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Computer Simulation of Interactions in the NH_3–CO_2–H_2O System

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Abstract—Computer simulation of interactions in the NH_3–CO_2–H_2O system was performed using a quantum-chemical method B3LYP/6-31G(d,p) for the simulation of the possible routes of the reactions and the estimation of the energy parameters: interaction energy between molecules in complexes, activation energy of forward and reverse reactions, and the heat of the reaction. A new version of termolecular reaction mechanism is proposed and investigated. The probability of realization of various paths of interaction in the NH_3–CO_2–H_2O system was shown to be determined by the temperature: at low temperatures the termolecular mechanism is more probable, while at the temperatures close to the standard conditions carbamate and bimolecular mechanisms are preferable.

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Natural, liberated from oil at oil production, and technological gases contain acidic components, including carbon dioxide, that should be removed before further use of the gas [1, 2]. Among the processes of gas purification, the leading place in the world belongs to the processes of absorption by aqueous solutions of ammonia or alkanolamines [2–4]. Thermodynamic and kinetic investigatons of the carbon dioxide extraction with ammonia showed a possibility of the formation of two products: carbamate and (or) ammonium hydrogen carbonate [5]. However, the reactions occurring in the NH_3–CO_2–H_2O system has not been adequately investigated and their mechanism is tentative (Table 1). The problem concerning intermediate states and the compounds formed at different stages of the reaction is controversial [10].

The results of the computer simulation of the reaction between the molecules 1 and 2 using quantum-chemical methods at different levels of

Table 1. Mechanisms of interaction of carbon dioxide and ammonia

Mechanism	Reaction	References
Carbamate	$\text{I. }\underset{1}{NH_3} + \underset{2}{CO_2} \xrightleftharpoons{\text{limit.}} \underset{3}{NH_2COOH}$	[5]
	$\text{II. }\underset{1}{NH_3} + \underset{3}{HOOCNH_2} \rightleftharpoons \underset{4}{(NH_4)^+(OOCNH_2)^-}$	
Zwitterionic	$\text{I. }\underset{1}{NH_3} + \underset{2}{CO_2} \xrightleftharpoons{\text{limit.}} \underset{5}{(NH_3)^+\text{–}COO^-}$	[5–8]
	$\text{II. }\underset{1}{NH_3} + \underset{5}{(NH_3)^+\text{–}COO^-} \rightleftharpoons \underset{4}{(NH_4)^+(OOCNH_2)^-}$	
Bicarbonate	$\text{I. }\underset{2}{CO_2} + \underset{6}{H_2O} \xrightleftharpoons{\text{limit.}} \underset{7}{H_2CO_3}$	[5]
	$\text{II. }\underset{1}{NH_3} + \underset{7}{H_2CO_3} \rightleftharpoons \underset{8}{(NH_4)^+(HCO_3)^-}$	
Termolecular	$\underset{1}{NH_3} + \underset{6}{H_2O} + \underset{2}{CO_2} \rightleftharpoons \underset{4}{(NH_4)^+(OOCNH_2)^-}$	[9]

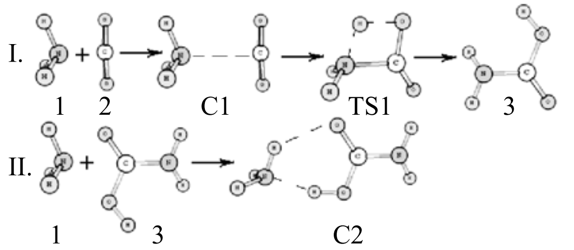

Fig. 1. The route of interactions in the NH_3–CO_2–H_2O system by carbamate mechanism.

theory have been reported [11–18]. As a rule they include analysis of carbamate mechanism, without comparison of the energy parameters of all possible routes of interaction. Now we performed the computer simulation of the interaction in the NH_3–CO_2–H_2O system at different temperatures (0 K and 313 K).

Research methods. Computer modeling of interactions in the NH_3–CO_2–H_2O system was performed using quantum-chemical methods of calculation in the framework of density functional theory (DFT) [19] using B3LYP/6-31G(d,p) (GAMESS) software [20, 21]. Identification of stationary points and refinement of the values of energy parameters was carried out by by vibrational analysis, the thermochemical calculation was carried out at $T = 313$ K, $P = 1$ at (conditions of the industrial process of extracting carbon dioxide with ammonia). The scaling factor at the calculation of the stretching vibrations frequencies by the B3LYP/6-31G(d,p) method is 0.9614 [22].

