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Alcohol Associates as Catalysts of Tautomeric Transformations

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Abstract—The B3LYP/6-311++G(df,p) quantum-chemical simulation has revealed that linear associates of methanol catalyze the ketone–enol, nitro–aci-nitro, and carbamate–azomethinenol tautomeric transformations. All the reactions proceed via the coherent transition states. The catalytic effect is enhanced with the increased alcohol degree of association. The acid-base properties of methanol are changed similarly.

Keywords: hydrogen bond, complex, tautomerism, catalysis, reactivity

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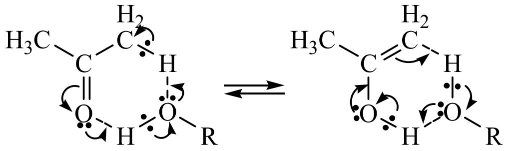
Tautomeric transformations have been studied in detail so far [1–3]. Monomolecular tautomeric interconversions proceed via the synchronous (coherent) transition states, with the bonds rupture and formation occurring simultaneously. Catalysis of such reactions via the Brønsted–Lowry acids and bases gives rise to ionic transition states [4]. Water-catalyzed tautomeric transformations have been discussed in a number of reports [3, 5–8]. Enhancement of the catalytic action of water dimers as compared to that of water monomer has been revealed. The water-catalyzed reactions occur via the synchronous mechanism as well. However, the mechanism of the catalytic action has not been elucidated in [3, 5–8].

Catalytic tautomeric reactions involving hydroxyl-containing species can be explained in view of the Brønsted acid-base interactions. The approach is illustrated below using the acetone keto-enol tautomerism as an example.



In the course of the interaction, proton of the alcohol hydroxyl group is attached at the carbonyl atom of acetone. Proton of the acetone methyl group is attached at the alcohol oxygen atom. Hence, the alcohol molecule simultaneously acts as an acid and a base in the Brønsted–Lowri terms. Therefore, the tautomeric transformation should be catalyzed more efficiently by the hydroxyl-containing compounds possessing the stronger acid-basic properties, the latter being expressed by the gas-phase acidity-basicity parameters (pK_a and pK_B). The gas-phase proton affinity of water clusters grows up with the molecules association [9]. Enthalpy of the heterolytic dissociation of water monomer (a measure of the Brønsted acid properties) is of 1633 kJ/mol in the gas phase [10]. Using the data from [11, 12], we have computed the dissociation enthalpies of water dimer, trimer, and tetramer in the gas phase (1537, 1476, and 1425 kJ/mol, respectively). Hence, the Brønsted acid properties of water clusters are enhanced owing to the molecules association as well. In view of this, the increased catalytic activity on the tautomeric transformations of water dimer as compared to that of the isolated molecules can be rationalized.

If the acid-base interactions are indeed the key ones determining the catalytic action of water associates in the tautomeric transformations, the above-discussed trends should be general. Indeed, our simulations presented in this paper have confirmed that the similar features are observed in the case of linear alcohol associates.

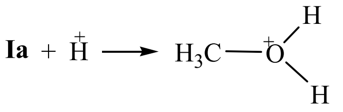
Acid-base properties of linear methanol associates. We explored the effect of alcohols association on their acid-base properties using methanol as an example. In

Table 1. Parameters of acidity and basicity of methanol linear associates **Ia–Ic** in gas phase at 298 K

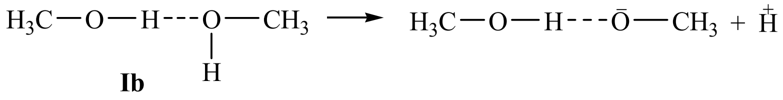
Associate	ΔG_A, kJ/mol	ΔH_A, kJ/mol	*GB*, kJ/mol	*PA*, kJ/mol
Ia	1543	1575	712	743
Ib	1454	1483	830	871
Ic	1395	1430	894	930

particular, we performed the B3LYP/6-311++G(df,p) hybrid quantum-chemical simulations to assess the parameters of gas-phase acidity and basicity of linear methanol associates (Table 1).

