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Quantum-Chemical Study of Thermodynamics of Hydrogen-Bonded Methylamine–Methanol Complexes Reaction with Dimethyl Carbonate

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Abstract—Thermodynamic parameters of the reactions of dimethyl carbonate *cis–cis* and *cis–trans* conformers with methylamine, methylamine dimer, and methylamine complexes involving linear methanol associates have been computed with the B3LYP and WB97XD quantum-chemical methods. The both methods have given similar results. Thermodynamically, reactions of the *cis–trans* conformer are preferred over the analogous reactions of the *cis–cis* conformer, and the reactions with methylamine dimer and methylamine–methanol trimer complex are preferred over the reactions with methylamine monomer. The acid–base properties of the hydrogen-bonded methanol complexes are significantly enhanced with increasing degree of association. Stability of the methylamine complexes with methanol clusters is increased with more of the alcohol molecules involved.

Keywords: hydrogen-bonded complex, thermodynamics, acidity, basicity, aminolysis

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Reactions of dimethyl carbonate with primary amines have been intensively studied experimentally [1–6]. Such reactions are interesting because thermal decomposition of their products, carbamates, allows for phosgene-free production of isocyanate [7–10].

$$RNH_2 + CH_3OCOOCH_3 \rightarrow RNHCOOCH_3 + CH_3OH,$$

$$RNHCOOCH_3 \rightarrow RN{=}C{=}O + CH_3OH.$$

This technology does not involve any highly toxic compounds and meets the requirements of green chemistry.

Choice of the proper reaction conditions requires knowledge of the reaction thermodynamics. Li et al. estimated thermodynamic parameters of the aniline reaction with dimethyl carbonate using the empirical Benson's method [11]. Gao et al. studied thermodynamics of ammonia reaction with dimethyl carbonate using the PW91 density functional theory method [12]. In the both studies several important complications were neglected. First, potentially different reactivity of dimethyl carbonate conformers was not studied. Second, participation of the hydrogen-bonded forms of the amine, including its complexes with methanol (the reaction product) in the reaction was not considered. Furthermore, alcohols are known to catalyze aminolysis of esters [13–15]. Indeed, the autocatalysis phenomenon was revealed in reactions of primary amines with dimethyl carbonate [16]. Thermodynamic parameters of a number of reactions of hydrogen-bonded complexes much differed from those in the case of non-associated compounds [17–20].

In view of the above, the present work aimed to compare thermodynamic parameters of the reactions of dimethyl carbonate with methylamine, its hydrogen-bonded dimer, and its hydrogen-bonded complexes with methanol.

Thermodynamic parameters of conformational equilibrium of dimethyl carbonate. As shown with IR spectroscopy [21], X-ray scattering [22], gas-phase electron diffraction [23], and quantum-chemical simulation [24, 25], dimethyl carbonate consisted of a

Table 1. Thermodynamic parameters of dimethyl carbonate *cis–cis* → *cis–trans* transition in the gas phase at 298 K as computed with the B3LYP and WB97XD methods

Parameter	B3LYP/6-311++G(df,p)	WB97XD/6-311++G(df,p)
ΔG, kJ/mol	12.5	12.3
ΔH, kJ/mol	12.1	15.1
ΔS, J K^{-1} mol^{-1}	–1.2	9.3

Table 2. Ratio of equilibrium constants of the analogous reactions involving dimethyl carbonate *cis–trans* and *cis–cis* conformers ($K_{cis–trans}/K_{cis–cis}$) as function of temperature

Simulation method	Temperature, K			
	298	373	423	473
B3LYP	153	57	36	25
WB97XD	145	43	24	15

mixture of two major conformers: *cis–cis* and *cis–trans*. The *cis–trans* conformer was found less stable than the *cis–cis* form. According to the available experimental data, fraction of the *cis–trans* conformer in the liquid phase was of 1% [21, 22]. Figure 1 shows geometry parameters of dimethyl carbonate conformers, as computed using the B3LYP and WB97XD methods. Table 1 lists thermodynamic parameters of the transition of dimethyl carbonate *cis–cis* conformer into the *cis–trans* conformer.

