Exchange Reactions of Urethanes with Proton-Donating Compounds: Kinetics of the Reactions of Phenyl-*N*-Phenylurethane with Butyl Alcohols

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Abstract—The exchange reactions of phenyl-*N*-phenylurethane with aliphatic alcohols, namely, *n*-butyl, *sec*-butyl, and *tert*-butyl alcohols, in *ortho*-dichlorobenzene and in the media of the corresponding alcohols were studied. In the absence of a catalyst and proton-donating compounds, the monomolecular cleavage of phenyl-*N*-phenylurethane to isocyanate and alcohol proceeds at a noticeable rate starting only at 250°C. Between 40 and 80°C, the exchange reactions take place via direct exchange between urethane and the photon-donating compound and are second-order up to high conversions (until the almost complete disappearance of the initial urethane). Activation energies and apparent rate constants have been determined for the exchange reactions of phenyl-*N*-phenylurethane with butyl alcohols. The rates of the exchange reactions in the alcohol medium are compared with those in *ortho*-dichlorobenzene.

Exchange reactions of urethanes with proton-donating compounds are widely used in the modern production of polyurethanes, polyureas, polyisocyanurates, epoxyurethane, epoxyisocyanurate, and some other polymers, as well as in the processing of polymer production waste. The kinetics and mechanisms of the exchange reactions forming the basis of these processes should be known for rational control of the technologies of polyurethane synthesis and waste processing and for modifying polymers of other classes.

Two routes of the exchange reactions of urethanes with proton-donating compounds are usually discussed [1]: urethane cleavage to an isocyanate and an alcohol followed by the addition of the coreactant to the isocyanate via reactions (I) and (II) and the direct urethane–nucleophile (NuH) exchange similar to ester interchange (III). Under some conditions, both reaction routes can occur simultaneously.

$$\underset{\text{RNHCOR'}}{\overset{\overset{\text{O}}{\|}}{}} \rightleftharpoons \text{RNCO} + \text{R'OH}, \qquad \text{(I)}$$

$$\text{RNCO} + \text{NuH} \rightleftharpoons \underset{\text{RNHCONu}}{\overset{\overset{\text{O}}{\|}}{}}, \qquad \text{(II)}$$

$$\underset{\text{RNHCOR'}}{\overset{\overset{\text{O}}{\|}}{}} + \text{NuH} \rightleftharpoons \underset{\text{RNHCONu}}{\overset{\overset{\text{O}}{\|}}{}} + \text{R'OH}. \qquad \text{(III)}$$

Many publications, especially those concerning the destruction of urethanes and their use as solidifying agents, simply postulate that the exchange reactions involve a monomolecular urethane decomposition step [2–4]. More detailed kinetic studies were carried out only in [5, 6]. However, it is mentioned [1] that the kinetic regularities found are not properly substantiated and are not confirmed by further studies, and some conclusions even contradict the experimental data.

This work is aimed at elucidating the influence of the structure of the proton-donating compound on the kinetic parameters of the exchange reactions of phenyl-*N*-phenylurethane with aliphatic alcohols (*n*-butyl, *sec*-butyl, and *tert*-butyl alcohols).

EXPERIMENTAL

Phenyl isocyanate (Fluka, >98%) was purified by vacuum distillation (10 Torr) at 90°C. Phenol (analytical grade, for medical applications) was sublimed at 120°C.

Butyl alcohols were treated using standard procedures [7].

1,2-Dichlorobenzene (DCB) (Fluka) was purified by fractionation, and the medium fraction with the boiling point 179.7°C was used in further studies.

The catalyst, tin dibutyldilaurinate (TDBDL) (Aldrich, 95%), was used without additional purification.

Phenyl-*N*-phenylurethane (PPU), *n*-butyl-*N*-phenylurethane (*n*-BPU), *sec*-butyl-*N*-phenylurethane (*sec*-BPU), and *tert*-butyl-*N*-phenylurethane (*tert*-BPU) were synthesized by the reactions of phenyl isocyanate with the corresponding alcohol in an inert gas atmo-

sphere at 60°C and [NCO]/[OH] = 1. The completeness of urethane formation was checked by IR spectroscopy on a Specord M-82 spectrophotometer from the intensity of the absorption band $\nu(NCO) = 2270$ cm^{-1}, which is due to the antisymmetric stretching vibrations of the NCO groups. The synthesized urethanes were purified by sublimation and analyzed by IR spectroscopy.

