

# Kinetics of Urethane Formation from Isophorone Diisocyanate: The Catalyst and Solvent Effects

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Received December 4, 2015

**Abstract**—The dependence of the kinetic parameters of urethane formation in the reaction between isophorone diisocyanate and alcohols of different structure (*n*-propanol, isopropanol, propargyl alcohol, 1,3-diazidopropan-2-ol, and phenol) in diluted solutions on the natures of solvent (toluene, carbon tetrachloride) and catalyst (dibutyltin dilaurate, diazobicyclooctane) was found using an original IR spectroscopic procedure. The ratio of the apparent rate constants for the reactions involving the aliphatic and cycloaliphatic NCO groups of isophorone diisocyanate was determined, and the efficiency of catalysis in these reactions was estimated. The reaction conditions under which the difference between the reactivities of isocyanate groups can reach 40 were determined.

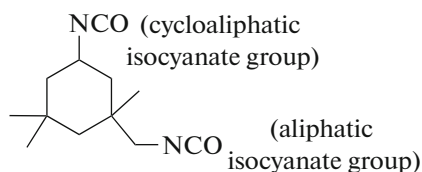
**Keywords:** isophorone diisocyanate, urethane formation, kinetics, catalysis, *n*-propanol, isopropanol, 1,3-diazidopropan-2-ol, propargyl alcohol, phenol, reactivity of isocyanate groups

**DOI:** 10.1134/S0023158416040066

## INTRODUCTION

Isophorone diisocyanate (IPDI) is extensively used in the production of different-purpose polyurethanes (coatings, rubbers, filling compositions, and glues). Of utmost interest is application of IPDI in the preparation of water-based or solventless polyurethane compositions [1–4], radiation-curable urethane acrylates [5], isocyanate-containing prepolymers, blocked polyisocyanates [6], etc. This is due to the fact that IPDI is characterized by an excellent compatibility with coreagents and different solvents and IPDI-based products possess a set of various good properties, such as light resistance, mechanical qualities, and chemical stability.

The main feature of IPDI is the presence of aliphatic and cycloaliphatic isocyanate groups therein, which exhibit different reactivities in urethane formation [7, 8].



It is obvious that the selectivity<sup>1</sup> of the isocyanate groups of IPDI and its controllability play a key role in

<sup>1</sup> Hereafter, the selectivity shall be understood as the ratio between the kinetic constants for urethane formation involving the cycloaliphatic and aliphatic NCO groups of IPDI.

selection of a procedure for the synthesis of block copolymers and prepolymers with a controlled molecular weight distribution and a low content of the residual monomeric diisocyanate. A high selectivity is very important also in the synthesis of mainly monosubstituted diisocyanate derivatives [9–12], for example, in the reaction between equimolar amounts of IPDI and 1,3-diazidopropan-2-ol (DAPOL), which can be used as precursors for the synthesis of AB<sub>2</sub>-type monomers and new hyperbranched poly(urethane-*co*-triazoles) based thereon [13].

There are a number of works dealing with the kinetics of urethane formation from IPDI and the selectivity of the NCO groups of diisocyanate in these reactions [7, 8, 14–18]. However, in many cases the differences between the reactivities of NCO groups were not taken into account [14, 15] and kinetic studies were not performed in the works where the selectivity was studied [8, 17]. In [17], the selectivity of the NCO groups of IPDI in the solventless reaction with butan-1-ol and butan-2-ol ([NCO]/[OH] = 2) was studied both in the absence of catalyst and in the presence of several Lewis acids and bases. Almost all metal-containing catalysts showed a considerably higher efficiency than the amino catalysts. Moreover, the selectivity of the NCO groups of IPDI depended on the catalyst nature. For example, the ratio of the apparent rate constants for the reactions involving the cycloaliphatic ( $k_{app,cal}$ ) and aliphatic ( $k_{app,al}$ ) NCO

groups in the absence of catalyst was on average 4–5.5 and changed from 12 for butan-1-ol to 17 for butan-2-ol upon catalysis with dibutyltin dilaurate (DBTDL, Lewis acid), and to 0.18 for butan-1-ol upon catalysis with 1,4-diazobicyclo[2.2.2]octane (DABCO, Lewis base). At the same time, according to the data from [8], the selectivity in the noncatalytic solventless reaction between IPDI and butan-1-ol ( $[\text{NCO}]/[\text{OH}] = 4$ ) was 1.6, about 12 in the presence of DBTDL, and 0.83 in the presence of DABCO. All of this suggests that the selectivity depends on the catalyst nature, the  $[\text{NCO}]/[\text{OH}]$  ratio, and the reactant concentrations, i.e. on the features of associative interactions between the hydroxyl groups in the reaction mass [19]. Thus, changing the reaction conditions one can vary the selectivity of IPDI in a wide range.