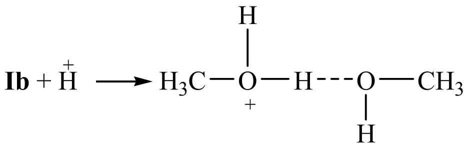
$$\underset{\mathbf{Ia}}{CH_3OH} \longrightarrow CH_3\bar{O} + \overset{+}{H} \qquad (1)$$



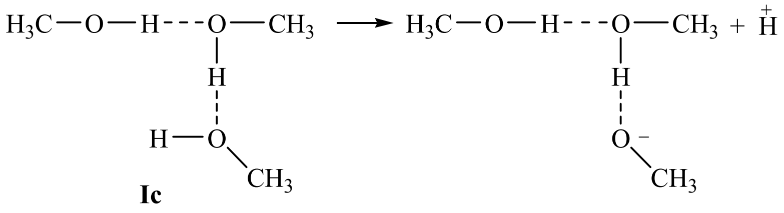
$$\mathbf{Ia} + \overset{+}{H} \longrightarrow H_3C-\overset{+}{O}H_2 \qquad (2)$$



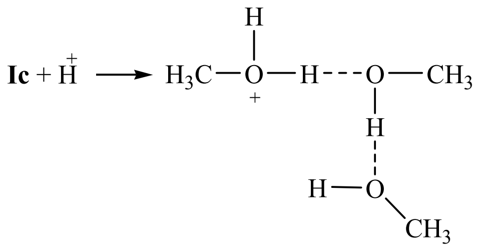
$$\underset{\mathbf{Ib}}{H_3C-O-H\cdots O(H)-CH_3} \longrightarrow H_3C-O-H\cdots\bar{O}-CH_3 + \overset{+}{H} \qquad (3)$$



$$\mathbf{Ib} + \overset{+}{H} \longrightarrow H_3C-\overset{+}{O}(H)-H\cdots O(H)-CH_3 \qquad (4)$$



$$\underset{\mathbf{Ic}}{H_3C-O-H\cdots O(CH_3)-H\cdots O(H)CH_3} \longrightarrow H_3C-O-H\cdots O(CH_3)-H\cdots \bar{O}CH_3 + \overset{+}{H} \qquad (5)$$

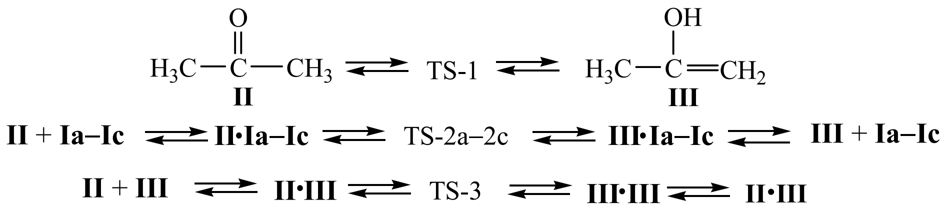


$$\mathbf{Ic} + \overset{+}{H} \longrightarrow H_3C-\overset{+}{O}(H)-H\cdots O(CH_3)-H\cdots O(H)CH_3 \qquad (6)$$

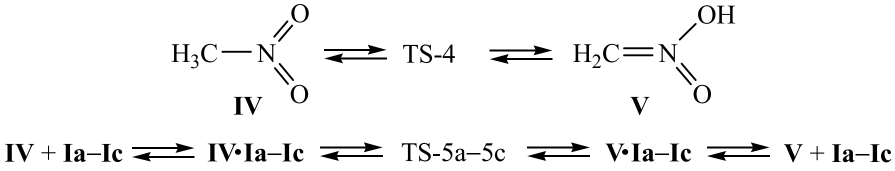
Experimental values of ΔG_A and ΔH_A for monomeric methanol are of 1571 and 1597 kJ/mol, respectively, at 298 K [13], whereas the experimental values of its gas-phase basicity and proton affinity are of 724 and 754 kJ/mol, respectively [14]. The simulated parameters of gas-phase acidity and basicity deviated from the experimental values by less than 2%, thus confirming the validity of the performed simulation.

