Spectroscopic Kinetic Study of the Interaction of Urethanes with Amines

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Abstract—The exchange reactions of phenyl-*N*-phenylurethane with amines varying in structure and nature have been investigated in *o*-dichlorobenzene. In the absence of a catalyst and proton-donating compound, the unimolecular decomposition of phenyl-*N*-phenylurethane into isocyanate and alcohol takes place at a noticeable rate starting at 250°C. The exchange reactions at $60-80^{\circ}$ C proceed as a direct exchange between the urethane and the proton donor and are second-order up to high conversions, practically until the disappearance of the entire urethane. The activation energies and apparent rate constants of the exchange reactions of phenyl-*N*-phenylurethane with various amines have been determined. The results have been explained in terms of the dependence of kinetic parameters of the reaction on the amine nature, structure, and nucleophilicity, on the steric accessibility of the amino group, and on the molecular organization of the solution.

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Investigation of polyurethanes is among the most rapidly developing areas of polymer chemistry. The steadily increasing production of polyurethane materials strongly needs efficient methods of utilization of waste and worn-out goods for improving the environmental situation [1, 2]. There are a number of polyurethane waste processing methods: thermal decomposition (incineration) and physical and chemical processing. In the latter case, wide use is made of the ability of urethanes to react with compounds containing active hydrogen, namely, alcohols, amines, and water-glycolysis, aminolysis, and hydrolysis, respectively. For efficient control over the polyurethane waste processing technology, it is necessary to know the underlying kinetic regularities and the mechanisms of the exchange reactions of the urethanes with proton-donating compounds.

Earlier, we thoroughly investigated the kinetics of the catalytic exchange reactions of phenyl-*N*-phenylurethane (PPU) with aliphatic alcohols [3]. Amines are an equally interesting and promising class of proton donors.

An analysis of the literature on the exchange reactions of urethanes with amines suggests that, while there are numerous purely technological studies, there are only a few works dealing with the kinetics and mechanism of urethane-amine reactions [4–8]. There have been kinetic studies on urethane aminolysis in a large excess of amine (pseudofirst-order reaction) and in the absence of a catalyst [6–8]. The kinetics and thermodynamics of the reactions of N-phenylurethanes and secondary aliphatic amines were investigated at a stoichiometric ratio of the reactants [9]. Experiments conducted in o-dichlorobenzene solution at 55-178°C demonstrated that the rate of the reaction obeys a second-order equation. It was hypothesized that secondary amines used as the coreactant catalyze the urethane deblocking reaction. However, that study [9] suffers from some obvious inconsistencies. It is not quite clear whether the second order of the exchange reaction is consistent with the elimination-addition mechanism suggested by the authors, since they themselves claim that the rate-limiting step of the reaction is urethane decomposition into isocyanate and blocking agent, while the reaction between the isocyanate and the amine occurs rapidly. In addition, the urethane deblocking temperatures are higher than some experimental temperatures, for example, in the 55–70°C range, while urethanes do not dissociate to a significant extent below 170°C.

Thus, the kinetics and mechanism of the exchange reactions of urethanes with amines have been insufficiently studied to date.

Here, we report the kinetics of the catalytic exchange reactions phenyl-*N*-phenylurethane with amines varying in their structure and nature, namely, aniline (An), benzylamine (BA), phenylethylamine (PEA), octylamine (OA), butylamine (BuA), and dibutylamine (DBuA), at an equimolar or near-equimolar amine : urethane ratio.

Product	Empirical formula	T. mp.,°C	ν , cm ⁻¹
Phenyl- <i>N</i> -phenylurethane	C ₁₃ H ₁₁ NO ₂	124	3319, 1534 (N–H); 1720 (C=O); 1590, 1492, 693 (aryl); 1200 (C–N)
Phenylphenylurea	$C_{13}H_{12}N_2O$	247	3327, 3290 (sh.), 1555 (N–H); 1648 (C=O); 1592, 1495, 700 (phenyl)
Benzylphenylurea	$C_{14}H_{14}N_2O$	175	3329, 3308 (sh.), 1555 (N–H); 1631 (C=O); 1605, 1499, 700 (aryl); 2930, 2917, 2876, 1450, 1440 (CH ₂)
Phenylethylurea	$C_{15}H_{16}N_2O$	155	3346, 3305 (sh.), 1566 (N–H); 1647 (C=O); 1596, 1496, 702 (aryl); 2940 (sh.), 2924, 2860, 1450, 1441 (CH ₂)
Octylphenylurea	$C_{15}H_{24}N_2O$	155	3346, 3307 (sh.), 1565(N–H); 1645 (C=O); 1592, 1499, 701 (aryl); 2943 (sh.), 2926, 2857, 1450, 1440 (CH ₂)

