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Computational study of the reaction of dimethyl carbonate with methyl amine

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A B S T R A C T

A detailed study on mechanism of the reaction between dimethyl carbonate and methyl amine have been investigated theoretically. Thermodynamics parameters have been described at wB97XD/6-311++G(df,p), M06/6-311++G(df,p) and PBE1PBE/6-311++G(df,p) levels. The calculations show that the presence of hydrogen-bonded methyl amine dimer or hydrogen-bonded complexes of methyl amine with methanol can noticeably reduce the energy barrier. These complexes possess higher electron-donor properties than free alcohol molecules thus increasing the activity of complexes in the reaction with dimethyl carbonate. All conversions occur through cyclic late transition states.

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1. Introduction

Isocyanates are substances that have great commercial value; they are used in production of polyurethanes and herbicides. In modern industry isocyanates are produced by synthesis, in the process of interaction of amines with phosgene:

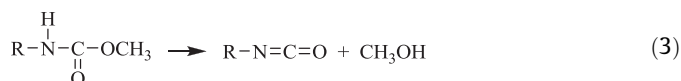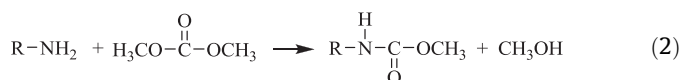$$R-NH_2 + \underset{\overset{\parallel}{O}}{Cl-C-Cl} \longrightarrow R-N=C=O + 2HCl \tag{1}$$
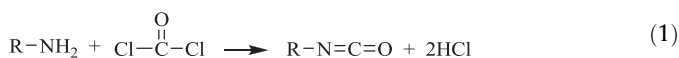
Given process has several essential disadvantages. Phosgene is extremely toxic substance without antidote. Besides, in reaction (1) hydrochloric acid is formed. Acid causes corrosion of equipment and requires equimolar amount of alkali for its neutralization [1,2]. Therefore advisable to develop such methods of isocyanates' production that exclude the use of phosgene.

Such "non-phosgenic" methods do exist. Among them we could mention reductive carbonylation of nitro compounds [3], oxidative carbonylation of amines [4], alcoholysis of substituted ureas [5]. But all mentioned methods require high temperature, high pressure, and expensive catalysts. In addition, they are aggravated by side reactions, leading to low selectivity of given processes.

Therefore the method in which isocyanates are obtained in the process of methoxy carbonylation of amines by dialkyl carbonates (for instance, by dimethyl carbonate, or DMC) looks like an attractive option [6–8]. This method includes two steps. On the first step,

carbamates are obtained from amine and DMC. Then, on the second step, thermal decomposition of these carbamates into isocyanates and methanol is carried out:

$$R-NH_2 + H_3CO-\underset{\overset{\parallel}{O}}{C}-OCH_3 \longrightarrow R-\underset{\overset{\parallel}{O}}{N}-\overset{\overset{H}{|}}{C}-OCH_3 + CH_3OH \tag{2}$$

$$R-\overset{\overset{H}{|}}{\underset{\underset{O}{\parallel}}{N}}-C-OCH_3 \longrightarrow R-N=C=O + CH_3OH \tag{3}$$

DMC, which is used in the given process, is environmentally safe substitute of phosgene, dimethyl sulphate and methyl halides. Also, DMC is non-mutagenic compound [9,10]. However, there was no a single example in the literature where thermodynamics of these reactions has been described. Because of this fact there is no possibility to choose intentionally temperature interval in which interactions of DMC with primary amines should be conducted. This paper is dedicated to quantum-chemical determination of thermodynamic parameters of interaction between DMC and primary amines using model reaction between DMC and methyl amine as an example.

2. Computational details

All calculations were carried out using Gaussian 09 [11] program. Optimization in the geometries of the reactants, intermediates, transition states (TS) and products was achieved using the

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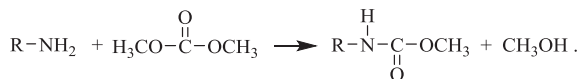 *E-mail address:* ysamuilov@yandex.ru (A.Y. Samuilov).

density functional theory [12,13] with long range corrected wB97XD/6-311++G(df,p) functional of Chai and Head-Gordon [14]. We have also used M06/6-311++G(df,p) [15] and PBE1PBE/6-311++G(df,p) [16] methods. All geometry optimization calculations have been performed without any symmetry restrictions. Frequency analysis was used to verify the optimized geometries of TS, which are characterized by one imaginary frequency (IF) and stationary points with no imaginary frequency. The intrinsic reaction coordinate (IRC) calculation was carried out to check the energy profile connecting each TS to the two associated minima of the proposed mechanism.

3. Results and discussion

3.1. Thermodynamics of reactions of dimethyl carbonate's conformers in interactions with methyl amine

Characterization of thermodynamic parameters of discussed interactions is aggravated by fact that DMC is conformationally flexible compound. According to IR-analysis [17] and X-ray scattering [18], DMC exists in liquid state in the form of two conformers which are defined as cis–cis and cis–trans conformers (Fig. 1). Cis–trans conformer is considerably less stable in comparison with cis–cis one. According to experimental data we possess, content of cis–trans conformer in liquid state is 1% [17,18]. Both conformers can participate in interaction. Due to this fact, thermodynamic characteristics for interaction of primary amines with both cis–cis and cis–trans conformers of DMC should be obtained.