To construct the energy profiles of the routes of interaction of ammonia with carbon dioxide we used the values of the relative energies E_{rel} (G_{rel}), kJ mol^{-1}. For each route the sum of total energies (Gibbs energies) of the reagents was taken as zero, E_{rel} (G_{rel}) = 0. The interaction energy E_{int} of the molecules in the complex was calculated as a difference between the total energy of the complex and the sum of the total energies of the molecules in the complex: $E_{\text{int}} = E_{\text{AB...}} = (E_{\text{A}} + E_{\text{B}} + ...)$ (value of the G_{int} was defined similarly).

Results and discussion. The simulation of variations interactions in the NH_3–CO_2–H_2O system shows that at the implementation of the carbamate mechanism of the interaction of molecules 1 and 2 complex C1 is first formed, and the formation of carbamic acid 3 proceeds through transition state TS1 (Fig. 1). The reaction of molecule 3 with a second molecule 1 ends with the formation of the complex C2, a six-membered cyclic structure with two hydrogen bonds.

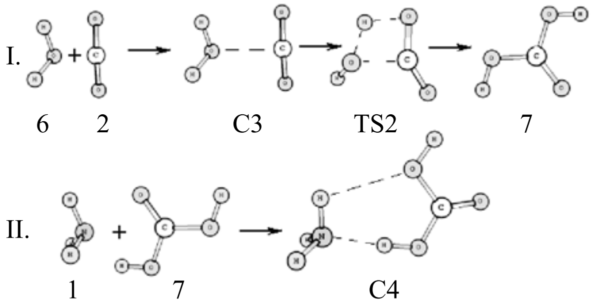

Fig. 2. The route of interactions in the NH_3–CO_2–H_2O system by the bicarbonate mechanism.

Bicarbonate mechanism (Fig. 2) involves the interaction of molecules 2 and 6 with the formation of the complex C3. The formation of carbonic acid proceeds through transition state TS2. The reaction of molecules 7 and 1 ends with the formation of molecular complex C4.

Note the similarity of the structures of complexes C1 and C3, C2 and C4, and the transition states TS1 and TS2 (Figs. 1, 2) forming at the occurrence of the carbamate and bicarbonate mechanisms, as well as the proximity of the calculated energy parameters (Table 2), which may lead to a competitive implementation of these mechanisms.

The termolecular mechanism includes interaction of molecules 1, 2, and 6. Depending on the arrangement of molecules in the arising termolecular complex, a possibility of two routes is expectable. The route A (Fig. 3) includes first the formation of termolecular complex C5 and then through the transition state TS3 bimolecular complex C6 is formed consisting of molecules of carbamate 3 and water 6. Next, the reaction between a second molecule 1 and the complex

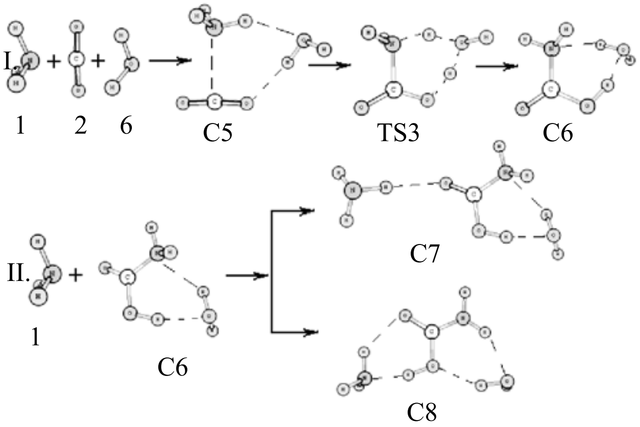

Fig. 3. Route A of the interactions in the NH_3–CO_2–H_2O system by termolecular mechanism.

Table 2. Calculated energy parameters of the routes of interactions in the NH_3–CO_2–H_2O system, kJ mol^{-1} $T = 0$ K (E) and 313 K (H, G)

Parameter		Carbamate mechanism		Bicarbonate mechanism		Termolecular mechanism			
						A		B	
		I	II	I	II	I	II[a]	I	II[a]
E_{int}	E	–14.6	–95.4	–14.6	–54.0	–47.7	–87.9	–55.1	–26.9
	H	–8.2	–87.4	–7.5	–48.1	–34.0	–81.4	–46.3	–21.2
	G	–3.6	–45.8	–1.3	–12.1	16.6	–40.9	10.9	7.1
E_a^{forward}	E	178.2	–	184.1	–	86.9	–	74.6	–
	H	168.6	–	173.2	–	73.1	–	71.8	–
	G	192.7	–	192.0	–	97.9	–	88.0	–
E_a^{backward}	E	143.9	–	180.7	–	72.4	–	84.7	–
	H	130.7	–	163.6	–	53.7	–	71.5	–26.9
	G	131.6	–	161.5	–54.0	60.6	–	79.4	–21.2
Δ_r	E	19.7	–95.4	–11.3	–48.1	–33.3	–87.9	–65.2	7.1
	H	29.7	–87.4	2.1	–12.1	–14.6	–81.4	–46.1	
	G	57.5	–45.8	31.8		53.8	–40.9	19.6	
$\Sigma\Delta_r$	E	–75.7		–65.3		–121.1		–92.1	
	H	–57.7		–46.0		–96.0		–67.3	
	G	11.7		19.7		12.9		26.7	

[a] The energy parameters are calculated for more stable complexes C8 and C12.