An earlier study was devoted to the kinetic features of urethane formation in the reaction of IPDI with a series of alcohols: *n*-propanol (PA), isopropanol (IPA), propargyl alcohol (PrA), 1,3-diazidopropan-2-ol (DAPOL), and phenol in toluene at the stoichiometric ratio of reactive groups [18]. The activation parameters of the reactions were determined, the order of activity was established, and the selectivity of the NCO groups of IPDI was shown to be 1.4–1.7 (2.3 in the reaction with DAPOL), and almost did not depend on the temperature in the range of 20–90°C at the reagent concentrations from 0.5 to 2 g-equiv/L.

The aim of the present work was to study the kinetic regularities of urethane formation from IPDI involving alcohols of different structures in the presence of DBTDL and DABCO catalysts and to search for conditions providing the highest selectivity of NCO groups.

## EXPERIMENTAL

IPDI and cyclohexyl isocyanate (CHI) (Aldrich) were purified by vacuum distillation at 60°C ( $2 \times 10^{-2}$  Torr) and 50°C (20 Torr), respectively. The content of isocyanate groups measured by the chemical method [20] was 99.9% of the theoretical one. Alcohols (PA, IPA, PrA, and phenol) and solvents were purified prior to use according to the standard procedures [21, 22]. DAPOL was synthesized according to a published procedure [23], the degree of its purity was at least 98.0% according to IR and  $^1\text{H}$  NMR spectroscopic and elemental analysis data. DBTDL and DABCO with a purity of 95 and 98%, respectively, were obtained from Aldrich and used as received.

IR spectra were recorded on an ALPHA FT-IR spectrometer (Bruker, Germany) using constant-thickness (0.0024, 0.0583, and 0.1 cm)  $\text{CaF}_2$  cells in the wavenumber range from 4000 to 1000  $\text{cm}^{-1}$  at 23°C. The number of scans was 16, and the resolution was 4  $\text{cm}^{-1}$ .

The urethane formation reactions were performed in dry argon-blown flasks in toluene or  $\text{CCl}_4$  at 23°C under vigorous stirring on a magnetic stirrer