The data collected in Table 1 showed that increasing of methanol association degree significantly enhanced its acid [reactions (1), (3), and (5)] as well as base [reactions (2), (4), and (6)] properties. Therefore, we suggested that alcohol associates, similarly to water ones, should catalyze the tautomeric transformations, and their catalytic effect should be more pronounced for the higher association degrees. We further verified

Scheme 1.



Scheme 2.



the assumption by performing the quantum-chemical simulation of the following non-catalytic as well as methanol-catalyzed tautomeric transformations: ketone–enol, nitro–aci-nitro, and carbamate–azomethinenol. All the simulations were performed taking advantage of the B3LYP/6-311++G(df,p) method.

Catalysis of ketone–enol tautomeric transformation with linear methanol associates Ia–Ic. We considered the non-catalytic as well as a number of catalytic pathways of acetone enolization (Scheme 1).

The reactions **IIa**–**IIc** catalyzed by methanol associates proceed via formation of the pre- and post-reaction complexes. We studied the autocatalytic reaction as well. Figure 1 displays the ball-and-stick models of the TS-1–TS-3 transition states of the considered tautomeric transformations.

All the studied transformations involved formation of the coherent transition states, the rupture and formation of the chemical bonds occurring simultaneously. The nature of the interactions in the transition states TS-2 and TS-3 pointed at the bifunctional acid-base properties of the alcohol and its associates. The calculated enthalpy of transformation of the ketone form of acetone **II** into the enol form was of 53.5 kJ/mol, and the entropy of that process was of 6.7 J K^{-1} mol^{-1}. Experimental enthalpy of this tautomeric transformation ranges from 50 to 58 kJ/mol [5, 15]. Table 2 lists the determined thermodynamic parameters of activation of the studied processes.

The non-catalytic enolization of the ketone **II** revealed high enthalpy of activation and relatively low activation entropy.

The reactions **IIa**–**IIc** involving the methanol associates showed lower activation enthalpies and large negative activation entropies. Nevertheless, the free energy change was determined by the enthalpy contribution. The free energy and the activation enthalpy were lower when the corresponding alcohol associates revealed more pronounced acid-base properties (i.e., at higher association degree). Catalysis of the keto-enol tautomeric transformation by alcohols has been experimentally demonstrated in [16].

Enol **III** is capable of catalyzing the tautomeric transformation of the starting acetone **II**. The autocatalytic pathway of ketones enolization should be predominant in an inert medium (for example, in hydrocarbons). Such possibility has been pointed out in the experimental study of 2-nitrocyclohexanone tautomerism in cyclohexane [17].

Catalysis of nitro–aci-nitro tautomeric transformation with linear methanol associates Ia–Ic (Scheme 2). Similarly to the previous case, tautomeric transformation of nitromethane can occur via the monomolecular mechanism as well as under the alcoholic catalysis. The catalytic reactions involve formation of pre- and post-reaction complexes.

Figure 2 displays the transition states structure of the considered reactions.

All the studied transformations proceeded via the coherent transition states. Their structures confirmed that the methanol associates showed both the acid and the base properties.

Transition of nitromethane into the aci-nitro form was endothermic, the calculated reaction enthalpy

