

# Quantum-Chemical Study on the Reaction of Phenyl Isocyanate with Linear Methanol Associates. Addition at the C=N Bond

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**Abstract**—Quantum-chemical calculations at the B3LYP/6-311++G(*df,p*) level of theory showed that reactions of phenyl isocyanate with methanol associates involve formation of pre- and post-reaction complexes. The reactions proceed through late asymmetric cyclic transition states. The height of the energy barrier decreases as the degree of association of the alcohol increases. The relative change in the Gibbs energy in the reaction of phenyl isocyanate with methanol also becomes smaller as the degree of alcohol association increases.

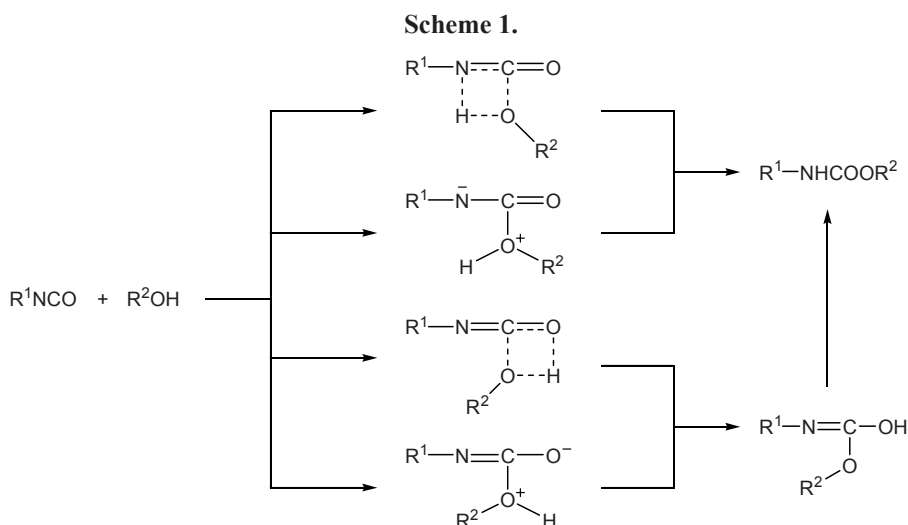
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Reactions of isocyanates with alcohols underlie large-scale processes for manufacture of polyurethanes which are widely used in industry, building construction, and medicine [1–4]. These reactions were assumed to follow both two-step ionic and synchronous mechanisms involving addition of the hydroxy group in alcohol at both C=N bond and carbonyl group of isocyanate (Scheme 1) [1].

Development of the ionic mechanism concept was favored by the observed acceleration of the process in the presence of electron-withdrawing substituents in isocyanates [5–7] and electron-donating substituents in

alcohols [8]. The ionic mechanism is very consistent with the fact that such transformations are catalyzed by Lewis acids, in particular by tertiary amines [1–3]. On the other hand, such kinetic parameters of reactions of alcohols with isocyanates as small energies (enthalpies) of activation, large negative entropies of activation [9–13], weak sensitivity to the solvent nature [14–17], and small  $\rho$  values in the Hammett equations [5–8] are more typical of synchronous mechanisms.

Consideration of problems related to the reactivity of alcohols and isocyanates toward each other is complicated due to the fact that these transformations could



involve not only monomeric alcohol molecules but also their associates [15, 16, 18–20]. As a result, interpretation of the experimental kinetic data becomes difficult. These obstacles can be overcome with the aid of quantum-chemical calculations which have already been used to study the mechanism of reaction of isocyanates with alcohols [21–24]. However, in these studies only variation of potential energy during the process was examined, and the calculations were performed by semiempirical methods which now attract interest only from the historical viewpoint. Equilibrium constants of chemical reactions are determined by variation of the Gibbs energy during the process, and a free energy barrier exists on the reaction coordinate. Therefore, a deeper insight into mechanisms of chemical reactions requires complete description of thermodynamic parameters of the process as the reaction system moves from the initial reactants through transition state to final products. We followed an analogous approach while studying the reaction of phenyl isocyanate with methanol associates.

The calculations were performed using Gaussian 03 software package [25, 26] with B3LYP/6-311++G(*df,p*) basis set. The geometric parameters were preliminarily optimized by Priroda 6 program [27] using L11 basis set (an analog of cc-pCVDZ [28]). Transition state was identified by the first negative Hessian eigenvalue and was verified by descent from the transition state point toward both directions with the aid of the IRC procedure, followed by geometry optimization of the resulting pre- and post-reaction complexes.