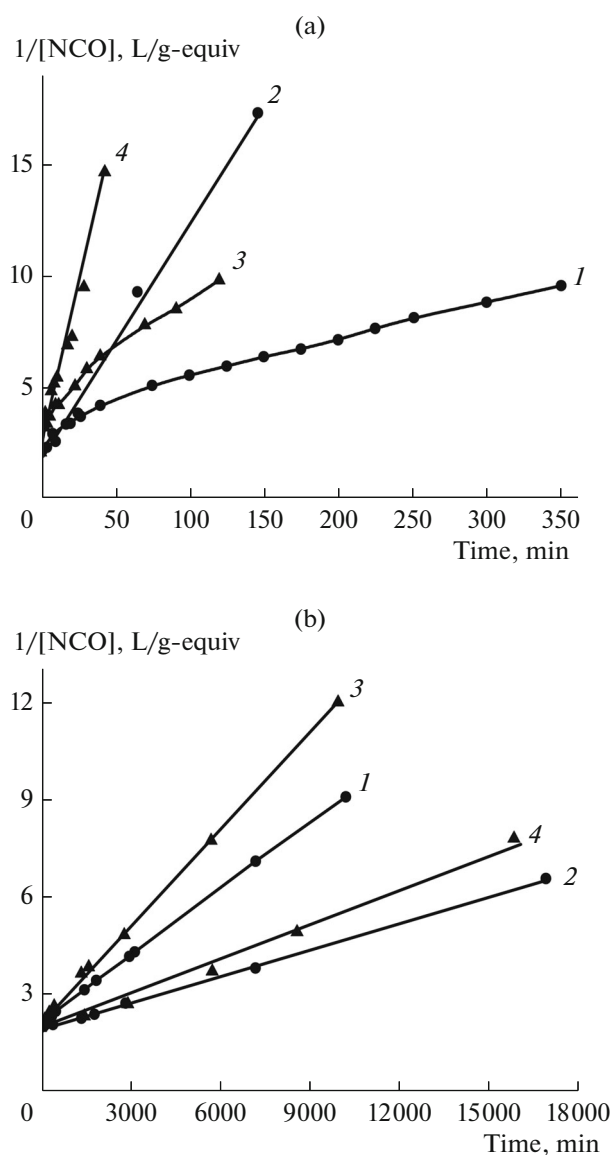
( $\sim 400 \text{ min}^{-1}$ ) at the stoichiometric ratio of NCO and OH groups ( $[\text{NCO}] = [\text{OH}] = 0.5 \text{ g-equiv/L}$ ). The reaction mixture was sampled at regular intervals after initiation of the reaction and the samples were analyzed on the IR spectrometer in constant-thickness cells. The intensities of absorption bands corresponding to the antisymmetric stretching vibration of the NCO group at 2270  $\text{cm}^{-1}$  (the molar extinction coefficients of the NCO groups were 1115  $\text{L g-equiv}^{-1} \text{ cm}^{-1}$  in toluene and 1076  $\text{L g-equiv}^{-1} \text{ cm}^{-1}$  in  $\text{CCl}_4$ ). The concentration of unreacted NCO groups was estimated using the Beer–Lambert–Bouguer law.

The ratio between the concentrations of the unreacted cycloaliphatic and aliphatic NCO groups of IPDI were measured from the IR spectra of reaction samples diluted in  $\text{CCl}_4$  ( $\sim 0.05 \text{ g-equiv/L}$  based on the starting concentration of the NCO groups) in the 3500–3200  $\text{cm}^{-1}$  region using the difference between the N–H stretching vibration frequencies of urethanes formed involving the cycloaliphatic and aliphatic NCO groups [24]. The detailed procedure for calculation of the constants  $k_{\text{app,cal}}$  and  $k_{\text{app,al}}$  in urethane formation has been described in [18]. The calculation error was not higher than 10%.

## RESULTS AND DISCUSSION

The catalytic reactions of IPDI with PA, IPA, DAPOL, PrA, and phenol in toluene at  $[\text{NCO}] = [\text{OH}] = 0.5 \text{ g-equiv/L}$  were studied and the anamorphoses of kinetic curves in the second-order equation coordinates were plotted (Fig. 1).

As can be seen from Fig. 1, the anamorphoses of the kinetic curves for the reactions between IPDI and the alcohols have two sections, fast and slow (Fig. 1a, curves 1, 3), for catalysis with DBTDL and remain almost rectilinear up to high conversions for catalysis with DABCO (Fig. 1b, curves 1, 3), as in the case of the noncatalytic reactions [18]. It was shown [18] that the anamorphoses of kinetic curves in urethane formation from diisocyanates containing the NCO groups differing in reactivity are satisfactorily linearizable in the second-order equation coordinates when the ratio of the  $k_{\text{app}}$  for the reactions involving these group is less than 3, which also takes place in the reaction between IPDI and studied alcohols in the presence of DABCO. The constants  $k_{\text{app,cal}}$  and  $k_{\text{app,al}}$  in urethane formation from IPDI and the same alcohols using DBTDL as the catalyst, which were calculated from the corresponding anamorphoses, differ more than 8-fold (Table 1). Thus, when DABCO is used, the selectivity of the NCO groups of IPDI can be determined only using a special procedure described in detail in [24]. But if DBTDL is used as the catalyst, it can be determined both by the above-mentioned procedure and using the anamorphoses of kinetic curves. It should be noted that the resulting data coincide within the limits of measurement error. The



**Fig. 1.** Typical anamorphoses of kinetic curves for the reactions (1) IPDI + IPA, (2) CHI + IPA, (3) IPDI + PA, and (4) CHI + PA in the presence of catalysts: (a) DBTDL ( $5.0 \times 10^{-3}$  mol/L) and (b) DABCO ( $5.0 \times 10^{-2}$  mol/L).

kinetic parameters of the reactions under study are given in Table 1.