The exchange reactions of urethanes with alcohols in the absence and presence of the TDBDL catalyst were studied in the temperature interval from 40 to 80°C in DCB at a nearly equimolar alcohol-to-urethane ratio and in solutions of reacting alcohols at an alcohol-to-urethane molar ratio of ≈100 : 1. For studying the reaction kinetics, samples of the reaction mixture were sealed in tubes, which were then placed in a thermostat. At certain time intervals, the tubes were withdrawn from the thermostat and cooled rapidly to terminate the reaction. The PPU concentration was determined in solution by IR spectroscopy from the absorption band intensities at 1755, 1490, and 1193 cm^{-1} (the molar absorption coefficients are 698, 724, and 1484 l mol^{-1} cm^{-1}, respectively). The data corresponding to different absorption bands were averaged in order to enhance the accuracy of measurements. The PPU conversion in the reaction can be calculated from the concentrations determined.

The temperature interval of the monomolecular reactions of urethane decomposition was determined with a differential microcalorimeter capable of working in the scanning and isothermal modes [8] at heating rates of 0.5–2 K/min in the 30–350°C temperature interval. A weighed sample of urethane was placed into a glass tube and evacuated for 30 h under a pressure of 10^{-2} Torr. Then the tube was sealed in a vacuum. The activation energy of the monomolecular decomposition was estimated using the stepwise scanning mode. For this purpose, the reaction rates were determined within one entry at different temperatures and low of conversions.

An MK-2 calorimeter (Calvet type) was used in isothermal kinetic measurements and in the estimation of the heat of the exchange reaction. Experiments were carried out in sealed glass tubes at 60°C.

RESULTS AND DISCUSSION

Thermal Decomposition of Urethanes

Published data [1] indicate that urethanes dissociate to the starting isocyanate and alcohol under certain conditions. To solve the problem stated in this work, specifically, to study the kinetics of the exchange reactions of PPU with aliphatic alcohols, it was necessary to select such a temperature interval in which no monomolecular dissociation of the urethanes will occur.

In order to determine correctly the temperature at which PPU decomposes with an appreciable rate to the starting alcohol and isocyanate, we studied the behavior of the urethane samples in the temperature interval 250–300°C by differential scanning calorimetry
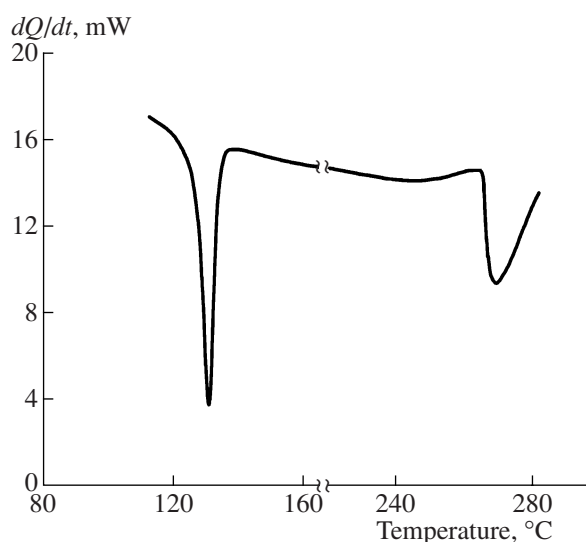
Fig. 1. DSC curve of phenyl-*N*-phenylurethane.

(DSC). The thermoanalytical curve shown in Fig. 1 contains two endotherms. The first of them corresponds to PPU melting at 130.5°C. At 265°C PPU begins to decompose noticeably to phenol and phenyl isocyanate, which is confirmed by the IR analysis of the contents of the tube after it was heated to 300°C followed by fast cooling. The IR spectra exhibit the absorption bands characteristic of phenol ($\nu(OH) = 3590$ cm^{-1}), phenyl isocyanate ($\nu(NCO) = 2270$ cm^{-1}), initial urethane ($\nu(C=O) = 1753$, $\nu(C–O) = 1192$, $\delta(NH) = 1521$, and $\nu(NH) = 3432$ cm^{-1}), isocyanurate (product of phenyl isocyanate cyclotrimerization, $\nu(C=O) = 1705$ cm^{-1}), and allophanate ($\nu(C=O) = 1725$ cm^{-1}) formed upon the reaction of isocyanate with urethane. Under the same conditions, we carried out experiments where PPU was subjected to thermal decomposition in the presence of TDBDL, as well as PPU dissolved in thoroughly dehydrated DCB. In both cases, no urethane decomposition was observed below 250°C.