The structures of most energetically favorable conformers and energy barriers to internal rotation were determined in terms of PM3 semiempirical approximation with variation of dihedral angles through a step of 10 deg. The geometric parameters of conformers thus obtained were then used in the subsequent calculations.

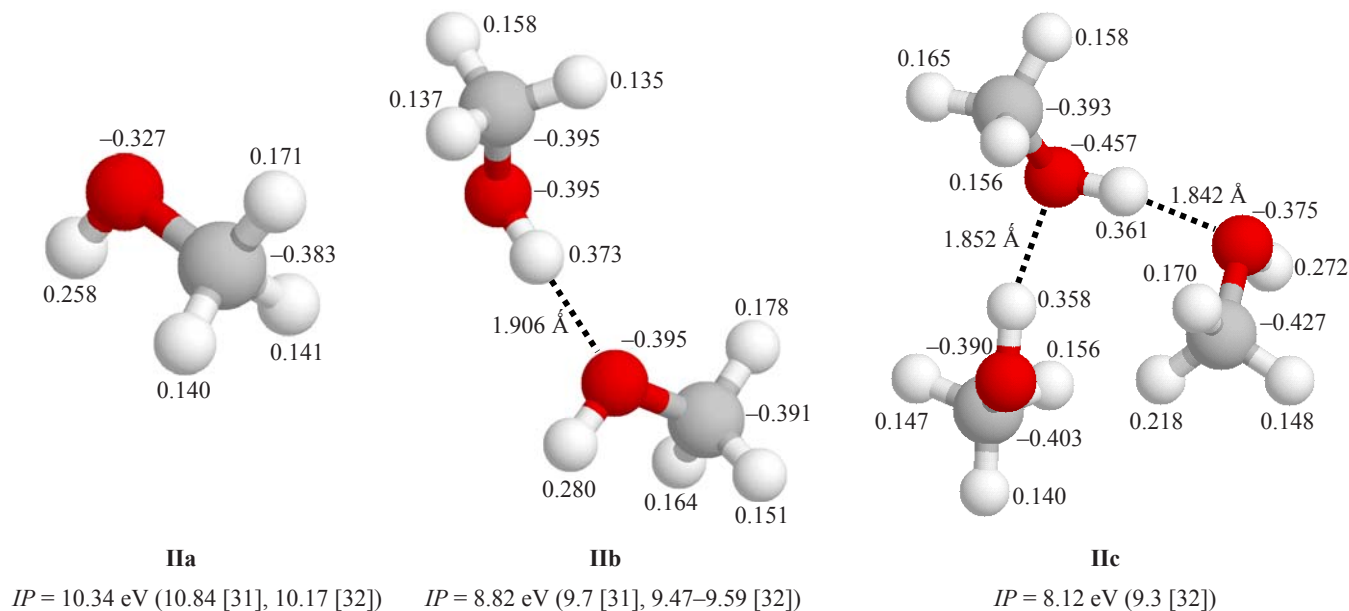
**Structure of phenyl isocyanate (I).** The calculations showed that the most stable conformer of **I** has planar structure (the dihedral angle CCNC is 0.063°).

The isocyanato group slightly deviates from linearity: the bond angle NCO is 174.0°. The barrier to rotation of the isocyanato group in molecule **I** is insignificant (3.5 kJ/mol). According to the microwave spectroscopy data, it does not exceed 22 kJ/mol [29]. From the viewpoint of molecular orbital structure, the isocyanato group in phenyl isocyanate consists of two orthogonal 1,3-dipolar systems and is not a heterocumulene system. The partial charges on the nitrogen, carbon, and oxygen atoms in the NCO group are equal to –0.126, +0.546, and –0.258 (electron charge units), respectively. Molecule **I** is weakly polar: the calculated dipole moment is 2.66 D. According to different authors, the experimental dipole moment of phenyl isocyanate ranges from 2.23 to 2.91 D [30].