The given data suggest that the cycloaliphatic NCO group of IPDI exhibits higher reactivity in the presence of DBTDL, whereas the aliphatic NCO group exhibits higher reactivity in the presence of DABCO, which does not contradict the literature data [8, 17].

To simulate the reactions involving the cycloaliphatic NCO group of IPDI, the kinetics of urethane formation from CHI containing only the cycloaliphatic NCO group and PA, IPA, PrA, DAPOL, and phenol was studied and the corresponding  $k_{\text{app}}$  were calculated (Fig. 1, Table 1). The comparison of typical

anamorphoses show that, upon catalysis with DBTDL, the rate of the reaction of alcohols with CHI is considerably higher than that with IPDI (Fig. 1a), while, in the presence of DABCO, the situation was strictly antipodal (Fig. 1b). At the same time, the cycloaliphatic NCO group of IPDI is more reactive compared to the NCO group of CHI both in the absence [18] and in the presence of DBTDL and DABCO; i.e., the cycloaliphatic groups of IPDI and CHI show different reactivities (Table 1). One can assume that this is due to the presence of alkyl substituents in the IPDI molecule, which have a noticeable effect on the molecular structure of this isocyanate: a possible lower degree of molecular association of IPDI provides a higher availability and, consequently, a higher reactivity of the cycloaliphatic NCO group.

It can also be seen from the data given in Table 1 that the structural features of alcohol play a significant role in the studied reactions. In all considered catalytic reactions of IPDI, the primary alcohol (PA) is much more reactive than the secondary one (IPA). Introduction of two azide groups (DAPOL) into the IPA molecule has no noticeable effect on the reactivity of the OH groups upon catalysis with DABCO: the constants  $k_{\text{app}}$  on the reactions of DAPOL and IPA with IPDI and CHI are close to each other. However, when DBTDL is used as the catalyst, the reactivity of the NCO groups of CHI and IPDI in the reaction with IPA is 1.3–1.5 times higher compared to the reaction with DAPOL. The introduction of a triple bond (PrA) into the PA molecule increases the reactivity of the alcohol by a factor of about 2.5 in the reactions with IPDI and CHI catalyzed by DABCO and by a factor of 2.5 and  $\sim 6.5^2$  in the reactions with IPDI and CHI catalyzed by DBTDL, respectively. A comparison between the reactivities of aromatic (phenol) and primary aliphatic alcohols showed that, in the presence of DBTDL, phenol is almost an order of magnitude less reactive than propanol and, in the presence of DABCO, phenol is 2.2 times more reactive than propanol.

Thus, the studied alcohols depending on the reactivity in the reaction with IPDI are arranged in the following orders:

- PrA > PA  $\gg$  IPA > DAPOL  $\gg$  phenol  
in the presence of DBTDL;
- PrA > phenol > PA > DAPOL  $\sim$  IPA  
in the presence of DABCO.

Table 1 gives also the coefficients of catalysis efficiency in the reaction involving the cycloaliphatic and aliphatic NCO groups of IPDI ( $\alpha_{\text{cal}}$  and  $\alpha_{\text{al}}$ , respectively) which was calculated as the ratio between the corresponding  $k_{\text{app}}$  for the catalytic and noncatalytic reactions. As it has been shown in [18], the alcohol

<sup>2</sup> This value was estimated with account taken of the differences in the DBTDL concentration.