The both methods applied gave similar results. The computed data were in complete agreement with the experiment and other simulation results, confirming the higher stability of *cis–cis* conformer of dimethyl carbonate. For example, the energy gap between *cis–trans* and *cis–cis* conformers of dimethyl carbonate as computed in this work was of 12.3–12.5 kJ/mol, its experimental estimate being of 10.9±2.1 kJ/mol [21]. The energy gap obtained with the MP2 method ranged from 12.3 to 14.6 kJ/mol depending on the applied basis [24, 25]. The activation (rotation) barrier of the *cis–cis* conformer transformation into the *cis–trans* one was of 42 kJ/mol [24]. The rotation entropy being low, the rate of the *cis–cis* ⇄ *cis–trans* transformation at 298 K was of about 10^5 s^{-1}. Hence, the equilibrium between the conformers of dimethyl carbonate should be established almost immediately.

As seen from Table 1, the enthalpy term gave the major contribution into the difference of the conformers Gibbs energy, whereas the entropy factor was of minor importance.

From the above-discussed results it follows that the reaction of dimethyl carbonate *cis–trans* conformer is always thermodynamically preferential over the same reaction of the *cis–cis* conformer, provided that their products are structurally similar.

As seen from Table 2, thermodynamic preference of the *cis–trans* conformer reaction over the same reaction with the *cis–cis* conformer somewhat decreased upon heating, remaining fairly large over the whole studied range of temperature.

Thermodynamics hydrogen bonding of methylamine to give self-associates and complexes with linear methanol associates. Amines and alcohols readily form hydrogen-bonded complexes via self- and hetero-association in the gas and liquid states [26–28]. Methylamine can act as proton donor or proton acceptor to form two types of hydrogen-bonded complexes with methanol and its linear associates. In the present work we considered complexes between methylamine and linear methanol associates with methylamine acting as proton acceptor.

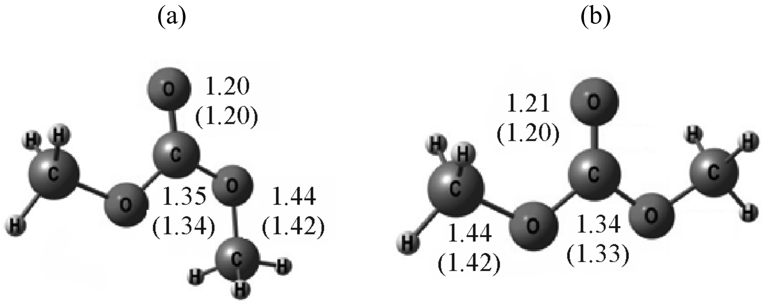
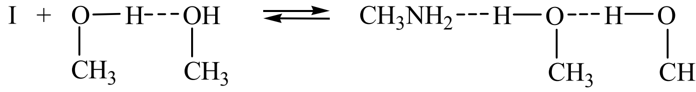


Fig. 1. The Stewart−Briegleb models of dimethyl carbonate (a) *cis–trans* and (b) *cis–cis* conformers as obtained with the B3LYP (WB97XD) simulation. Interatomic distances are given in Å.

We computed thermodynamic parameters of methylamine dimerization [Eq. (1)], its association with methanol [Eq. (2)] and with linear methanol associates [Eqs. (3), (4)].