**Structure of methanol associates IIa–IIc.** Figure 1 shows the electronic structures of monomeric methanol molecule **IIa**, dimer **IIb**, and trimer **IIc**. Association of methanol molecules is accompanied by insignificant change of charges on the oxygen and hydrogen atoms in the hydroxy groups. On the other hand, increase in the number of methanol molecules leads to considerable enhancement of electron-donating properties of the associates. Presumably, increased electron-donating power of clusters formed via intermolecular hydrogen bonds is a typical pattern which is also observed for associates of ammonia, primary and secondary amines, ethylene, allene [33], acetylene [34], etc. The polarity of different methanol associates depends only slightly on their size. The calculated dipole moments of associates **IIa–IIc** are 1.87, 3.20, and 1.12 D, respectively. The experimental estimates of the dipole moment of methanol range from 1.61 to 1.71 in the gas phase and from 1.58 to 1.91 D in solution [30]. The fraction of monomeric species in pure methanol is 2.7%, while the fractions of dimers, trimers, and tetramers are 25.4, 68.2, and 3.6%, respectively [35, 36]. In the gas phase in the presence of helium, the corresponding fractions are 90.1 ( $n = 1$ ), 5.4 ( $n = 2$ ), 3.6 ( $n = 3$ ), and 0.9% ( $n = 4$ ) [37]. Table 1 contains the calculated thermodynamic parameters for

**Table 1.** Variations in the Gibbs energies ( $\Delta G$ ) at 298 K, enthalpies ( $\Delta H$ ), and entropies ( $\Delta S$ ) in the formation of methanol associates **IIb** and **IIc** from monomeric species **IIa** and the corresponding experimental data for the gas phase

Reaction	Calculated values			Experimental data [38]	
	$\Delta G_{298}$ , kJ/mol	$-\Delta H_{298}$ , kJ/mol	$-\Delta S_{298}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$-\Delta H_{298}$ , kJ/mol	$-\Delta S_{298}$ , J mol <sup>-1</sup> K <sup>-1</sup>
<b>2IIa</b> ↔ <b>IIb</b>	11.8	17.2	97.6	13.5–18.0	69.0–104.2
<b>3IIa</b> ↔ <b>IIc</b>	26.4	43.3	234.1	19.2–52.4	74.5–185.0
<b>IIa + IIb</b> ↔ <b>IIc</b>	14.6	26.1	136.6	–	–



**Fig. 1.** Ball-and-rod models of linear methanol associates **IIa–IIc**. Given are partial charges on atoms, hydrogen bond lengths, and calculated and experimental (in parentheses) ionization potentials.

the formation of associates **IIa–IIc** from monomeric methanol molecules. In addition, the corresponding experimental values for the gas phase [38] are given; these values were obtained by averaging of the data reported in a number of publications.

The enthalpies of the processes under study are typical of interactions involving hydrogen bonding. Such equilibria are characterized by large negative entropies, which are usually observed when a single species is formed from two or more species in an elementary step. The relative variation of the corresponding Gibbs energies (and hence equilibrium constants) is governed by change of the entropies. The processes described in Table 1 conform to the isokinetic relationship

$$\Delta H = 536.8 + 188.4\Delta S; r = 0.998.$$

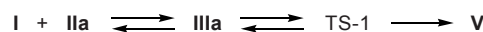
It should be noted that processes involving formation of hydrogen bonds generally fit isokinetic relationship [39, 40].

**Structure of methyl phenylcarbamate (V).** The methyl group in carbamate **V** can be oriented *syn* or *anti* with respect to the carbonyl group. The available published data [41] suggest that the *syn* conformer is preferred. Therefore, just the *syn* conformer of methyl phenylcarbamate was used as initial structure in our calculations. The barrier to internal rotation about the N–C bond (variation of the dihedral angle CNCO) in molecule **V** is 18.9 kJ/mol. Two conformers of **V** are possible. Among these, the most stable is that with

a dihedral angle CNCO of 30°, and the CNCO angle in the other less stable conformer is 210°. The calculated difference in the energies of these conformers is 4.2 kJ/mol. According to Moraczewski et al. [42], the difference in the energies of alkyl phenylcarbamate conformers arising from rotation about the C–N bond is equal to 7.5 kJ/mol.

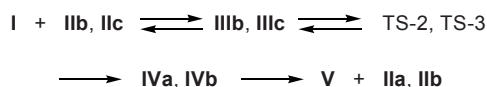
**Thermodynamic characterization of the reaction of phenyl isocyanate (I) with linear methanol associates IIa–IIc.** We examined the potential energy surfaces for the reactions of phenyl isocyanate (**I**) with linear methanol associates **IIa–IIc**. The reaction with monomeric methanol **IIa** involves pre-reaction complex **IIIa** which is transformed into carbamate **V** through transition state TS-1 (Scheme 2).