The temperatures of the onset of noticeable decomposition of some other phenylurethanes were determined:

N-phenylbutylurethane, C$_4$H$_9$O(O)CNHPh, 222°C;

N-phenyl-*sec*-butylurethane, C$_4$H$_9$O(O)CNHPh, 245°C;

N-phenyl-4-methoxyphenylurethane, 1,4-(C$_6$H$_5$NHC(O)OC$_6$H$_4$OMe), 233°C;

N-cyclohexylphenylurethane, C$_6$H$_{11}$NHC(O)OPh, 236°C;

bis(*N*-phenyl)-1,4-phenylenediurethane, 1,4-(C$_6$H$_5$NHCOO)$_2$C$_6$H$_4$, 233°C;

N-*meta*-chlorophenylphenylurethane, 3-ClC$_6$H$_4$NHC(O)OC$_6$H$_5$, 235°C.

Based on the data on the decomposition rates of PPU in the stepwise heating regime in the temperature interval from 233 to 261°C, we estimated the activation
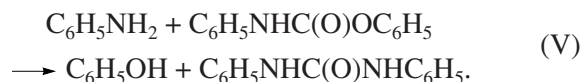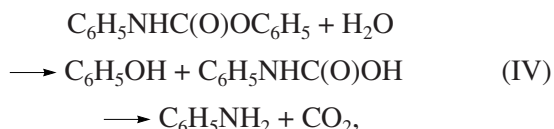
energy and preexponential factor for this reaction. They are 171 ± 12 kJ/mol and $10^{13 \pm 1}$ s^{-1}, respectively. The rate constants of the monomolecular PPU decomposition calculated from these kinetic parameters are very low, at 80°C ranging from 10^{-11} to 10^{-13} s^{-1}. Even at 180°C, the rate constants determined by extrapolation are as low as 10^{-6} to 10^{-7} s^{-1}.

The results obtained change the common concepts on the strength of the urethane bond. The data presented indicate that, in the absence of proton donors, the urethane bond is cleaved at higher temperatures than is commonly accepted. In particular, up to 265°C, PPU undergoes no noticeable dissociation. Two conclusions hence follow. First, at substantially lower temperatures the reactions of urethane exchange cannot proceed through the preliminary step of monomolecular urethane decomposition and are, most likely, bimolecular. Second, to study the exchange reactions of PPU with alcohols, one can choose a temperature interval of 40–80°C without the possible occurrence of the competitive monomolecular reaction.

Kinetics of the Reactions of Phenyl-N-Phenylurethane with Butyl Alcohols in a DBC Medium

The kinetics of the exchange reactions of PPU with alcohols in DCB was studied by IR spectroscopy, which virtually has not been used for these purposes up to the present in spite of its high accuracy and reliability. Low-volatile DCB was chosen as the solvent to exclude the possibility of changing the concentration in the solution due to solvent evaporation during analysis. The concentrations of the reactants were restricted by the solubility of PPU, which does not exceed ~0.1 mol/l in most solvents, including DCB.

Since the purpose of this work was to simulate the real processes of polyurethane processing, the reactants were not dried thoroughly. However, water is undoubtedly involved in the exchange reactions: in many cases, a precipitate of N,N'-diphenylurea virtually insoluble in DCB is formed in the reaction mixture. N,N'-Diphenylurea is formed via the following reactions:

$$C_6H_5NHC(O)OC_6H_5 + H_2O$$
$$\longrightarrow C_6H_5OH + C_6H_5NHC(O)OH \qquad (IV)$$
$$\longrightarrow C_6H_5NH_2 + CO_2,$$
$$C_6H_5NH_2 + C_6H_5NHC(O)OC_6H_5 \qquad (V)$$
$$\longrightarrow C_6H_5OH + C_6H_5NHC(O)NHC_6H_5.$$

To obtain correct data, it was necessary to study the influence of the water present in the reaction system on the kinetics of the exchange reaction between alcohol and urethane. For this purpose, we carried out a series of kinetic experiments in an isothermal calorimeter at 60°C in sealed tubes.