**Table 1.** Kinetic parameters of the reactions of IPDI and CHI with alcohols of different structures in toluene\*

Isocyanate	Catalyst	$k_{app} \times 10^4$ (L g-equiv <sup>-1</sup> s <sup>-1</sup> ) and their ratio	Alcohol				
			PA	PrA	IPA	DAPOL	Phenol
IPDI	Without catalyst [18]	$k_{app}$	0.017	0.0016	0.008	0.0007	~0.00009
		$k_{app,cal}$	0.023	0.0019	0.0095	0.0009	****
		$k_{app,al}$	0.014	0.0012	0.0065	0.0004	****
		$k_{app,cal}/k_{app,al}$	1.6	1.6	1.5	2.3	****
	DABCO	$k_{app}$	0.78	1.90	0.22	0.23	1.70
		$k_{app,cal}$	0.58	1.60	0.12	0.18	1.10
		$k_{app,al}$	1.0	2.30	0.40	0.30	2.20
		$k_{app,cal}/k_{app,al}$	0.60	0.70	0.30	0.60	0.50
		$\alpha_{cal}^{**}$	25	850	13	200	~20000
	$\alpha_{al}^{**}$	71	1900	62	750		
	DBTDL	$k_{app,cal}$	120	30****	31.5	21.5	8.0
		$k_{app,al}$	8.2	2.7****	2.4	2.5	0.7
		$k_{app,cal}/k_{app,al}$	15	11**	13	8.6	11.4
		$\alpha_{cal}$	5200	15800****	3300	24900	~100000
		$\alpha_{al}$	590	2250****	380	6300	
CHI	Without catalyst [18]	$k_{app}$	0.0046	0.001	0.001	****	****
	DABCO	$k_{app}$	0.22	0.53	0.06	0.06	*****
		$\alpha_{cal}$	48	530	60	—	
	DBTDL	$k_{app}$	48	30****	18	14	
		$\alpha_{cal}$	10500	30000****	18000	—	

\* [NCO] = [OH] = 0.5 g-equiv/L, [DABCO] =  $5 \times 10^{-2}$  mol/L, [DBTDL] =  $5 \times 10^{-3}$  mol/L.

\*\*  $\alpha_{cal}$  and  $\alpha_{al}$  are the coefficients of catalysis efficiency equal to the ratio of  $k_{app}$  for the catalytic and noncatalytic reactions.

\*\*\* In view of the high reaction rate, the DBTDL concentration equal to  $5 \times 10^{-4}$  mol/L was used.

\*\*\*\* No reaction occurs at room temperature.

\*\*\*\*\* The reaction was not studied.

The dashes mean that we failed to determine the  $\alpha_{cal}$  value due to the absence of data on the rate of noncatalytic reaction.

under study are arranged by the content of free OH groups, which are typically more reactive in the catalytic reactions of urethane formation, in the order: phenol > DAPOL > PrA  $\gg$  IPA  $\gg$  PA. The highest catalysis efficiency is observed in the reaction with phenol and the lowest one in the reaction with PA and IPA (Table 1).

The content of free OH groups in DAPOL and PrA does not correlate with the  $\alpha_{cal}$  and  $\alpha_{al}$  values. For example, in the presence of DABCO the  $\alpha_{cal}$  and  $\alpha_{al}$  values in the reaction with PrA are highest than those in the reaction with DAPOL. This can be due to the fact that the steric hindrances in the reaction with DAPOL are more significant than those in the reaction with PrA. In the presence of DBTDL, the coefficients  $\alpha_{cal}$  and  $\alpha_{al}$  in the reaction of IPDI with DAPOL are higher than those in the reaction with PrA; how-

ever, this is most likely due to the fact that the amount of DBTDL in the reaction with PrA was 10-fold lower<sup>3</sup> than that in the reaction with DAPOL.

Thus, the coefficients of catalysis efficiency  $\alpha_{cal}$  and  $\alpha_{al}$  in the reaction between IPDI and alcohols in toluene decrease in the following orders:

—phenol > PrA > DAPOL > PA  $\gg$  IPA  
in the presence of DABCO;

—phenol > (PrA  $\approx$  DAPOL) > PA  $\gg$  IPA  
in the presence of DBTDL.

The study of the selectivity of IPDI NCO groups in the catalytic urethane formation involving PA, PrA, IPA, and DAPOL in the toluene medium (Table 1)

<sup>3</sup> DBTDL was used at a low concentration because of the high rate of the reaction between IPDI and PrA.