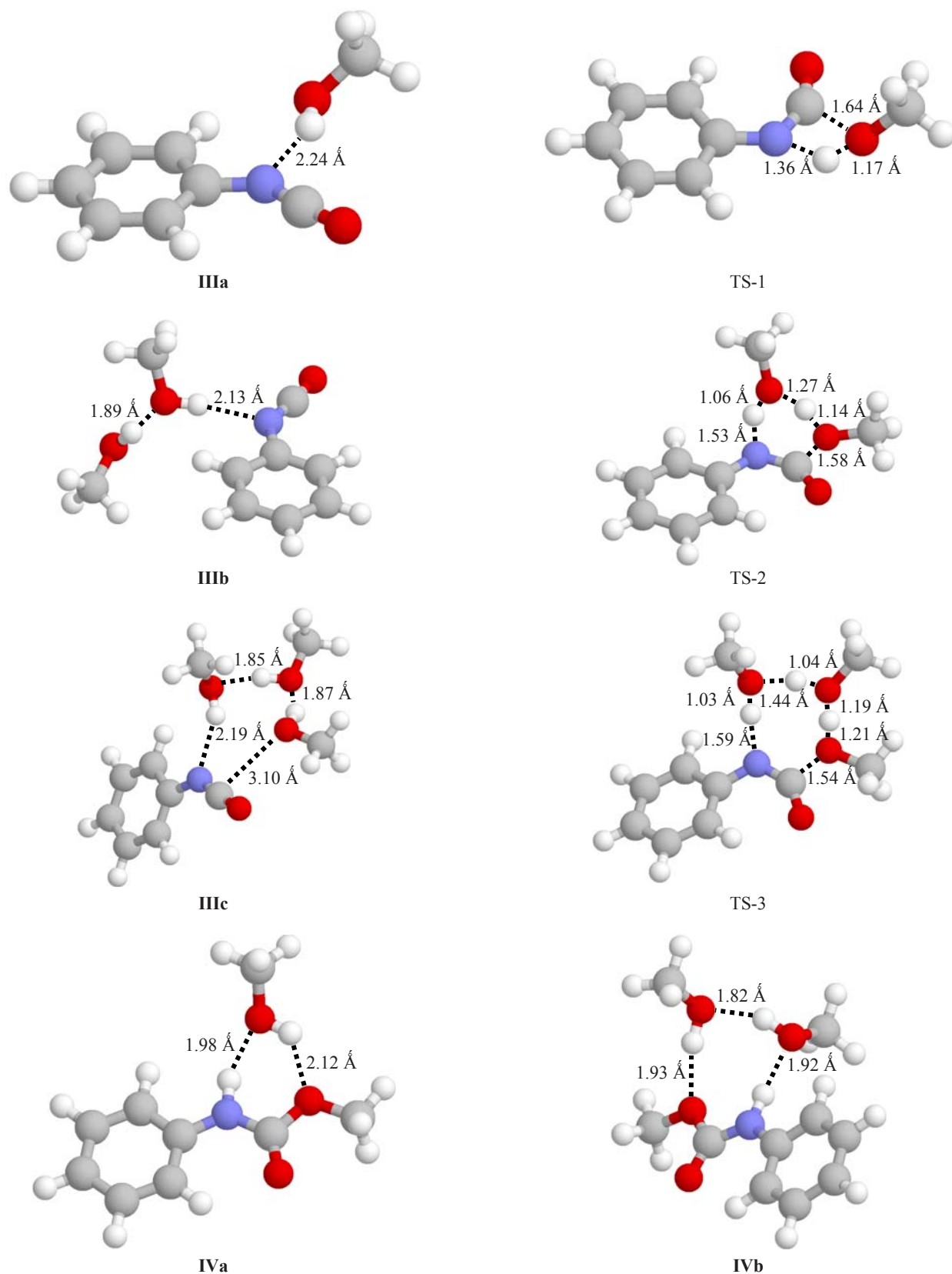
**Scheme 2.**



In the reactions of **I** with associates **IIb** and **IIc**, the corresponding pre-reaction complexes **IIIb** and **IIIc** are also formed, but transition states TS-2 and TS-3 are initially converted into post-reaction complexes **IVa** and **IVb** which lose methanol molecule, yielding carbamate **V** (Scheme 3).