Table 1. IR spectroscopic data for the synthesized phenylureas and phenyl-*N*-phenylurethane

EXPERIMENTAL

Chemicals

Phenyl isocyanate C₆H₅NCO (Fluka, >98%, bp 160–164°C, d^{25} = 1.093 g/cm³, n_D^{20} = 1.536) was purified by vacuum distillation at 90°C (10 Torr).

Phenol C₆H₅OH (analytical grade for medical purposes, USSR Specifications TU 6-09-40-3245-88, $d^{41} = 1.05760$ g/cm³, $n_{\rm D}^{41} = 1.5478$, crystallization temperature of 40.6°C) was purified by sublimation at 120°C.

Aniline $C_6H_5NH_2$ (pure grade, USSR State Standard 6006-51, $d^{25} = 1.01750$ g/cm³, $n_D^{20} = 1.5854$, bp 184.4°C) was purified by keeping it for several weeks over potassium hydroxide and was then distilled, and the middle fraction was used in the experiments.

Benzylamine C₆H₅CH₂NH₂ (99%, bp 184– 185°C, $d^{25} = 0.981$ g/cm³, $n_D^{20} = 1.5430$), phenylethylamine C₆H₅CH₂CH₂NH₂ (99%, bp 197–200°C, $d^{25} = 0.965$ g/cm³, $n_D^{20} = 1.5330$), octylamine CH₃(CH₂)₇NH₂ (99%, bp 175–177°C, $d^{25} = 0.782$ g/cm³, $n_D^{20} = 1.4290$), butylamine CH₃(CH₂)₃NH₂ (99%, bp 78°C, $d^{25} = 0.740$ g/cm³, $n_D^{20} = 1.4010$), and dibutylamine CH₃(CH₂)₃NH(CH₂)₃CH₃ (99%, bp 129.25°C, $d^{25} = 0.767$ g/cm³, $n_D^{20} = 1.4170$), all purchased from Aldrich, were used as received.

1,2-Dichlorobenzene (DCB) $C_6H_4Cl_2$ (Fluka, bp 179–180°C, $d^{25} = 1.305$ g/cm³, $n_D^{20} = 1.552$) was purified by fractional distillation, and the middle fraction was used in the experiments.

Dibutyltin dilaurate (DBTDL) $[CH_3(CH_2)_{10}CO_2]_2Sn(C_4H_9)_2$ (Aldrich, 95%, $d^{25} = 1.066 \text{ g/cm}^3$, $n_D^{20} = 1.4710$) was used as received.

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Synthesis of Phenyl-N-Phenylurethane and Phenylureas

For kinetic experiments, we synthesized urethane based on phenyl isocyanate and phenol,

$RNCO + R'OH \rightarrow RNHC(O)OR'$ isocyanate urethane

and a number of ureas based on phenyl isocyanate and the amines to be examined,

$$RNCO + R'NH_2 \rightarrow RNHC(O)NHR'.$$

isocyanate urea

Phenyl isocyanate was placed in a flask with a ground-glass joint, and a proton donor was then added. (Its amount was adjusted so that the reacting groups were in equimolar proportions, [NCO] : [proton donor] = 1 : 1.) The reaction mixture was stirred, and the flask was then placed in an oven preheated to 60° C. The completeness of the reaction was checked by IR spectroscopy as an absorption band at 2270 cm⁻¹, which is due to the antisymmetric stretching vibrations of the NCO group. The reaction was performed until the ~100% conversion of the NCO groups. The resulting urethane and ureas were identified by IR spectroscopy and melting point measurements (Table 1).