The study of the behavior of PPU dissolved in undried DCB in the presence of TDBDL (0.04 mol/l)

showed that, in the absence of alcohol, water contained in DBC reacts with PPU according to the second-order law and the reaction rate constant is about 1.9×10^{-3} l mol^{-1} s^{-1}. According to the data of IR spectroscopy, about 26% of the initial PPU is consumed, and long needlelike crystals of N,N'-diphenylurea are formed in the reaction mixture. It follows from the experimental results that the moisture content in the solvent used is ~0.013 mol/l (it was accepted in the calculation that two urethane molecules are consumed per one water molecule). Thus, the water concentration in the reaction mixture is lower than the PPU concentration only by an order of magnitude.

When undried reagents are used, the reaction of PPU with sec-butanol occurs in two steps: the fast interaction with water is followed by a considerably slower reaction of PPU with alcohol. In the coordinates of the second-order equation with allowance for the PPU consumption for the reaction with water,[1] the kinetic curve of heat release corresponding to the slow (second) step remains linear up to 90% conversion. At a TDBDL concentration of 0.04 mol/l, the rate constant is 1.85×10^{-4} l mol^{-1} s^{-1}. In this case, a urea precipitate is also formed in the reaction mixture.

In an experiment with dehydrated reagents, dosed amounts of PPU and the catalyst were introduced in an argon counterflow into a preliminarily degassed tube. Next, DCB dried above molecular sieves was condensed into the tube in vacuo. After PPU was dissolved, freshly distilled, and stored above CaH_2, sec-butanol was condensed into the tube, and the tube was filled with argon and sealed. To accelerate the reaction, sec-butanol was taken in slight excess with respect to PPU. In this entry, the curve of heat release in the coordinates of the second-order reaction at the nonstoichiometric ratio of the reactants also remains linear up to the conversion >80%. Under these conditions, the rate constant of the second-order reaction at the same catalyst concentration as in the previous experiment is also 1.85×10^{-4} l mol^{-1} s^{-1}, and no precipitate is formed in the reaction mixture.

The thermal effects of the reactions of PPU with water and sec-butanol are 18.8 and 33.4 kJ/mol, respectively.

Thus, the calorimetric studies showed that a water admixture exerts no noticeable effect on the alcohol–urethane exchange reaction rate; however, the urethane consumption for the interaction with water and the corresponding change in the ratio of concentrations of the main reactants should be taken into account when processing the kinetic dependences and determining the rate constants.

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[1] The coordinates of the considered dependence at the nonstoichiometric ratio of the reactants are the following: $\frac{1}{\Delta} \ln\left(1 + \frac{\Delta}{[\text{PPU}]}\right) - t$, where $\Delta = ([\text{OH}]_0 + 2[\text{H}_2\text{O}]_0 - [\text{PPU}]_0)$ and t is the reaction time.
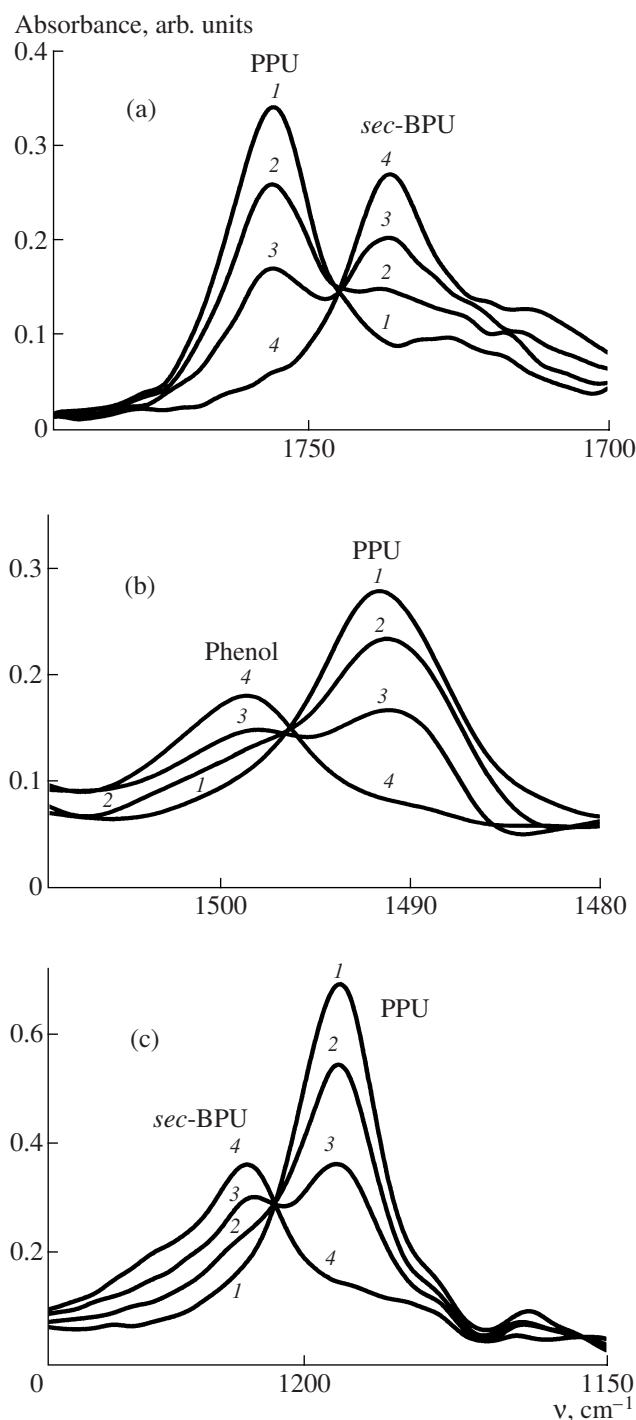
Absorbance, arb. units

