xylene, (5) *ortho*-dichlorobenzene, and (6) phenetole.

As can be seen from correlation (3), the basicity of the solvent exerts a favorable effect on the rate of urea dissociation. If urea isomerization is the rate-determining step in the decomposition of urea, an increase in the solvent basicity will increase the constant $k_{\text{diss}}^{\text{cat}}$. Indeed, in this case, the solvent's basicity will stabilize isourea **III**, a more acidic compound,



and will facilitate proton transfer from the nitrogen atom to the oxygen atom in transition state **II** (Scheme 1).

Thus, the kinetic data obtained in the present work are self-consistent and are in agreement with the reaction schemes proposed (Schemes 1, 2).

The kinetics study of the reaction between symmetrical dioctylurea and *n*-octanol catalyzed by tin dibutyldilaurinate outlined the mechanism of the catalytic process. However, some details require further refinement and will be discussed elsewhere.

ACKNOWLEDGMENTS

The authors are grateful to M.Ya. Zayats for the kindly presented catalyst.

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