**Table 2.** Kinetic parameters of the reactions between IPDI and alcohols of different structures in  $\text{CCl}_4$ \*

Catalyst	$k_{\text{app}} \times 10^4$ (L g-equiv <sup>-1</sup> s <sup>-1</sup> ) and their ratio	Alcohol		
		PA	IPA	DAPOL
Not available	$k_{\text{app}}$	0.055	0.02	**
	$k_{\text{app,cal}}$	0.070	0.022	
	$k_{\text{app,al}}$	0.038	0.018	
	$k_{\text{app,cal}}/k_{\text{app,al}}$	1.8	1.2	
DABCO	$k_{\text{app}}$	1.24	0.23	0.33
	$k_{\text{app,cal}}$	1.33	0.20	0.36
	$k_{\text{app,al}}$	1.50	0.25	0.30
	$k_{\text{app,cal}}/k_{\text{app,al}}$	0.88	0.80	1.2
	$\alpha_{\text{cal}}$	19	9.1	–
	$\alpha_{\text{al}}$	40	14	–
DBTDL	$k_{\text{app,cal}}$	110	17	60
	$k_{\text{app,al}}$	7.1	1.5	1.5
	$k_{\text{app,cal}}/k_{\text{app,al}}$	15	11	40
	$\alpha_{\text{cal}}$	1500	760	–
	$\alpha_{\text{al}}$	190	83	–

\* [DABCO] =  $5 \times 10^{-2}$  mol/L, [DBTDL] =  $5 \times 10^{-3}$  mol/L, [NCO] = [OH] = 0.5 g-equiv/L.

\*\* The reaction almost does not proceed at room temperature.

The dashes mean that we failed to determine the  $\alpha_{\text{cal}}$  and  $\alpha_{\text{al}}$  values due to the absence of data on the rate of noncatalytic reaction.

allows to conclude that, upon catalysis with DABCO, the aliphatic NCO groups of IPDI is at most 3 times more reactive than the cycloaliphatic one. Use of DBTDL enhances the selectivity of the NCO groups of IPDI almost by one order of magnitude over the selectivity observed in the noncatalytic reaction (Table 1). The observed effects can be explained by the difference in the mechanisms of catalysis using Lewis acids versus bases.

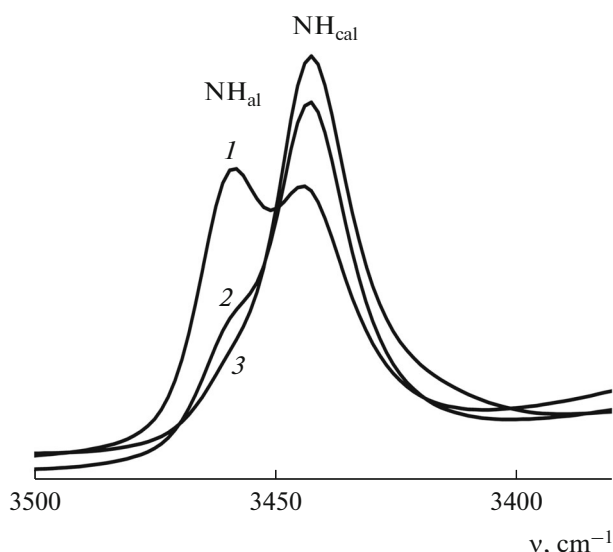
The structural features of alcohols have also a noticeable effect on the  $k_{\text{app,cal}}/k_{\text{app,al}}$  ratio. For example, in the presence of DABCO the selectivity of the NCO groups of IPDI in the reactions with PA and DAPOL is two-fold lower than that in the reaction with IPA and, in the presence of DBTDL, the selectivity of these groups in the reaction with IPA is 1.5-fold higher than that in the reaction with DAPOL, but is 1.2-fold lower than that in the reaction with PA (Table 1).

As is well known, the kinetics of urethane formation can be influenced by different factors, such as the structural features of starting reagents (isocyanate and alcohol), the nature of catalyst, the reaction medium, etc. [25]. The effect of first two factors studied in toluene has been described and discussed above. The next step was a kinetic study of urethane formation from IPDI and PA, IPA, and DAPOL in the  $\text{CCl}_4$  (Table 2).

The comparison between the kinetic regularities which were observed in toluene and  $\text{CCl}_4$  (Tables 1, 2) allows one to conclude that the reaction medium and a possible cause of this fact is medium has an effect on the catalysis efficiency. For example, in the reaction of IPDI with PA and IPA the highest efficiency was achieved when toluene was used as reaction medium and a possible cause of this fact is a higher concentration of free OH groups in this medium compared to  $\text{CCl}_4$ . It should be emphasized that the selectivity of the NCO groups in the reactions of IPDI with studied alcohols is defined by the nature catalyst and does not depend on the reaction medium, and the highest ratio  $k_{\text{app,cal}}/k_{\text{app,al}} = 15$  was obtained in the reaction between IPDI and PA catalyzed by DBTDL.