(a) PPU *1*, *2*, *3*, *4*, sec-BPU *4*, *3*, *2*, *1*

1750   1700

(b) Phenol *4*, *3*, PPU *1*, *2*, *3*, *4*

1500   1490   1480

(c) sec-BPU *4*, *3*, *2*, *1*, PPU *1*, *2*, *3*, *4*

1200   1150
ν, cm⁻¹

Fig. 2. IR spectra of the reaction mixture during the catalytic reaction of PPU with sec-butanol in DCB at the degrees of conversion x = (1) 0, (2) 32, (3) 70, and (4) 100%: (a) in the region of absorption of the carbonyl group (ν_{PPU} = 1755 cm⁻¹, $\nu_{sec\text{-}BPU}$ = 1730 cm⁻¹); (b) in the region of skeletal vibrations of the aromatic ring (ν_{PPU} = 1491 cm⁻¹, ν_{phenol} = 1498 cm⁻¹); (c) in the region of skeletal vibrations of the C–N bond (ν_{PPU} = 1193 cm⁻¹, $\nu_{sec\text{-}BPU}$ = 1211 cm⁻¹). The reaction temperature was 80°C, [TDBDL] = 0.0522 mol/l.

Absorbance, arb. units

$\nu_{C=O}$ = 1735 *1*, *2*, $\nu(C=O)$ = 1712 *2*, *1*, *3*
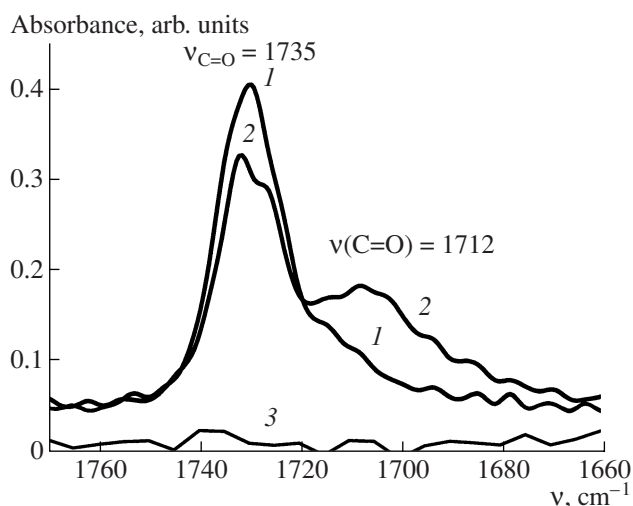
1760   1740   1720   1700   1680   1660
ν, cm⁻¹

Fig. 3. IR spectra in a DCB medium of (1) BPU, (2) a mixture of BPU with phenol, and (3) phenol; [BPU] = [phenol] = 0.1 mol/l.