**Scheme 3.**





**Fig. 2.** Structures of pre-reaction complexes **IIIa–IIIc**, transition states **TS-1–TS-3**, and post-reaction complexes **IVa** and **IVb**. Interatomic distances are given.

**Table 2.** Variations of the Gibbs energies ( $\Delta G$ ), enthalpies ( $\Delta H$ ), and entropies ( $\Delta S$ ) in intermediate stages in the reactions of phenyl isocyanate (**I**) with linear methanol associates **IIa–IIc**

Reaction	$\Delta G_r^\circ$ , kJ/mol	$\Delta H_r^\circ$ , kJ/mol	$\Delta S_r^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup>
<b>I + IIa</b> → <b>IIIa</b>	26.1	-4.6	-103.1
<b>IIIa</b> → TS-1	153.1	131.7	-71.7
TS-1 → <b>V</b>	-201.3	-202.1	-2.9
<b>I + IIb</b> → <b>IIIb</b>	27.3	-5.3	-109.3
<b>IIIb</b> → TS-2	96.8	58.8	-127.0
TS-2 → <b>IVa</b>	-140.8	-131.1	32.6
<b>IVa</b> → <b>V + IIa</b>	-17.2	19.7	123.7
<b>I + IIc</b> → <b>IIIc</b>	32.4	-7.3	-133.2
<b>IIIc</b> → TS-3	84.6	51.4	-111.2
TS-3 → <b>IVb</b>	-136.4	-126.3	33.9
<b>IVb</b> → <b>V + IIb</b>	-17.2	33.4	169.6

**Table 3.** Parameters  $f$  for transition states TS-1–TS-3 in the reactions of phenyl isocyanate (**I**) with linear methanol associates **IIa–IIc**

Transition state	$f_{C-N}$	$f_{C-O}$	$f_{N-H}$
TS-1	62.9	82.6	74.1
TS-2	60.5	85.7	65.8
TS-3	61.7	88.0	63.2

**Table 4.** Variations of the Gibbs energies ( $\Delta G_r$ ), enthalpies ( $\Delta H_r$ ), and entropies ( $\Delta S_r$ ) in the reactions of phenyl isocyanate (**I**) with linear methanol associates **IIa–IIc** at 298 K

Reaction	$\Delta G_r^\circ$ , kJ/mol	$\Delta H_r^\circ$ , kJ/mol	$\Delta S_r^\circ$ , J mol <sup>-1</sup> K <sup>-1</sup>
<b>I + IIa</b> → <b>V</b>	-22.1	-74.9	-177.6
<b>I + IIb</b> → <b>V + IIa</b>	-33.9	-57.7	-80.0
<b>I + IIc</b> → <b>V + IIb</b>	-36.7	-48.8	-41.0

Figure 2 shows the structures of pre-reaction complexes **IIIa–IIIc**, transition states TS-1–TS-3, and post-reaction complexes **IVa** and **IVb**, and Table 2 contains the thermodynamic parameters characterizing the above transformations.

Many authors [15, 43] presumed that isocyanates react with alcohols through intermediate complexes. The formation of complexes **IIIa–IIIc** is governed mainly by hydrogen bonding between protons in the free hydroxy groups of associates **IIa–IIc** and nitrogen atom in isocyanate **I**. Complexes **IIIa–IIIc** may be regarded as weak: their formation is characterized by

relatively small enthalpies and large negative entropies (Table 2). The stability of the complexes decreases in going from monomeric methanol **IIa** to trimer **IIc**. The relative variation in the Gibbs energies of complex formation of isocyanate **I** with associates **IIa–IIc** is determined by variation in the entropy. The enthalpy–entropy compensation effect is observed for the above equilibria:

$$\Delta H = -4410.7 + 88.1 \Delta S; r = 0.999.$$

In all cases, pre-reaction complexes **IIIa–IIIc** are transformed into cyclic transition states TS-1–TS-3 where formation of new bonds and rupture of old bonds occur simultaneously, i.e. the transformations under study follow a concerted synchronous mechanism. Analogous transition states were found while studying the reaction of isocyanic acid with linear methanol associates by the MP2 method [24].