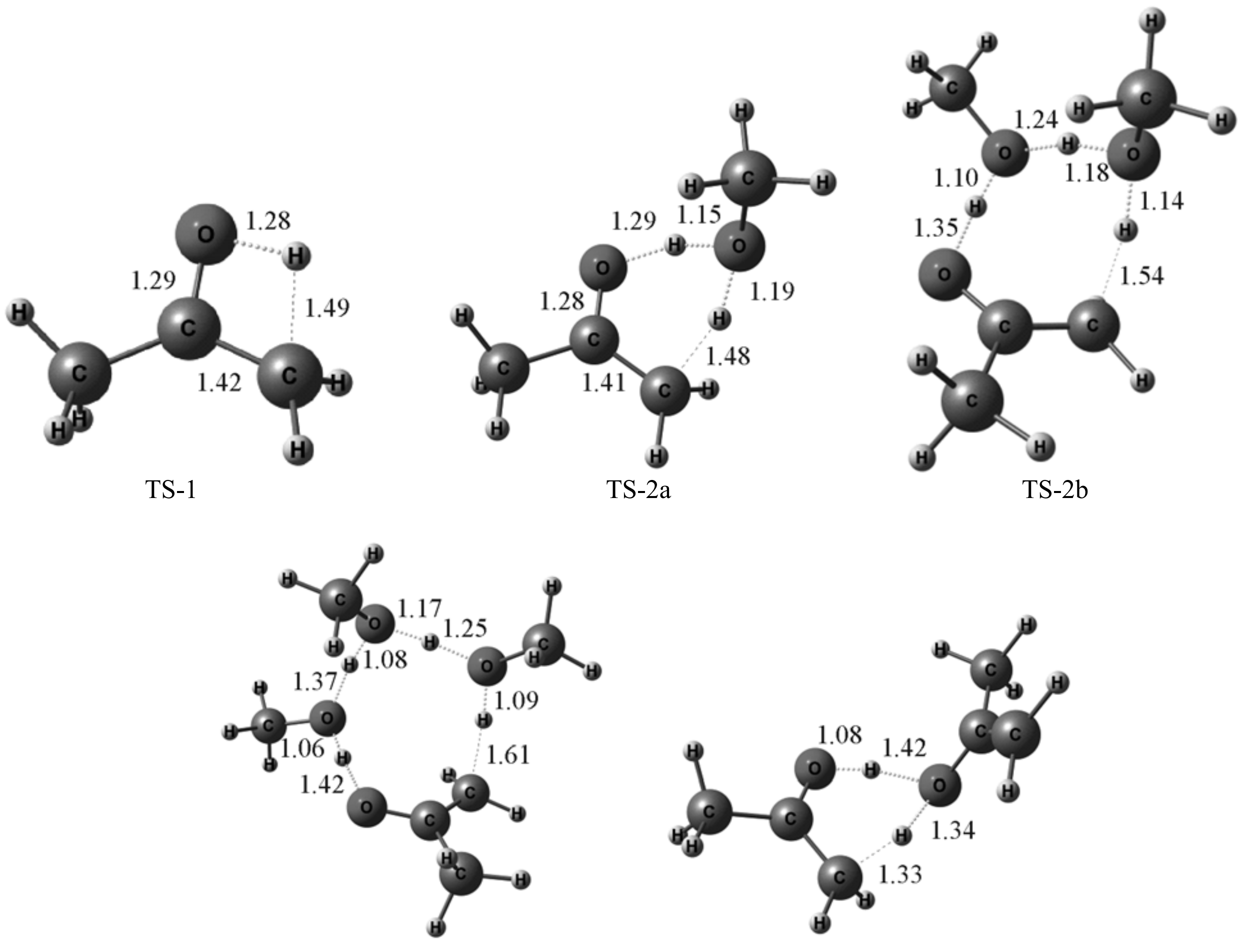


Fig. 1. Ball-and-stick models of transition states of the non-catalytic (TS-1), catalyzed by the methanol associates (TS-2a–2c), and auto-catalytic (TS-3) acetone enolization.

being of 82.2 kJ/mol; the reaction entropy was fairly low, –6.4 J K^{-1} mol^{-1}. The following values of the process enthalpy have been earlier determined via a number of methods: 80.8 kJ/mol, MP4/6-311++G**; 75.6 kJ/mol, MP4/(+ZPE) 6-311++G**; and 95.7 kJ/mol, MP2/6-31G* [18].

