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Computational study of the reaction of dimethyl carbonate with methyl amine on Zn_4O_4 cluster

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Reactions of dimethyl carbonate with primary amines resulting in carbamates are important step of phosgene-free method for producing of isocyanates. Isocyanates are monomers to produce large scale polymers. Many questions about the mechanism of reactions of dimethyl carbonate with primary amines are unknown. In this study a structure of Zn_4O_4 cluster and mechanism of the reaction between dimethyl carbonate and methyl amine on Zn_4O_4 cluster 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 participating in the reaction of ZnO cluster noticeably reduce the energy barrier compared with non-catalytic reaction. All conversions occur through cyclic late transition states. Using the hydrogen-bonded complexes of methylamine with methanol as well as methylamine itself in the reaction was also shown to lower the activation barrier.

1. Introduction

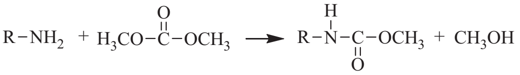
Isocyanates are commercial substances being produced in a large scale. They are generally used in polyurethane, carbamate, and urea production. Carbamates and ureas are also commonly used substances. They find application in herbicides, fungicides, dyes, pharmaceuticals, cosmetic products, and act as protective groups [1,2].

Originally, isocyanates were prepared by the reaction of amines with phosgene [3]:

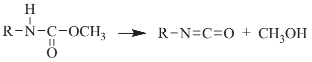
$$\mathrm{R{-}NH_2 + Cl{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl \longrightarrow R{-}N{=}C{=}O + 2HCl} \tag{1}$$

This reaction produces hydrogen chloride which causes corrosion of equipment [4]. Phosgene is very toxic. Therefore, a lot of efforts were taken to develop alternative methods of isocyanate synthesis to avoid these disadvantages. These methods are oxidative carbonylation of amines [5], reductive carbonylation of nitro derivatives [6], and methoxycarbonylation of amines using carbonyl-containing reagents, such as CO, CO_2 and dimethyl carbonate (DMC) [7].

Among the phosgene-free methods mentioned the most advanced is the carbonate method [8,9]. It involves two stages. The first one is the reaction of amine with DMC to give carbamates; the second one is thermal decomposition of carbamates yielding isocyanates and methanol:



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



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

DMC used in this reaction is a versatile compound that represents an attractive eco-friendly alternative to both methyl halides or dimethyl sulphate and phosgene for methylation and carbonylation processes because of its nontoxicity in comparison with other carboxylating or alkylating agents. Using DMC for these processes does not result in inorganic salts; the leaving methylcarbonate species decomposes into only methanol and CO_2 as side products. DMC is therefore safe in handling and does not require special safety precautions as in the case of toxic and mutagenic methyl halides and extremely toxic phosgene [10,11].

Earlier we studied a non-catalytic interaction of DMC with primary amines exemplified by a model reaction of DMC with methylamine [12]. This reaction is catalysed by Lewis acids, such as carboxylates [13], zinc carbonate [8], lead, iron, and zirconium oxides [14], zinc oxide on titanium dioxide [15], magnesium oxide on zirconium dioxide [16].

This study is aimed at computational determination of thermodynamic characteristics of the reaction of DMC with primary

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amines exemplified by the model zinc oxide-catalysed reaction of DMC with methylamine.

2. Computational details

All calculations were carried out using Gaussian 09 [17] program. Optimisation in the geometries of the reactants, intermediates, transition states (TS) and products was achieved using the density functional theory [18,19] with long range corrected wB97XD functional of Chai and Head-Gordon [20]. We have also used M06 [21] and PBE1PBE [22] methods. Different DFT methods used to find out, does accounting method of the exchange–correlation potential affect at the patterns of reactions. All geometry optimisations (including minima and transition states) were carried out with the 6-311++G(df,p) basis set for all elements except the transition metal (Zn), for which the effective core potential LANL2DZ basis set was used. All calculations have been performed without any symmetry restrictions. Frequency analysis was used to verify the optimised geometries of TS, which are characterised 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. Natural bond orbital (NBO) [23] analysis was used to provide the natural charge distribution.

3. Results and discussion

3.1. Structure of zinc oxide Zn_4O_4 clusters

The zinc oxide Zn_4O_4 cluster can form the wurtzite-like [24] and the rocksalt-like [25] three-dimensional structures (Fig. 1). In wurtzite-like structure, each zinc atom, placed in the centre of the tetrahedron is surrounded by four oxygen atoms and vice versa. In rocksalt-like structure, each zinc atom is surrounded by 6 oxygen atoms and vice versa. For the bulk structures wurtzite-like structure is thermodynamically more stable [26]. Fig. 1 demonstrates Zn_4O_4 clusters, which underlie at the basis of these structures.