Kinetic Study of Phenyl-N-Phenylurethane Aminolysis

The kinetics of the exchange reactions between PPU and amines was studied in a DCB medium at $60-80^{\circ}$ C and a stoichiometric ratio of the reactants. The concentration of the catalyst—DBTDL—was varied between 0 and 5 × 10⁻² mol/L. The reactant concentrations were limited by the solubility of PPU and DCB and did not exceed ~0.1 mol/L.

The kinetics of the exchange reactions was investigated by IR spectroscopic monitoring using a tube technique [10]. The accuracy of rate constant determination was $\pm 5\%$.

The aminolysis products—phenol and ureas were identified by IR spectroscopy. The IR spectra of filtered products, recorded as KBr pellets, were comAbsorbance, arb. units



Fig. 1. IR spectra of solutions of the reaction mixture in DCB in the region of the stretching vibrations of the carbonyl bond of urethane under conditions of the catalytic reaction between PPU and aniline at urethane conversions of (1) 0, (2) 30, (3) 60, and (4) 95%. The reaction temperature is 80°C; $C_{\text{Cat}} = 0.0024 \text{ mol/L}$.

pared with the spectra of presynthesized samples of the corresponding ureas.

IR spectra were obtained on a Specord-M82 spectrophotometer (Carl Zeiss Jena, Germany).

RESULTS AND DISCUSSION

Earlier, we established that, in the absence of a proton donor and a catalyst, PPU is not deblocked up to 265°C [3]. In addition, we carried out experiments on the thermal decomposition of PPU in the presence of the DBTDL catalyst and on the decomposition of PPU dissolved in thoroughly dehydrated DCB. In both cases, there were no indications of urethane decomposition until 250°C. Therefore, the reaction of the urethane with proton-donating compounds at much lower temperatures cannot proceed via a preliminary deblocking stage and is apparently a bimolecular reaction. In order to rule out the thermal decomposition of the urethane into the starting isocyanate and alcohol, the exchange reactions between PPU and amines were conducted in the temperature range from 60 to 80°C.

As was demonstrated by qualitative and quantitative IR spectroscopic analyses of the reaction mixture, the exchange reactions of PPU with all of the amines examined here proceed with practically 100% PPU conversion (Fig. 1) and yield the corresponding ureas and phenol.¹



Fig. 2. IR spectra of (1) PPU and (2) PPUr.

In most cases, the resulting urea precipitated after the reaction mixture was cooled. The IR spectra of the filtered crystals were identical to the spectra of the ureas synthesized for identification (Table 1). By way of example, we present the IR spectrum of the starting PPU and phenylphenylurea (PPUr) isolated from the reaction mixture by filtration (Fig. 2).

Note that, as was demonstrated by a thorough analysis of the reaction mixture at high PPU conversions, in no case did the reverse reaction between the liberated phenol and the resulting urea occur.



Fig. 3. Typical anamorphoses of kinetic curves for the exchange reactions of PPU with amines: (1) dibutylamine, (2) octylamine, (3) phenylethylamine, (4) benzylamine, and (5) aniline. $C_{\rm PPU} = C_{\rm amine} \approx 0.1 \text{ mol/L}$; $C_{\rm Cat} = 1.7 \times 10^{-3} \text{ mol/L}$; $T = 70^{\circ}$ C.

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¹ The aminolysis products were identified using ureas synthesized by the direct reaction between phenyl isocyanate and an amine.

Until high conversions, the kinetic curves for the exchange reactions of PPU with the amines are linearizable in the coordinates of a second-order rate equation throughout the temperature and catalyst concentration ranges examined (Fig. 3). Using anamorphoses of the kinetic curves, we determined the apparent rate constants k_{app} for the reactions, and, from the temperature dependences of these constants, we derived the effective activation energies E_a (Table 2).