With a view to characterize the degree of rupture of old and formation of new bonds in transition states TS-1–TS-3 on a quantitative level we introduced a parameter  $f$  which was defined (for bond formation) as the ratio of bond length in the product and in the transition state:

$$f_f (\%) = d_{\text{prod}}/d_{\text{TS}} \times 100.$$

The parameter  $f_f$  reflects the degree of formation of new bonds in the transition state in percentage. The corresponding parameters  $f_r$  for rupture of old bonds was defined as the difference between the bond lengths in the transition state and in the initial reactant, divided by the difference between the bond lengths in the product and in the reactant, so that this parameter reflects the percent degree of bond rupture in the transition state:

$$f_r (\%) = (d_{\text{TS}} - d_{\text{react}})/(d_{\text{prod}} - d_{\text{react}}) \times 100.$$

As follows from the  $f_f$  and  $f_r$  values for different bonds (Table 3), transition states TS-1–TS-3 are characterized by considerable degrees of rupture of old bonds and formation of new bonds, so that these transition states may be regarded as late. In all cases, the degree of formation of new C–O bond is greater than the degree of formation of new N–H bond, i.e., transition states TS-1–TS-3 are asymmetric, and they reflect nucleophilic character of the addition of alcohols to isocyanates. The degree of rupture of the carbon–nitrogen bond in isocyanate **I** almost does not depend on the number of methanol molecules in the associate. On

the other hand, larger associates give rise to transition states with greater degree of formation of new C–O bond and smaller degree of formation of new N–H bond. The degree of rupture of the O–H bond in the alcohol (which is responsible for the formation of N–H bond) decreases in parallel. In the reaction of **I** with monomeric methanol **IIa**, the O–H bond in the transition state extends by 22%, while in the reactions with dimer **IIb** and trimer **IIc**, by 11 and 8%, respectively. Increase in the number of methanol molecules in the associate reacting with phenyl isocyanate is accompanied by increase in the transition state asymmetry, though the transition states remain late. Increased asymmetry leads to increased polarity, and the dipole moments of transition states TS-1, TS-2, and TS-3 are 2.7, 4.6, and 7.2 D, respectively.

In keeping with the data in Table 2, the Gibbs energies of the reactions of isocyanate **I** with methanol associates **IIb** and **IIc** are considerably lower than that calculated for the reaction of **I** with monomeric species **IIa**. These findings indicate that the main channels for the formation of methyl phenylcarbamate (**V**) are reactions of isocyanate **I** with methanol dimers and trimers and that the contribution of the reaction with monomer **IIa** should be insignificant. Enhanced reactivity of methanol associates **IIb** and **IIc** is consistent with their greater electron-donating power as compared to monomer **IIa**. Addition of alcohols to isocyanates is a particular case of nucleophilic addition at multiple bonds of compounds having a labile hydrogen atom. In terms of intermolecular donor–acceptor orbital interactions, such reactions are favored by electron-donating properties of nucleophiles [44, 45], which can be characterized on a quantitative level by ionization potentials.

Increase in the degree of methanol association favors the process under study not only from the kinetic but also from the thermodynamic viewpoint. The calculated thermodynamic parameters (Table 4) indicate that all the examined transformations are exothermic. The largest heat effect was found for the reaction of isocyanate **I** with monomeric methanol **IIa**. On the other hand, this reaction is characterized by the lowest entropy. In going to methanol dimer and trimer, the enthalpy of the reaction decreases, while the entropy increases. Decrease in the reaction enthalpy ( $\Delta H$ ) is related to the gain in energy upon association (Table 1). Decomposition of associates during the process implies energy consumption. Increased entropy  $\Delta S$  of the reaction with methanol associates is consistent with the fact that the process is not accompanied by loss of translational and rotational degrees of

freedom, while only their numerical values change. In the reaction with monomeric methanol, three translational and three rotational degrees of freedom are lost completely.

Thus the results of our study show that the reactions of phenyl isocyanate with methanol associates are more favorable than the reaction with monomeric methanol in both kinetic and thermodynamic aspects. These reactions involve formation of pre- and post-reaction complexes and cyclic transition states in which rupture of old bonds and formation of new bonds occur simultaneously. The transition states are late and asymmetric. We believe that increase in the reactivity with rise in the degree of association of methanol molecules is related to reduced ionization potentials of the associates. The relative change in the Gibbs energies is determined mainly by variation of the entropy.

In the present work we considered the reaction of phenyl isocyanate with methanol associates as a model process. Nevertheless, we believe that the conclusions drawn from the results of this study are general for all reactions of isocyanates with alcohols.

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