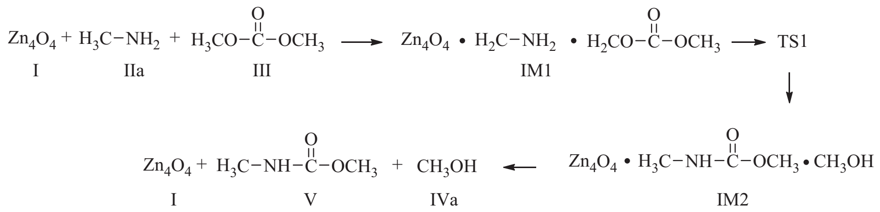
As seen from Table 1, all the methods result in similar dimensions of Zn_4O_4 clusters. The partial charges at the Zn and O ions, obtained by NBO population analysis by M06 method are smaller than the formal oxidation states of +2 and −2. In the rocksalt-like structure they are equal to ±1.501 for all atoms. In the wurtzite-like structure, the threefold coordinate ions exhibit slightly different charges than the twofold coordinate ones; typical values are ±1.534 for threefold coordinated atoms of zinc and oxygen respectively; for twofold coordinated atoms charges equal to ±1.426.

Table 1 demonstrates that for Zn_4O_4 nanoclusters rocksalt-like structure is more stable in comparison with wurtzite-like structure. This conclusion agrees with the results of [27,28]. Thermodynamic preference of wurtzite-like structure of zinc oxide in comparison with rocksalt-like structure is observed only in large clusters of zinc oxide [28].

Further calculations were carried out with thermodynamically more stable rocksalt-like Zn_4O_4 nanocluster.

3.2. Mechanism of catalytic reaction 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. The computational study of the reaction of DMC with methylamine showed that it proceeds through the following stages:



$$\underset{\mathrm{I}}{Zn_4O_4} + \underset{\mathrm{IIa}}{H_3C{-}NH_2} + \underset{\mathrm{III}}{H_3CO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3} \longrightarrow \underset{\mathrm{IM1}}{Zn_4O_4 \bullet H_2C{-}NH_2 \bullet H_2CO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3} \longrightarrow \mathrm{TS1}$$

$$\mathrm{TS1} \longrightarrow \underset{\mathrm{IM2}}{Zn_4O_4 \bullet H_3C{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3 \bullet CH_3OH} \longrightarrow \underset{\mathrm{I}}{Zn_4O_4} + \underset{\mathrm{V}}{H_3C{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3} + \underset{\mathrm{IVa}}{CH_3OH}$$

Initially, due to the interaction of zinc oxide Zn_4O_4 cluster (I), molecules methylamine (IIa), and DMC (III) the pre-reaction complex (IM1) is formed. Then, pre-reaction complex through transition state (TS1), in which the proton migrates from methylamine nitrogen to DMC oxygen, the pre-reaction complex (IM1) transforms into the post-reaction complex (IM2). The post-reaction

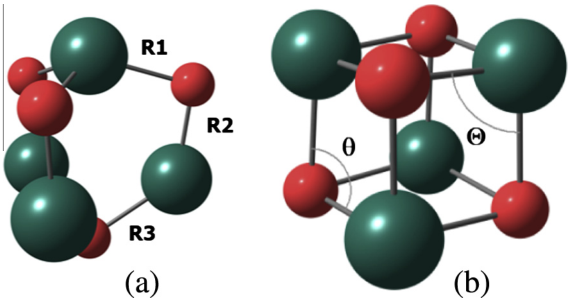


Fig. 1. Optimised structures of wurtzite-like (a) and rocksalt-like (b) Zn_4O_4 clusters calculated by M06 level in gas phase.

Table 1
Geometries and energies of wurtzite and rocksalt structures of Zn_4O_4 clusters.

Method	R1	R2	R3	R(Zn–Zn)	R(O–O)	ΔG°_f, kJ/mol
Wurtzite						
wB97XD	1.99	1.80	1.97	2.92	3.36	−2042.3
M06	1.98	1.80	1.96	2.87	3.40	−2074.0
PBE1PBE	1.99	1.80	1.97	2.89	3.39	−1929.4
	Θ/θ[a]	R(Zn–O)		R(Zn–Zn)	R(O–O)	ΔG°_f, kJ/mol
Rocksalt						
wB97XD	95.7/84.0	2.01		2.69	2.98	−2197.4
M06	96.2/83.4	2.01		2.67	2.99	−2221.0
PBE1PBE	96.0/83.7	2.01		2.68	2.99	−2090.4

[a] Valence angles at Zn and O, respectively.