The data presented in Table 2 suggest that the reactivity of the amines in their interaction with PPU throughout the catalyst concentration and temperature ranges examined here decreases in the following order: DBuA > BuA > OA > PEA > BA > An. These results can be explained under the assumption that, like the exchange reactions of PPU with aliphatic alcohols [10], the exchange reactions of PPU with the amines proceed via a bimolecular nucleophilic substitution mechanism. The kinetics of the exchange reactions depends at least on the structure and nature of the amine, which determine its nucleophilicity, and on the steric accessibility of the reacting functional groups.

Aromatic amines are generally less nucleophilic than aliphatic amines, because their benzene ring reduces the nucleophilicity of the molecule through the interaction between the lone electron pair of nitrogen and the delocalized π orbitals of the aromatic ring, while the alkyl radicals of the aliphatic amines increase the electron density on the nitrogen atom. As a consequence, the aliphatic amines are more reactive in the exchange reactions than the aromatic amines (Table 2). In the arylamine series, a lengthening of the alkyl moiety linking the amino group with the aromatic ring enhances the nucleophilicity of the molecule and, accordingly, the reactivity of the amine in its exchange reaction with the urethane (PEA > BA > An), since the insertion of an alkyl moiety between the benzene ring and the amino group weakens the interaction between the lone pair of nitrogen and the delocalized π orbitals of the aromatic ring.

It was demonstrated earlier that the kinetics of the exchange reactions of PPU with butyl alcohols depends on the spatial structure and acidity (basicity) of the proton donor [3]: the highest activity is shown by primary butanol, which is sterically least hindered and least basic. Conversely, the highest activity in the interaction of PPU with aliphatic amines is displayed by the secondary, sterically most hindered and most basic amine. Thus, in the exchange reactions of PPU with amines, as distinct from the same reactions of PPU with alcohols, the effect of proton donor basicity is stronger than the effect of the steric factor. Throughout the temperature and catalyst concentration ranges examined, the ratio of the k_{app} values for the reactions of PPU with DBuA, BuA, and OA is 4 : 2 : 1 (Table 2). The higher basicity of DBuA is confirmed by data available from the literature: the basicity of butylamines in chlorobenzene increases in the order

Table 2. Kinetic parameters of the exchange reactions of PPU with amines in DCB ($C_{PPU} = C_{amine} \approx 0.1 \text{ mol/L}$)

A !	$C_{\text{Cat}} \times 10^2,$ mol/L	$k_{\rm app} \times 1$	E_{α} .		
Amine		60°C	70°C	80°C	kJ/mol
DBuA	0	13.3	29.2	_*	72
	0.07	17.7	39.0	_	73
	0.21	19.6	46.8	_	79
BuA	0	4.2	10.0	_*	80
	0.10	7.2	15.0	_	70
	0.22	_*	17.0	_	_**
OA	0	2.3	5.5	11.6	80
	0.05	3.5	10.5	26.6	99
	0.10	3.7	12.9	32.1	106
	0.17	3.5	13.3	34.0	112
	0.26	3.6	16.0	34.0	111
PEA	0	1.2	2.5	10.5	106
	0.02	1.5	4.1	13.3	106
	0.05	1.9	5.3	17.5	108
	0.18	2.5	9.1	27.7	118
	0.38	2.8	13.9	43.7	135
BA	0	0.3	0.8	2.0	93
	0.17	2.1	6.7	16.7	102
	0.52	4.0	11.9	30.4	99
	0.95	3.6	11.9	30.4	99
	2.20	4.0	11.9	30.4	99
An	0	0	0	0	***
	0.04	0.4	1.9	8.3	148
	0.12	0.8	3.1	14.0	140
	0.24	1.0	4.2	22.0	145
	0.41	1.7	6.2	20.0	126
	0.80	2.7	9.1	29.0	120
	5.62	4.1	15.0	50.0	120

* The reaction was not investigated under these conditions.