The selectivity of the NCO groups of IPDI in the reaction with DAPOL is most interesting for practical application. As noted above, this is due to the fact that IPDI and DAPOL are substrates for diazidourethane isocyanate precursors for the synthesis of new hyperbranched poly(urethane-*co*-triazoles) [13].

The analysis of results from the kinetic studies of the reaction between IPDI and DAPOL suggests that, in  $\text{CCl}_4$ , the ratio  $k_{\text{app,cal}}/k_{\text{app,al}}$  is higher than that in toluene (Tables 1 and 2). For example, the  $k_{\text{app,cal}}/k_{\text{app,al}}$  ratio is less than 9 upon the reaction between IPDI and DAPOL in toluene (Table 1) and



**Fig. 2.** IR spectra of urethane solutions resulting from the reaction between IPDI and DAPOL (100% conversion by the OH groups) upon using DBTDL as the catalyst in  $\text{CCl}_4$  at  $[\text{NCO}]/[\text{OH}]$  ratios of (1) 1, (2) 1.8, and (3) 5.

reaches 40 under analogous conditions in  $\text{CCl}_4$ . The catalyst concentration has also a noticeable effect on the selectivity of the NCO groups of IPDI in the reaction with DAPOL in  $\text{CCl}_4$ :  $k_{\text{app,cal}}/k_{\text{app,al}} \approx 16$  at  $[\text{DBTDL}] = 5 \times 10^{-4}$  mol/L and this ratio is equal to 40 at  $[\text{DBTDL}] = 5 \times 10^{-3}$  mol/L. The catalyst concentration influences the activity of aliphatic and cycloaliphatic NCO groups of IPDI in different ways: the  $k_{\text{app,cal}}$  and  $k_{\text{app,al}}$  values are  $6.0 \times 10^{-3}$  and  $1.5 \times 10^{-4}$  L g-equiv $^{-1}$  s $^{-1}$  at  $[\text{DBTDL}] = 5 \times 10^{-3}$  mol/L and  $1.5 \times 10^{-3}$  and  $0.9 \times 10^{-4}$  L g-equiv $^{-1}$  s $^{-1}$  at  $[\text{DBTDL}] = 5 \times 10^{-4}$  mol/L, respectively. Thus, with an increase in the catalyst concentration by an order of magnitude,  $k_{\text{app,al}}$  increases only 1.7-fold, whereas  $k_{\text{app,cal}}$  increases by a factor of 4. To reveal the reasons for observed effects, special studies are needed.

An IR spectroscopic analysis of the products formed in the DBTDL-catalyzed reaction between IPDI and DAPOL in  $\text{CCl}_4$  at the  $[\text{NCO}]/[\text{OH}]$  ratios from 1 to 5 showed that, the relative concentration of cycloaliphatic urethane increases with an increase of the diisocyanate excess (Fig. 2) and the selectivity of the NCO groups of IPDI remains virtually unchanged.

Thus, the performed studies showed that the selectivity of the NCO groups of isophorone diisocyanate in the reactions with alcohol can be controlled varying the catalyst concentration, the catalyst type, and the solvent nature. The highest differences in the reactivity of the isophorone diisocyanate NCO groups are observed when it reacted with diazidopropanol in  $\text{CCl}_4$  and dibutyltin dilaurate was used as the catalyst. Under these conditions, the ratio of apparent rate con-

stants for the reactions involving the cycloaliphatic and aliphatic NCO groups of isophorone diisocyanate can reach 40. Not least important is the fact that the change in the ratio of reactive groups has no significant effect on the selectivity in the case when the reactions are performed in diluted solutions. The resulting data can be used for optimization of processes for the preparation of isophorone diisocyanate-based materials, coatings, and new polymers, in particular, hyperbranched poly(urethane-co-triazoles).

## ACKNOWLEDGMENTS

This work was supported by the Presidium of the Russian Academy of Sciences within Fundamental Research Program no. 1: "Nanostructures: Physics, Chemistry, Biology, and Principles of Technology" (Subprogram II: Nanomaterials).

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*Translated by K. Utegenov*