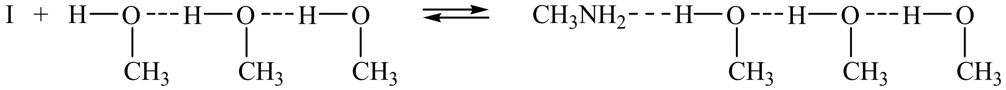
$$\underset{\textbf{I}}{2CH_3NH_2} \rightleftarrows \underset{\textbf{II}}{CH_3NH—H\text{---}NH_2CH_3} \qquad (1)$$

$$\text{I} + \underset{\textbf{IIIa}}{CH_3OH} \rightleftarrows \underset{\textbf{IVa}}{CH_3NH_2\text{---}H—O—CH_3} \qquad (2)$$



$$\text{I} + \underset{\textbf{IIIb}}{\underset{CH_3}{O}—H\text{---}\underset{CH_3}{OH}} \rightleftarrows \underset{\textbf{IVb}}{CH_3NH_2\text{---}H—\underset{CH_3}{O}\text{---}H—\underset{CH_3}{O}} \qquad (3)$$

IIIb **IVb**



$$\text{I} + \underset{\textbf{IIIc}}{H—\underset{CH_3}{O}\text{---}H—\underset{CH_3}{O}\text{---}H—\underset{CH_3}{O}} \rightleftarrows \underset{\textbf{IVc}}{CH_3NH_2\text{---}H—\underset{CH_3}{O}\text{---}H—\underset{CH_3}{O}\text{---}H—\underset{CH_3}{O}} \qquad (4)$$

IIIc **IVc**

Figure 2 shows the Stewart–Briegleb models of the mentioned complexes and of methyl *N*-methylcarbamate (**V**) as simulated with the B3LYP and WB97XD methods. Compound **V** is shown in the *trans* conformation which is most stable in the cases of carbamates according to simulations presented in [29–33]. Geometry parameters of the complexes as simulated with the B3LYP and WB97XD methods were similar.

Table 3 lists thermodynamic parameters of reactions 1–4 as derived with the B3LYP and WB97XD methods.

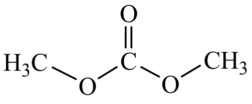
Thermodynamic parameters of complexes **II** and **IVa–IVc** formation as obtained with the B3LYP and WB97XD methods were close. The complexes formed via methylamine dimerization were the least stable. The corresponding Gibbs energy and enthalpy as computed with the MP2/aug-cc-pvdz method was of 24.4 and –9.43 kJ/mol, respectively [34], whereas experimental enthalpy of dimethylamine dimerization in krypton was of –6.34±0.35 kJ/mol [35]. The experimental value was well in agreement with by the B3LYP result, whereas the enthalpies derived from the MP2 and WB97XD simulations were significantly overestimated.

The hydrogen-bonded complexes of methylamine with linear methanol associates became more stable with more of methanol molecules in the cluster. Acidity and basicity of the hydrogen-bonded complexes were enhanced as compared with those of monomeric molecules [36–40]. Table 4 lists the thermodynamic basicity and acidity of linear methanol associates as determined with the B3LYP/6-311++G(df,p) simulation.