** The E_a value was not calculated.

*** The reaction does not occur under these conditions.

BuNH₂ < Bu₂NH < Bu₃N [11]. Note that basicity and nucleophilicity are not identical concepts, but there are some nucleophilic substitution reactions in which the reactivity of the attacking reactant increases with an increase in its basicity [11]. Note that the effective activation energy of the reactions of PPU with butylamines is practically independent of whether the amino group is primary (BuA) or secondary (DBuA), while the activation energy of the reaction between PPU and OA is substantially higher and is close to the E_a of the reactions of the urethane with arylamines, among which the reaction between PPU and aniline is characterized by the largest E_a value. It is clear from



Fig. 4. Apparent rate constants of the exchange reactions of PPU with amines at 70°C versus the catalyst concentration: (1) dibutylamine, (2) butylamine, (3) octylamine, (4) phenylethylamine, (5) benzylamine, and (6) aniline.

the data listed in Table 2 that, in almost all cases, an increase in the catalyst concentration causes a slight monotonic increase in the activation energy. This trend is most likely due to the specific features of the formation of the catalytic complexes involving one or both reactants. However, additional experiments are necessary to elucidate the mechanism of catalysis in the exchange reactions.

The dependences of the apparent rate constants of the reactions of PPU with the amines on the catalyst concentration are represented by curves tending to some limit, with plateauing observed at lower catalyst concentrations (Fig. 4) than in the case of the exchange reactions of PPU with butanols [3]. In addition, the apparent rate constants depend only weakly on the catalyst concentration (Fig. 4).

It is remarkable that the exchange reactions of PPU with the amines (except for aniline) in DCB can occur in the absence of a catalyst as well (Table 2), and this is not so for the reactions of PPU with aliphatic alcohols [3]. This can be explained by considering the effect of the form of the amino group in the reaction system, i.e., the molecular organization of the solution on the exchange kinetics. A similar situation was observed in urethane formation reactions [12–16], in which the highest activity in the absence of a catalyst was shown by hydroxyl group self-association species and, conversely, the unassociated groups were most active in the presence of a catalyst [17].

By analogy, it can be supposed that the amino groups in the reaction systems considered here can exist both in unassociated (monomeric) form and as



Fig. 5. Spectra of amine solutions in the region of NH bond vibrations (DCB solvent): (1) aniline (0.1246 mol/L), (2) butylamine (0.1123 mol/L), and (3) dibutylamine (0.1077 mol/L).

self-association species and heteroassociation species involving the urethane and amino groups.²

A comparison of the regions of NH group stretching vibrations $(3500-3100 \text{ cm}^{-1})$ in the IR spectra of amines—aniline, butylamine, and dibutylamine—in DCB at the same amine concentration as in the reaction mixture demonstrates that the self-association species content of these amines decreases in the order DBuA > BuA > An (Fig. 5), which coincides with the order of their activities in their exchange reactions with PPU. The spectrum of the aniline solution (Fig. 5, curve 1) contains practically no absorption bands characteristic of self-association species of NH groups. As in the case of urethane formation, this is due to the absence of noncatalytic interaction between PPU and aniline. In the solutions of butanols in DCB [10], as in aniline, the self-association species of OH groups at the concentration examined here are almost absent and, as a consequence, the noncatalytic exchange reactions of PPU do not take place.

However, the exchange reaction between PPU and aniline in an aniline medium, as distinct from the reactions in DCB, does occur without a catalyst but at a low rate ($k_{app} = 6 \times 10^{-7}$ L mol⁻¹ s⁻¹, $C_{PPU} =$ 0.5 mol/L, 60°C). This finding can be explained by the fact that, according to IR spectroscopic data, the amino groups of aniline in its own medium exist mainly as self-association species, which are the most reactive species in the noncatalytic exchange reaction. The same results were obtained for noncatalytic alcoholysis reactions of PPU in respective alcohols [3].

² All reactant molecules were solvated by the solvent.

Based on experimental data on the proportions of different amino group species in DCB solution, one might expect that aniline will be the most active amine in the catalytic exchange reactions, since almost all of its NH_2 groups are in monomeric (unassociated) form, and dibutylamine will be least reactive, because its solution contains more self-association species than the solutions of the other amines (Fig. 5, curve 3). In fact, as was mentioned above, the reactivity of the amines throughout the catalyst concentration range examined decreases in the order DBuA > BuA > OA > PEA > BA > An (Table 2). Therefore, both the association and amine nucleophilicity effects show themselves in the noncatalytic exchange reactions, while the catalytic reactions are governed by the nucleophilicity factor.

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