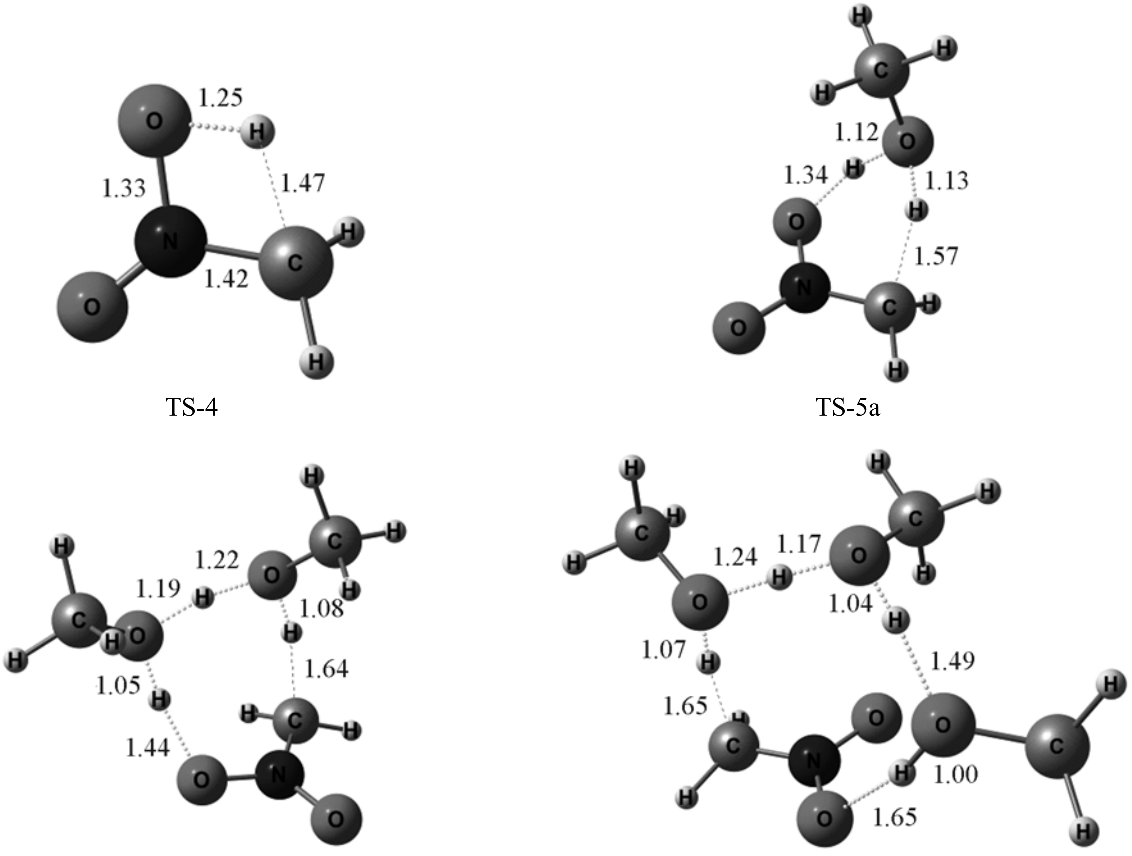
Table 3 lists the thermodynamic parameters of activation of nitromethane tautomeric transformations.

The non-catalytic transformation of nitromethane **IV** revealed the high activation enthalpy and the less significant activation entropy. The methanol-catalyzed reactions showed large negative activation entropies; on top of that, the activation enthalpy was much lowered. The activation enthalpy was lower in the cases of the methanol associates possessing the stronger acid-base properties. The relative free energy of the process activation was determined by variation of the activation enthalpy.

Catalysis of carbamate–azomethinenol tautomeric transformation with linear methanol associates Ia–Ic (Scheme 3). Azomethinenols are intermediates of

Table 2. Thermodynamic parameters of activation of acetone **II** enolization: the non-catalytic, catalyzed by the methanol associates **Ia–Ic**, and auto-catalytic

Reaction	$\Delta G^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
II → III	266.7	270.3	12.0
II + **Ia → III** + **Ia**	178.1	132.4	–153.1
II + **Ib → III** + **Ib**	147.6	87.3	–202.2
II + **Ic → III** + **Ic**	140.2	79.8	–202.3
II + **III → II· III**	185.5	141.0	–149.0

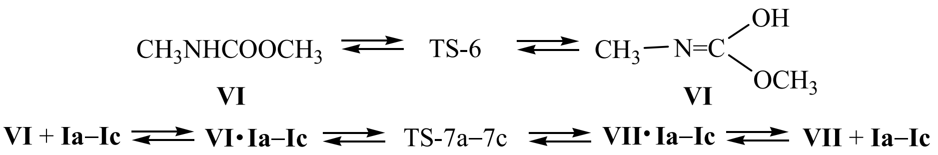


TS-4 TS-5a

TS-5b TS-5c

Fig. 2. Ball-and-stick models of transition states of the non-catalytic (TS-4) and catalyzed by the methanol associates (TS-5a–5c) conversion of nitromethane **IV** into aci-nitromethane **V** [B3LYP/6-311++G(df,p)].