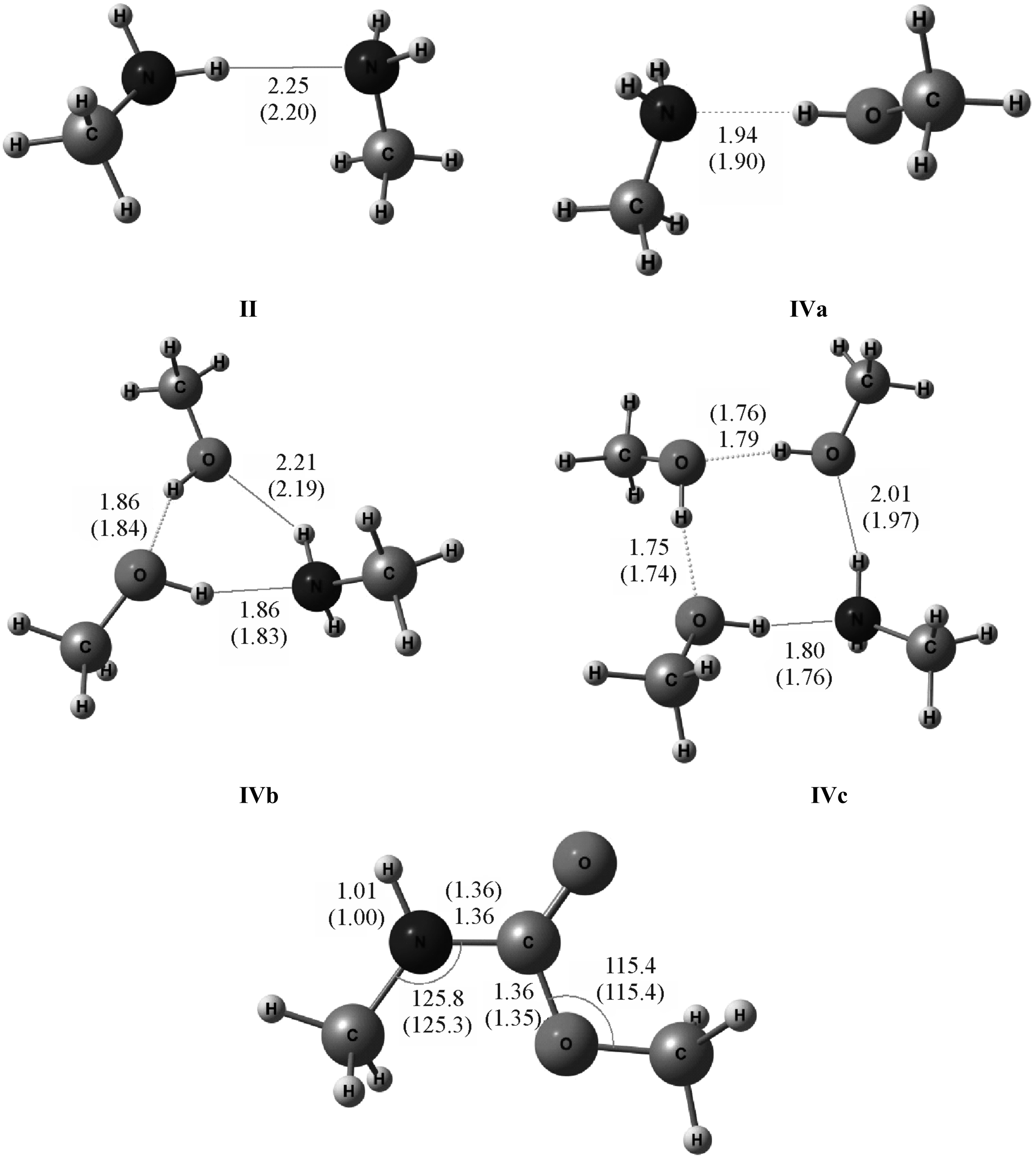
The corresponding experimental parameters were as follows (monomeric methanol at 298 K): ΔG_{acid} 1571 kJ/mol [41], ΔH_{acid} 1597 kJ/mol [41], gas basicity (GB) 724 kJ/mol [42], and proton affinity (PA) 754 kJ/mol [42]. Hence, deviation of the computed values from the experimental ones was below 2%. As follows from Table 4, stability of methanol hydrogen-bonded complexes with linear methanol associates changed in line with their acidity.

The acid–base properties of methanol associates enhanced substantially with increasing number of the associated alcohol molecules. Hence, transformations of alcohols in chemical reactions driven by the acid–base properties always involve alcohol associates.

Thermodynamic parameters of dimethyl carbonate reactions with methylamine and its hydrogen-bonded complexes with linear methanol associates. We performed quantum-chemical simulation of thermodynamic parameters of *cis–cis* dimethyl carbonate model reactions with methylamine [Eq. (5)], methylamine dimer [Eq. (6)], and methylamine hydrogen-bonded complexes with linear methanol associates [Eqs. (7)–(9)], all yielding methyl *N*-methylcarbamate (**V**).