We have carried out a computational study of thermodynamic parameters for model reaction – interaction of different DMC conformers with methyl amine leading to formation of N-methyl methyl carbamate according to reaction:

$$R-NH_2 \ + \ H_3CO-\underset{\overset{\|}{O}}{C}-OCH_3 \ \longrightarrow \ R-\underset{\overset{\|}{O}}{\overset{\overset{H}{|}}{N}}-C-OCH_3 \ + \ CH_3OH \ .$$

In Table 1 thermodynamic parameters of reactions (changes of Gibbs free energy, enthalpies and entropies) and equilibrium constants, which were calculated from these parameters at different temperatures, are given.
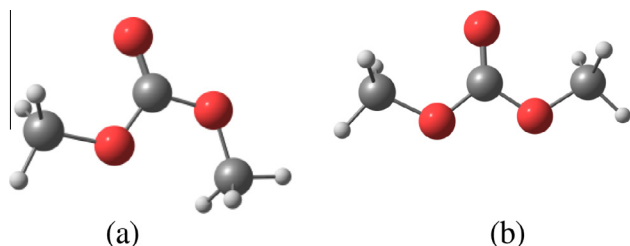

(a)   (b)

Fig. 1. Optimized structures of cis–trans (a) and (b) cis–cis DMC calculated by M06/6-311++G(df,p) level in gas phase.

As can be seen from Table 1, all computational methods show that interaction between methyl amine and both DMC conformers proceeds exothermically. And, in interaction with cis–trans DMC proceeds more exothermic than for cis–cis conformer. This fact affirms that cis–cis state is more stable.
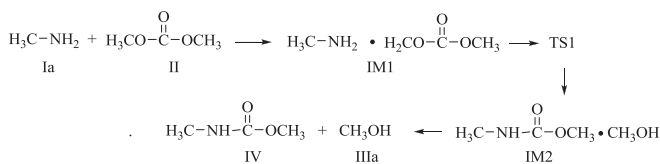
Changes of entropy for these reactions are negligible – because there is no loss of translational and rotational degrees of freedom (during interaction, two molecules of reagents turns into two molecules of products). There are just changes of their numerical values.

Changes of Gibbs free energy in interactions discussed are negative. Their values, in general, are determined by enthalpy.

From given in Table 1 equilibrium constants for interaction between cis–trans conformer of DMC and methyl amine follows that constants values stay quite large in the broad temperature interval (from 0 to 200 °C). As for reactions with cis–cis conformer of DMC, that reactions become noticeably reversible as temperature grows up.

3.2. Mechanisms of non-catalytic and autocatalytic interaction of dimethyl carbonate with primary amines

Mechanisms of reactions have been studied on example of interactions in which cis–cis conformer of DMC is participating. Computational study of interaction between DMC and methyl amine that we have carried out shows that non-catalytic interaction includes following steps:

$$H_3C-NH_2 + H_3CO-\underset{\overset{\|}{O}}{C}-OCH_3 \longrightarrow H_3C-NH_2 \cdot H_2CO-\underset{\overset{\|}{O}}{C}-OCH_3 \longrightarrow TS1$$

Ia II IM1

$$H_3C-NH-\underset{\overset{\|}{O}}{C}-OCH_3 + CH_3OH \longleftarrow H_3C-NH-\underset{\overset{\|}{O}}{C}-OCH_3 \cdot CH_3OH$$

IV IIIa IM2

Initially, due to interaction of molecules of methyl amine (Ia) and DMC (II), hydrogen-bonded pre-reaction complex (IM1) is formed. Then, pre-reaction complex through transition state (TS1) forms after-reaction complex (IM2). After-reaction complex splits into methanol (IIIa) and carbamate (IV).

Fig. 2 demonstrates ball-and-stick models for intermediates and transition states that are formed in interactions discussed. Table 2 shows thermodynamic parameters for all steps of interaction discussed.

In the given interaction between methyl amine (I) and DMC (II) pre-reaction complex (IM1) is formed. Complex formation is characterized by small negative values of enthalpies and large negative values of entropies changes.

Interaction of methyl amine (I) with DMC (II) goes through coordinated cyclic four-member transition state (Fig. 2) in which breaking "old" bonds and formation of "new" ones proceeds simultaneously.

Table 3 shows thermodynamic parameters of activation for interaction discussed.

From data given in Table 3 follows that interaction of methyl amine (I) and DMC (II) is characterized by high free energy barrier,

Table 1
Gibbs energies, enthalpies, and entropies of reactions of cis–trans and ci–cis DMC with methyl amine at 298 K and equilibrium constants (K_p) at various temperatures in the gas phase.

Method	Conformer	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))	K_{p273}	K_{p298}	K_{p373}	K_{p473}
wB97XD	Cis–trans	−28.0	−27.8	0.6	$2.1 \cdot 10^5$	$7.7 \cdot 10^4$	$8.1 \cdot 10^3$	$1.2 \cdot 10^3$
	Cis–cis	−15.7	−12.8	9.9	$9.1 \cdot 10^2$	$5.6 \cdot 10^2$	$2.0 \cdot 10^2$	84.1
M06	Cis–trans	−29.3	−26.1	10.6	$3.4 \cdot 10^5$	$1.3 \cdot 10^5$	$1.6 \cdot 10^4$	$2.7 \cdot 10^3$
	Cis–cis	−15.8	−16.6	−2.8	$1.0 \cdot 10^3$	$5.7 \cdot 10^2$	$1.5 \cdot 10^2$	48.1
PBE1PBE	Cis–trans	−33.9	−28.5	18.5	$2.5 \cdot 10^6$	$8.8 \cdot 10^5$	$8.8 \cdot 10^4$	$1.3 \cdot 10^4$
	Cis–cis	−20.8	−15.7	16.9	$7.5 \cdot 10^3$	$4.2 \cdot 10^3$	$1.2 \cdot 10^3$	$4.1 \cdot 10^2$