Scheme 3.



$$\underset{\textbf{VI}}{CH_3NHCOOCH_3} \rightleftarrows \text{TS-6} \rightleftarrows \underset{\textbf{VI}}{CH_3{-}N{=}C}\begin{matrix}\diagup OH\\ \diagdown OCH_3\end{matrix}$$

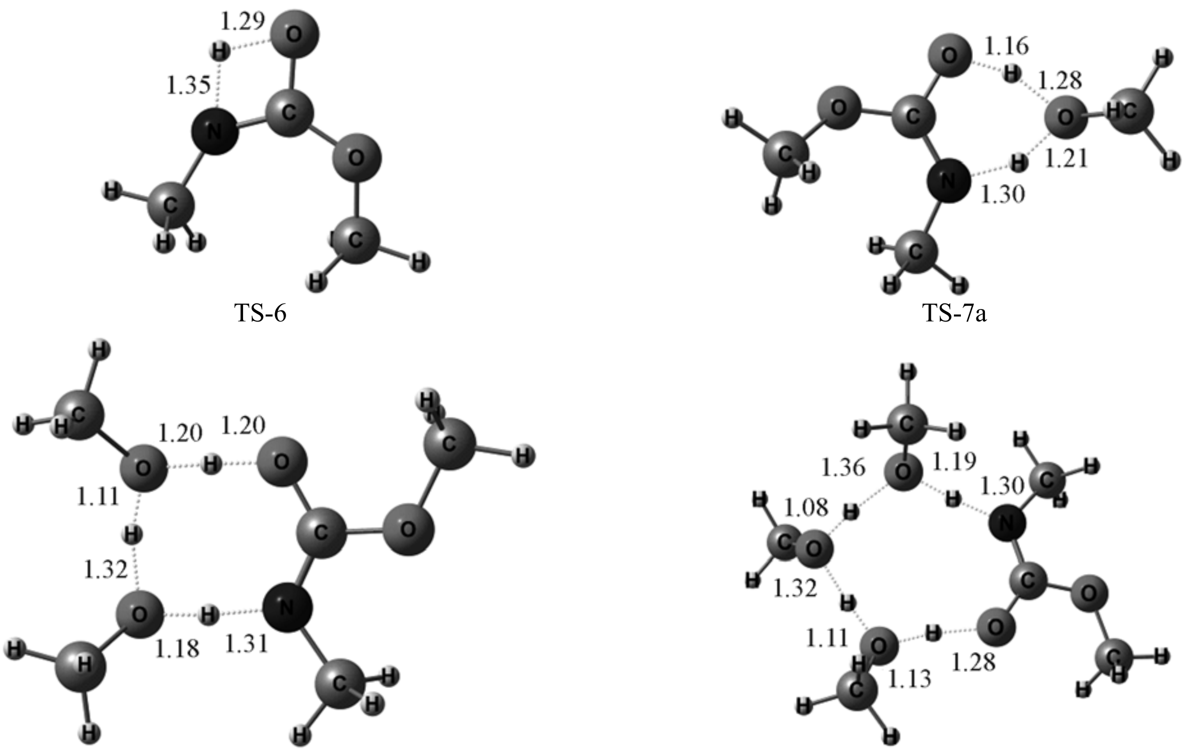
$$\textbf{VI} + \textbf{Ia–Ic} \rightleftarrows \textbf{VI}\cdot\textbf{Ia–Ic} \rightleftarrows \text{TS-7a–7c} \rightleftarrows \textbf{VII}\cdot\textbf{Ia–Ic} \rightleftarrows \textbf{VII} + \textbf{Ia–Ic}$$

Table 3. Thermodynamic parameters of activation of conversion of nitromethane **IV** into aci-nitromethane **V** in gas phase at 298 K: the non-catalytic and catalyzed by the methanol associates **Ia–Ic**

Reaction	$\Delta G^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
IV → **V**	263.0	256.7	–21.2
IV + **Ia** → **V** + **Ia**	185.7	131.3	–182.5
IV + **Ib** → **V** + **Ib**	155.1	88.1	–225.0
IV + **Ic** → **V** + **Ic**	134.6	63.6	–238.1

the addition of alcohol associates at the C=O bond of isocyanates [19, 20] as well as of the auto-catalytic addition of alcohols at the C=N bond of isocyanates [21]. In the latter case, carbamate molecules acting as catalyst are transformed into azomethinenols. We considered the monomolecular and the methanol-catalyzed isomerization of *N*-methylmethylcarbamate **VI** into the corresponding azomethinenol **VII**.