VI $+$ **I** $\rightleftarrows$ **V** $+$ **IIIa**, (5)



II **IVa**

IVb **IVc**

V

Fig. 2. The Stewart–Briegleb models of hydrogen-bonded complexes **II** and **IV** and of methyl *N*-methylcarbamate **V** as obtained from the B3LYP (WB97XD) simulation. The bond lengths are given in Å and bond angles are given in deg.

$$\mathbf{VI} + \mathbf{II} \rightleftarrows \mathbf{V} + \mathbf{IVa}, \quad (6)$$

$$\mathbf{VI} + \mathbf{IVa} \rightleftarrows \mathbf{V} + \mathbf{IIIb}, \quad (7)$$

$$\mathbf{VI} + \mathbf{IVb} \rightleftarrows \mathbf{V} + \mathbf{IIIc}, \quad (8)$$

$$\mathbf{VI} + \mathbf{IVc} \rightleftarrows \mathbf{V} + \mathbf{IIId}. \quad (9)$$

In Eq. (9), **IIId** stands for cyclic methanol tetramer.

Table 5 lists thermodynamic parameters of reactions (5)–(9) as computed with the B3LYP and WB97XD methods.

The following correlations were held:

$$\Delta G_{\mathrm{B3LYP}} = -1.150 + 1.128\Delta G_{\mathrm{WB97XD}}\ (r = 0.982),$$

$$\Delta H_{\mathrm{B3LYP}} = -4.830 + 0.992\Delta H_{\mathrm{WB97XD}}\ (r = 0.977).$$

Table 3. Thermodynamic parameters of reactions (1)–(4) in the gas phase at 298 K

Reaction	B3LYP			WB97XD		
	ΔG, kJ/mol	$-\Delta H$, kJ/mol	$-\Delta S$, J K^{-1} mol^{-1}	ΔG, kJ/mol	$-\Delta H$, kJ/mol	$-\Delta S$, J K^{-1} mol^{-1}
(1)	21.1	6.7	93.2	21.1	14.2	118.8
(2)	14.2	25.7	133.9	7.8	28.7	122.4
(3)	7.3	35.7	150.2	0.6	49.2	167.3
(4)	–9.5	52.4	143.7	–13.0	63.9	170.7

Table 4. Thermodynamic acidity and basicity parameters of linear methanol associates $(CH_3OH)_n$ in the gas phase at 298 K (see parameters definition in the text)

n	ΔG_{acid}, kJ/mol	ΔH_{acid}, kJ/mol	ΔS_{acid}, J K^{-1} mol^{-1}	GB, kJ/mol	PA, kJ/mol	$-\Delta S$, J K^{-1} mol^{-1}
1	1543	1575	106	712	743	103
2	1454	1483	97	830	871	140
3	1395	1430	119	894	930	120

Table 5. Thermodynamic parameters of reactions (5)–(9) in the gas phase at 298 K

Reaction	B3LYP			WB97XD		
	$-\Delta G$, kJ/mol	$-\Delta H$, kJ/mol	$-\Delta S$, J K^{-1} mol^{-1}	$-\Delta G$, kJ/mol	$-\Delta H$, kJ/mol	$-\Delta S$, J K^{-1} mol^{-1}
(5)	19.9	14.5	18	15.7	12.8	9.9
(6)	33.8	31.3	8.5	29.1	27.2	6.4
(7)	15.3	8.4	23.1	11.2	4.8	21.4
(8)	12.6 (20.3)[a]	3.2 (16.1)	31.6 (14.1)	12.2 (17.6)	–1.9 (9.8)	47.3 (26.1)
(9)	23.8	22.7	3.8	19.5	15.0	15.2

[a] Figures in parentheses refer to formation of cyclic methanol trimer.