C6 gives termolecular complexes C6, C7, and C8 consisting of molecules 1, 3, and 6. It is assumed that this mechanism in aqueous medium can lead to the formation of ammonium carbamate [9].

We have considered a possobility of the B route of the termolecular mechanism (Fig. 4) consisting of the formation of termolecular complex C9, which through transition state TS4 transforms into a bimolecular complex C10 containing the molecules of carbonic acid 3 and ammonia 1. Further, the reaction between 1 and a second molecule of complex C10 affords termolecular complexes C11 and C12 consisting of two molecules 1 and one molecule 7.

The calculation shows that in the gas phase approximation the zwitterionic mechanism is not realized. Also, as expected, there are no zwitterion 5 or ion complexes 4 and 8 on the potential energy surface, while the molecular complexes C1–C12 are securely fixed.

For the studied reactions at the temperatures $T = 0$ K (Fig. 5) and $T = 313$ K (Fig. 6) the following energy parameters were determined: the energy of intermolecular interactions in the complexes E_{int}, the activation energy of the forward and backward reaction E_a^{forward} and E_a^{backward}, and the heat of reaction Δ_r. The values obtained were refined by thermochemical calculations (Table 2).

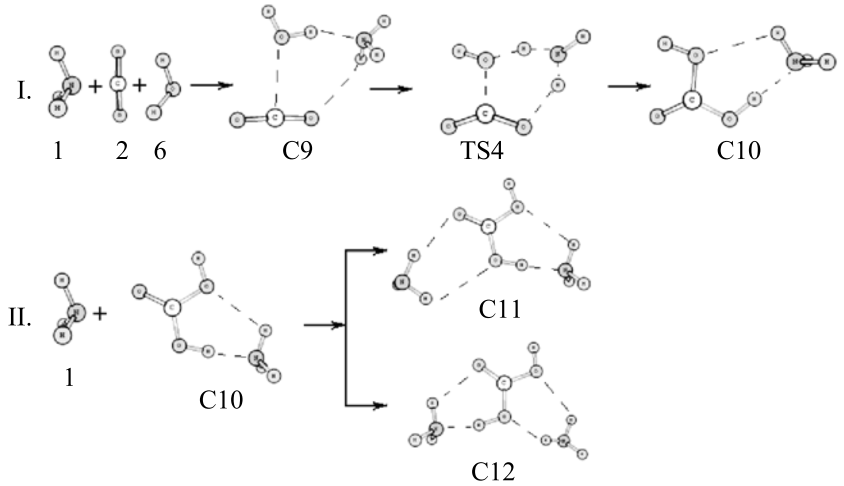

Fig. 4. Route B of the interactions in the NH_3–CO_2–H_2O system by termolecular mechanism.