The IR spectra of the reaction mixtures of PPU with sec-butanol corresponding to different degrees of conversion in the presence of the catalyst are presented in Fig. 2. Analogous spectra were obtained for the reactions of PPU with n- and tert-butanols. As can be seen, the catalytic exchange reactions occur to almost 100% conversion of PPU and no backward reactions between the BPU and phenol are observed under these conditions, which is not surprising if one takes into account the rather high exothermicity of the forward reaction. The high enthalpy of the exchange reaction with alcohol is due, possibly, to the formation of urethane complexes with phenol. The complex formation is indicated by a comparison of the IR spectra of n-BPU and its mixture with phenol (Fig. 3, curves 1, 2). The absorption band at 1712 cm⁻¹, which appears in the last case and is also observed in the spectra shown in Fig. 2a, can evidently be assigned to a BPU–phenol complex, because this band is absent from the spectra of individual phenol and BPU.

The kinetic curves of the catalytic exchange reactions of PPU with n- and sec-butanols are linearized in the coordinates of a second-order equation nearly throughout the conversion, temperature, and catalyst concentration ranges examined (Fig. 4). The difference in the rates of the reactions of PPU with water and the two alcohols indicated is not pronounced because of the relatively low water concentration in the reaction mixture. In the reaction involving tert-butanol, linearization in the second-order coordinates is observed only starting at a PPU conversion of about 20–25% (Fig. 5). This is related, obviously, to the fact that the reaction rates of PPU with water and this alcohol differ much more strongly than the rates of the reactions of PPU with water and the other two alcohols.

The kinetic parameters determined by us for the exchange reactions are presented in Table 1. It should
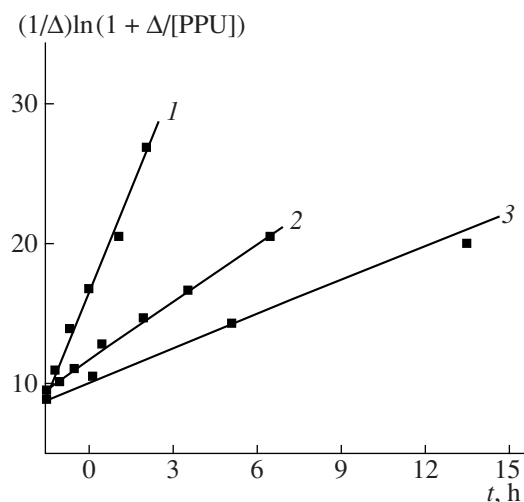
$(1/\Delta)\ln(1 + \Delta/[PPU])$

Fig. 4. Kinetics of the catalytic reactions of PPU with *n*- and *sec*-butanols in a DCB medium in the coordinates of the second-order equation: (*1*) *n*-butanol (80°C), (*2*) *n*-butanol (70°C), and (*3*) *sec*-butanol (70°C); [TDBDL] ≈ 0.005 mol/l.
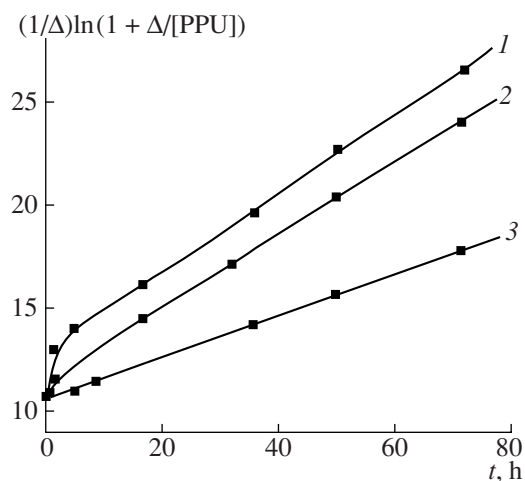
$(1/\Delta)\ln(1 + \Delta/[PPU])$

Fig. 5. Kinetics of the catalytic reaction of PPU with *tert*-butanol in a DCB medium at 80°C in the coordinates of the second-order equation at [TDBDL] = (*1*) 0.049, (*2*) 0.029, and (*3*) 0.0044 mol/l.

be mentioned that we observed no exchange reactions of PPU with the alcohols under study and water under the same conditions in the absence of the catalyst.

An analysis of the results given in Table 1 shows that in spite of the close activation energies (E_a) the apparent rate constants of the reaction of PPU with *sec*-butanol are much lower than the corresponding reaction rate constants with *n*-butanol, and the reactivity of *tert*-butanol is lower by 1.5 orders of magnitude.