In the both cases, the slope coefficient was close to unity. However, the WB97XD method produced systematically overestimated Gibbs energy and enthalpy of the studied reactions as compared to the B3LYP method.

Enthalpies of reactions (5)–(9) were different (cf. Table 5) and therefore revealed different temperature dependences of the equilibrium constants (Fig. 3). The equilibrium constants shown in Fig. 3 were calculated using the B3LYP-derived parameters at 298–473 K. As seen from the plots, in all the studied cases the equilibrium constant decreased with increasing temperature.

Dimethyl carbonate reaction with methylamine dimer (6) was thermodynamically the most favorable over the entire temperature range.

Thermodynamically, dimethyl carbonate reactions with methylamine complexes involving monomeric [Eq. (7)] and dimeric [Eq. (8)] methanol yielding linear methanol trimer were less favorable than the reaction with methylamine monomer [Eq. (5)]. However, if cyclic methanol trimer was considered the reaction product, equilibrium constants of reactions (5) and (8) turned almost equal.

Dimethyl carbonate reaction with methylamine associated with linear methanol trimer yielding

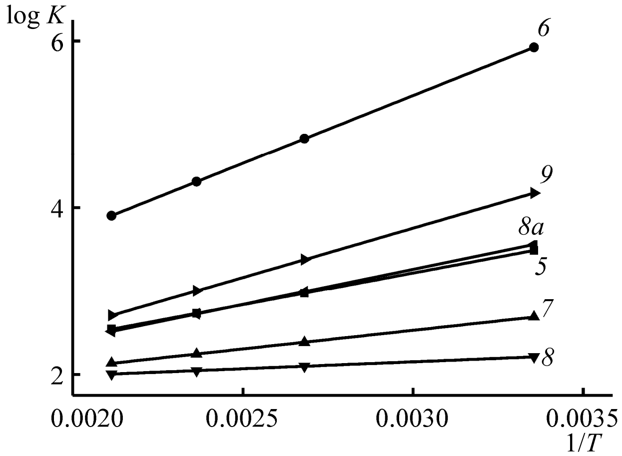


Fig. 3. (*5*–*9*) log Equilibrium constant of reactions (5)–(9) as function of reciprocal temperature; (*8a*) refers to the reaction of dimethyl carbonate *cis*–*cis* conformer with complex **IVb** leading to cyclic methanol trimer.

carbamate **V** and cyclic methanol tetramer was thermodynamically the most favorable of all the reactions involving methanol associates [Eqs. (7)–(9)].

Data in Fig. 3 relate to reactions of the *cis*–*cis* conformer of dimethyl carbonate. According to Table 2, similar reactions involving the *cis*–*trans* conformer are thermodynamically more favorable. In the dimethyl carbonate–methylamine–methanol system, a number of competitive reaction pathways are possible, involving both *cis*–*cis* and *cis*–*trans* forms of dimethyl carbonate. As the conformers interconversion rate is high, the reactions involving the *cis*–*trans* conformer are thermodynamically more favorable.

Monomeric methylamine, its dimer, and its hydrogen-bonded complexes with methanol associates are thermodynamically reactive towards dimethyl carbonate. Thermodynamic consideration has not allowed us to reveal the most favorable reaction pathways operative in the studied system; additional information on the reactions activation parameters is required to make the conclusion. Determination of these parameters will be discussed in our publication to follow.

EXPERIMENTAL

Quantum-chemical calculations were performed using GAUSSIAN 09 software [43, 44]. Full geometry optimization was performed with the B3LYP and WB97XD methods using the 6-311++G(df,p) basis set. Correspondence of the optimized structures to the potential energy minimum was confirmed by computation of real vibration frequencies at the same level of theory.

The standard enthalpy and the Gibbs energy of formation in the gas phase (298.15 K, 1 atm) were computed using the corresponding thermal corrections to the electron energy.

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