The catalytic reactions proceeded via the formation of pre- and post-reaction hydrogen-bonded complexes.



TS-6 TS-7a

TS-7b TS-7c

Fig. 3. Ball-and-stick models of transition states of the non-catalytic (TS-6) and catalyzed by the methanol associates (TS-7a–7c) tautomerization of carbamate **VI** into azomethinenol **VII** [B3LYP/6-311++G(df,p)].

Figure 3 displays the ball-and-stick models of the transition states: TS-**VI** and TS-**VIIa–VIIc**.

All the reactions involved the cyclic coherent transition states. Enthalpy of the **VI** → **VII** transformation was of 87.2 kJ/mol, the entropy being of 6.2 J K^{-1} mol^{-1}). The thermodynamic parameters of the studied reactions are collected in Table 4.

Again, the non-catalytic reaction revealed the high activation enthalpy, the activation entropy being negligibly lower. The methanol-catalyzed reactions revealed large negative activation entropies. On top of that, the activation enthalpy of the catalyzed reactions was much lower, leading to significant decrease of the activation free energy. The higher was the alcohol association degree, the lower were the activation enthalpy and free energy of the considered transformation.

In summary, catalysis of the tautomeric transformation with monomeric and associated molecules is not a special feature of water; similar behavior has been demonstrated in the case of methanol. The alcohol associates simultaneously act as the Brønsted–Lowri acid and base in such reactions. The increasing degree of association of alcohol molecules enhances their acid-base properties and, consequently, results in the more efficient catalytic action.

The improved catalytic activity of alcohol associates as compared to its monomeric molecules is not limited to the tautomeric transformations. The similar effect has been demonstrated in the case of urea decomposition into isocyanic acid and ammonia in ethylene glycol [22]. Moreover, the reactivity of alcohol associates as substrates is enhanced as compared to the monomeric alcohol molecules. This

Table 4. Thermodynamic parameters of activation of tautomerization of carbamate **VI** into azomethinenol **VII** in gas phase at 298 K: the non-catalytic and catalyzed by the methanol associates **Ia–Ic**

Reaction	$\Delta G^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
VI → **VII**	233.7	236.0	7.5
VI + **Ia** → **VII** + **Ia**	147.2	100.0	–158.7
VI + **Ib** → **VII** + **Ib**	89.6	27.7	–205.8
VI + **Ic** → **VII** + **Ic**	84.9	24.3	–203.0

has been shown for the alcohols reactions with alkyl- [23] and arylisocyanates [24] as well as isocyanic acid [25]; homo associates of phenol [26] and its mixed associates with methanol [27] are more reactive towards isocyanates than the monomeric alcohols; the same effect has been marked in the case of trans-esterification reactions [28]. The enhancement of reactivity upon association has been revealed for the hydrogen-bond complexes of amines: homo associates of amines [29] and their hetero associates with alcohols [30] are more reactive towards amides formation from esters as compared to the monomeric amines. The higher reactivity of methanol associates has been found in the cases of its addition at the Si=C bond [31] and at the triple carbon-carbon bond of 1,2-dehydrobenzene [32]. Hydrolysis of sulfur dioxide with water associates is remarkable for the negative activation energy, whereas the similar reaction with monomeric water shows a significantly high activation barrier [33]. The enhanced reactivity of water associates has been demonstrated for chlorosilanes hydrolysis [34]. Hence, a set of quantum-chemical simulation data leads to conclusion that the enhancement of the hydrogen-bonded complexes reactivity as compared to that of the monomeric components is likely a common feature of many organic reactions.

In this work the simulations were performed using the B3LYP/6-311++G(df,p) method [35, 36] implemented in the GAUSSIAN'09 software package [37].

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