This difference can be due to both steric factors and different acidity of the alcohols. The IR spectra of the alcohols under study in neutral and polar solvents were recorded to estimate the acidity. The measure of acidity was considered to be the shift of the absorption band corresponding to the stretching vibration of the OH group ($\Delta\nu(OH)$) in the spectra of solutions of the alcohols in carbon tetrachloride compared to their solutions in dioxane [9]. The $\Delta\nu(OH)$ values for *n*-, *sec*-, and *tert*-butanols are 138, 132, and 124 cm^{-1}, respectively; i.e., they are

Table 1. Kinetic parameters of the catalytic exchange reactions of PPU with alcohols in a DCB medium ([PPU] = [BuOH] ≈ 1 mol/l)

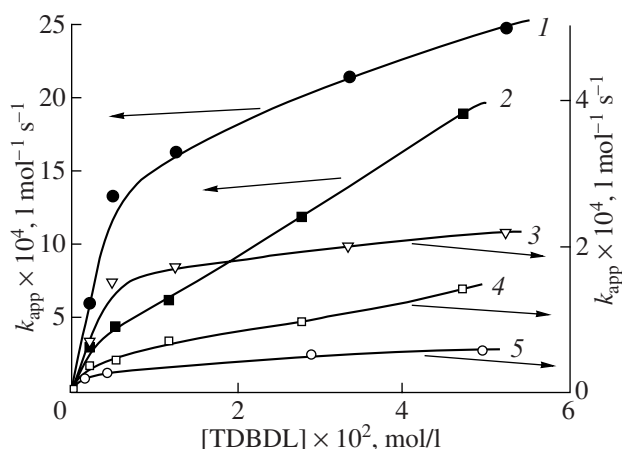| [TDBDL] × 10^2, mol/l	k_{app} × 10^4, l mol^{-1} s^{-1}			E_a, kJ/mol
	60°C	70°C	80°C	
n-Butanol				
0.23	0.7	–	6.0	113 ± 7
0.49	1.5	5.9	13.3	
1.25	1.7	–	16.3	
3.33	2.0	8.6	21.5	
5.22	2.2	8.9	24.9	
sec-Butanol				
0.23	0.36	1.0	3.0	113 ± 8
0.54	0.44	1.7	4.5	
1.17	0.70	2.6	6.3	
2.77	0.96	4.1	11.9	
4.71	1.41	5.8	19.0	
tert-Butanol				
0.17	0.011	0.055	0.19	127.5 ± 8
0.44	0.016	0.075	0.27	
2.90	0.046	0.160	0.53	
4.95	0.063	0.216	0.60	

Fig. 6. Plots of the apparent rate constants of the exchange reactions of PPU with aliphatic alcohols vs. catalyst concentration: (*1*) *n*-butanol (80°C), (*2*) *sec*-butanol (80°C), (*3*) *n*-butanol (60°C), (*4*) *sec*-butanol (60°C), and (*5*) *tert*-butanol (80°C).

Fig. 7. Kinetics of the catalytic exchange reactions of PPU with *n*-butanol in (*1, 2*) *n*-butanol and (*3, 4*) DCB media at 60°C; [TDBDL] = (*1, 3*) 0.0049 and (*2, 4*) 0.03 mol/l.

rather close to each other. Therefore, the difference in activity of the alcohols, most likely, is due to stronger steric screening of the hydroxyl group of *sec*-butanol and, even more so, of *tert*-butanol as compared to *n*-butanol.

The plots of the apparent rate constants of the exchange reactions vs. catalyst concentration in the temperature interval from 40 to 80°C (Fig. 6) represent the curves with saturation in almost all cases. In this sense, they are analogous to the corresponding dependences of urethane formation [10]; however, the necessary catalyst concentrations in the exchange reactions are two orders of magnitude higher than those in the urethane formation reactions.

Kinetics of the Reactions of PPU with Primary, Secondary, and Tertiary Butyl Alcohols in the Respective Alcohol

The reactions of PPU with alcohols in a medium of the corresponding alcohol can be considered as models for the real urethane exchange processes, which are used for the utilization of polymeric waste and worked-out products, because these processes are usually carried out in a medium of low-molecular-weight or oligomeric alcohols.