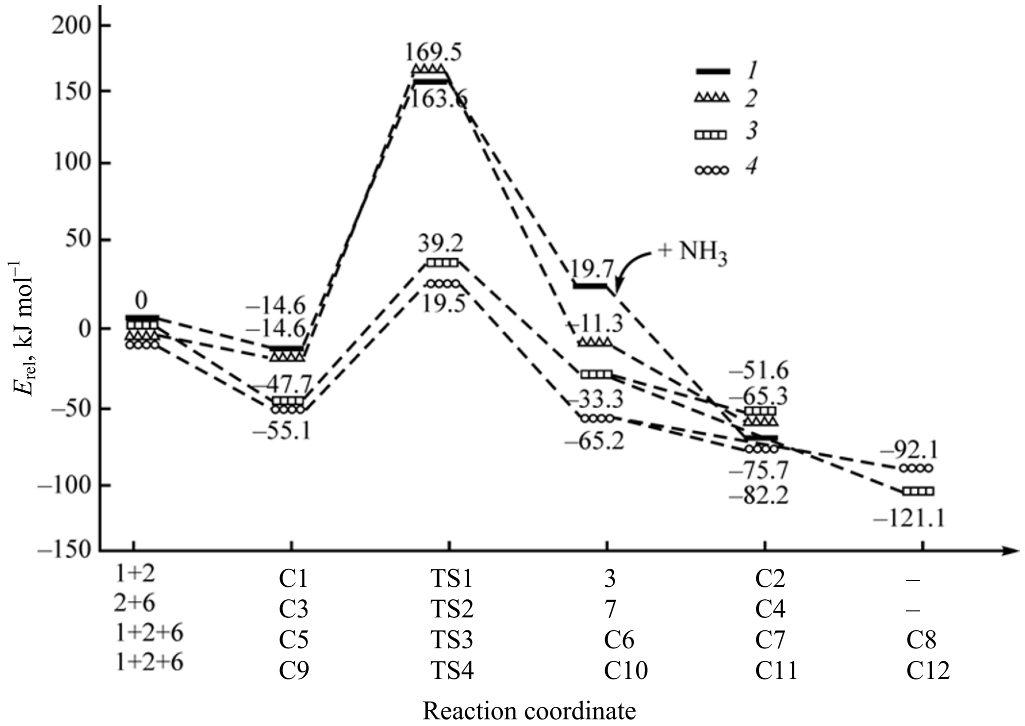

Fig. 5. The energy profiles of the possible routes of interactions in the NH_3–CO_2–H_2O system ($T = 0$ K). (*1*) carbamate mechanism, (*2*) bicarbonate mechanism, (*3*) termolecular mechanism A, and (*4*) termolecular mechanism B.

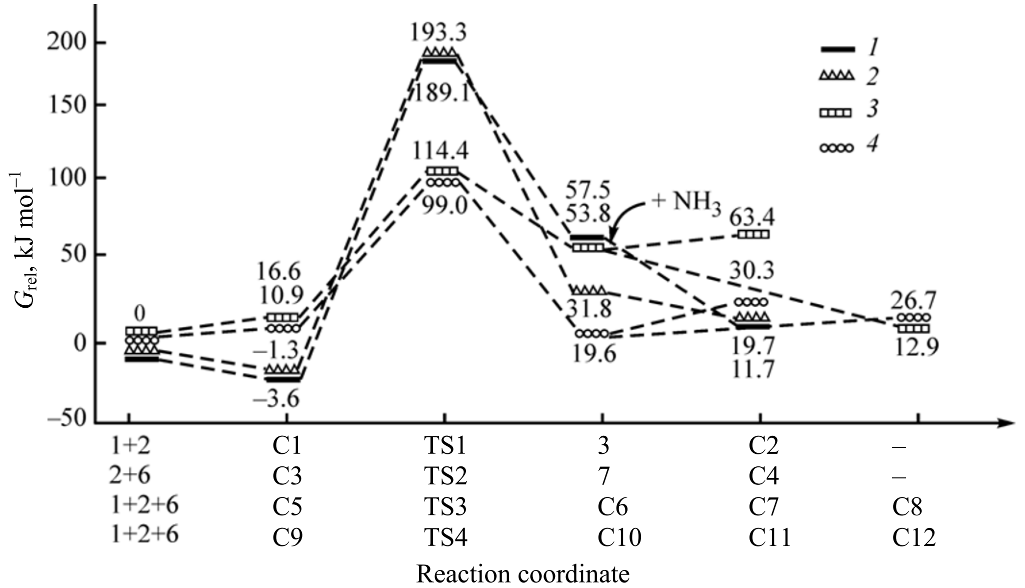

Fig. 6. The energy profiles of the possible routes of interactions in the NH_3–CO_2–H_2O system ($T = 313$ K). (*1*) carbamate mechanism, (*2*) bicarbonate mechanism, (*3*) termolecular mechanism A, and (*4*) termolecular mechanism B.

At $T = 0$ K, $\Sigma\Delta_r < 0$, so all studied reactions are exothermic. The comparison of the calculated energy profiles for the interaction routes at $T = 0$ K in the NH_3–CO_2–H_2O system shows that the first stage of the interaction by any mechanism is the spontaneous formation of molecular complexes: C1, C3, C5, and C9. The values of activation barriers in the limiting step determining the probability of a certain mechanism, for the termolecular mechanisms A and B are 86.9 and 74.6 kJ mol^{-1}, respectively. In the cases of carbamate and bicarbonate mechanisms these values are significantly higher: 178.2 and 184.1 kJ mol^{-1}, respectively. Therefore, at $T = 0$ the termolecular mechanism seems more likely, the activation energy of the limiting stage in the B route is the smallest one.

At the $T = 313$ K all the studied interaction pathways are endothermic, since the values $\Sigma\Delta_r > 0$. In contrast to $T = 0$ K, in the first stage the spontaneous formation is possible of molecular complexes C1 and C3, while termolecular complexes C5 and C9 do not form. This demonstrates the feasibility of both carbamate and bicarbonate mechanisms and their competition, since the activation barriers are comparable (Table 2).

Thus, we showed that the probability of various pathways of interaction in the NH_3–CO_2–H_2O system is determined by the temperature: at low temperatures the termolecular mechanism is more probable, while at the temperatures close to the ambient conditions the more probable are carbamate and bicarbonate mechanisms.

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