The results of studying the catalytic exchange reactions of PPU with *n*-, *sec*-, and *tert*-butanols in a medium of the corresponding alcohol are presented in Table 2. Note that, unlike the exchange reactions in DCB, analogous reactions of PPU in an alcohol medium occur without catalysts as well but their rates are low. In addition, the reactions are sharply inhibited at the 40–70% conversion, so that the complete conversion of PPU is not achieved within the noticeable time period. In the presence of the catalyst, the reaction rates are rather high and almost complete consumption of the starting PPU is achieved.
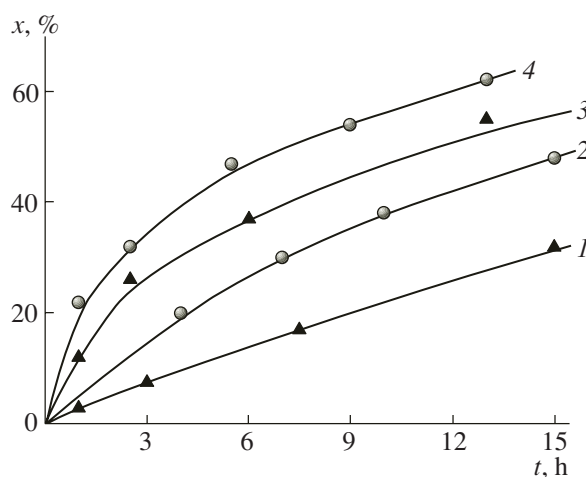
In a medium of *tert*-butanol possessing the lowest reactivity, the main reaction is the interaction of PPU with water to form diphenylurea, and only a minor portion of PPU interacts with alcohol. The rate of PPU consumption in *tert*-butanol is comparable with its consumption rates in *n*- and *sec*-butanols. However, no features of urea formation were observed in the last two cases (Table 2), although for a possible water content in alcohols of ~0.1% (which corresponds to ~0.05 mol/l) the water content is sufficient to convert the most part

Table 2. Catalytic exchange reactions of PPU with alcohols in a medium of the corresponding alcohol ([PPU] = 0.1 mol/l, reaction temperature 60°C)

| [TDBDL], mol/l	Time, h	Conversion, %	Reaction products (according to IR data)
n-Butanol			
0.0043	22	53	*n*-BPU and phenol
	44	69	
	164	96	
sec-Butanol			
0.0043	22	47	*sec*-BPU and phenol
	44	55	
	69	78	
	93	83	
	164	98	
tert-Butanol			
0.0021	22	46	N,N'-Diphenylureas (major product), *tert*-BPU, phenol
	44	92	
	69	90	
	164	~100	

of PPU to urea. This suggests that water is activated by alcohol in a *tert*-butanol medium.

A comparison of the catalytic exchange reactions of PPU with aliphatic alcohols in DCB (Figs. 4, 5) and in a medium of the corresponding alcohol (Fig. 7) indicates that they occur in different manners. For instance, in DCB the reaction rate of PPU with *n*-butanol is much higher than that with *sec*-butanol, whereas in a coreactant medium this difference is leveled, which is due, possibly, to different strengths of the formed self-associates of aliphatic alcohols.

At first glance it seems quite unexpected that the exchange reaction rate in an alcohol medium, i.e., with an increase in the reactant concentration by two orders of magnitude, remains almost the same as in a medium of DCB. In the reaction with *n*-butanol the rate of PPU consumption in an alcohol medium is even lower than that in a DCB solution (the time of achievement of the 50% conversion is doubled, see Fig. 7). This can be caused by the fact that, as shown by IR spectroscopy, in a DCB medium the hydroxyl groups of alcohols exist almost exclusively in the monomeric form, which is most reactive in the catalytic exchange reaction ($\nu(OH)$ for *n*-, *sec*-, and *tert*-butanol are 3614, 3588, and 3601 cm^{-1}, respectively), whereas in an alcohol medium they exist predominantly as poorly reactive associates [9].

Based on the data obtained, we can conclude that the catalytic exchange reactions of phenyl-*N*-phenylurethane with aliphatic alcohols at comparatively low temperatures proceed via the direct urethane–nucleophile exchange rather than urethane cleavage to isocyanate and alcohol followed by the addition of the coreactant to isocyanate. Presumably, the reaction proceeds through the step of equilibrium formation of an alcohol–urethane complex according to the following scheme:
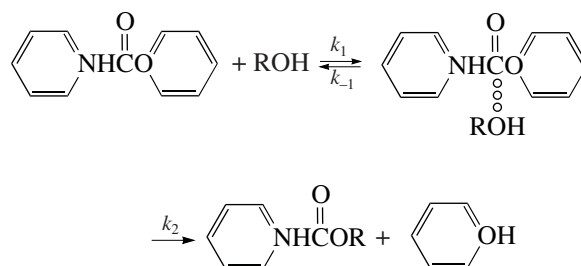
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