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Kinetics and quantum chemical aspects of the mechanism of the guanidine (TBD) catalyzed aminolysis of cyclocarbonate containing soybean oil triglycerides as the model process of green chemistry of polyurethanes

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Abstract

The kinetic regularities and the mechanism of the catalytic action of 1,5,7-triazabicyclo[4.4.0]decene-5 (TBD) in the reaction of *n*-butylaminolysis of cyclocarbonate-containing triglyceride based on soybean oil in DMSO have been studied. It is shown via DFT quantum chemical calculations of the model reaction of ethylene carbonate with methylamine under the action of TBD that the process proceeds by the bifunctional catalysis mechanism, whereby the catalyst molecule takes part in a number of equilibrium processes, resulting in a proton transfer from the amine molecule to cyclocarbonate. Within the framework of calculations by the DFT method, the effect of the solvent (DMSO) is first taken into account in the catalysis mechanism of the hydroxyurethane formation reaction. Based on the quantum chemical calculations of the model structures of the linoleic and oleic fragments of the oligomer, the anomalies of the kinetic curves of the reactions under investigation have been interpreted.

Keywords DFT · Aminolysis · Cyclocarbonate · Triglyceride · Catalysis · Kinetics

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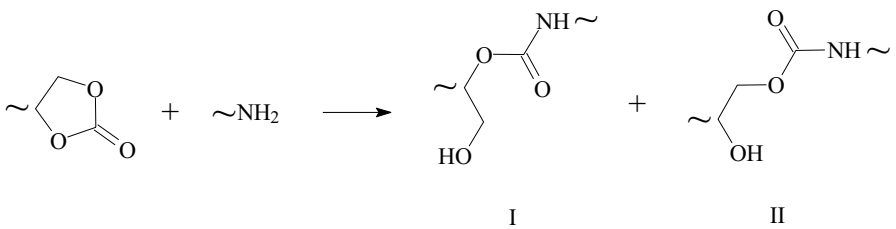
Introduction

The classical method of the polyurethane production is based on the interaction of NCO groups of di- or polyisocyanates with OH groups of di- or polyols. The world production of polyurethanes has already exceeded 18 million tons per year, although the production of these polymers is far from perfect in environmental terms. It is primarily due to high toxicity of the isocyanates themselves, moreover, they are obtained with the use of phosgene. Over recent years, a new trend has emerged in this field of research: the green chemistry of polyurethanes, the aim of which is to replace the urethane formation reactions involving isocyanates with safer reactions, including those based on renewable plant raw materials. A series of review articles published in recent years [1–10] indicate the relevance of work on the creation of nonisocyanate urethanes and certain progress of this area of polymer chemistry.

The most promising way to synthesize new urethanes is the reaction of primary amines with cyclocarbonates (Scheme 1).

The polyurethanes formed in this reaction contain hydroxyl groups—primary (Scheme 1, **I**) and/or secondary (Scheme 1, **II**) in equal or slightly different ratios depending on the structure of the reagents and the process conditions. The presence of OH groups in hydroxyurethanes promotes their hydrolytic and generally chemical stability due to the formation of the intra- and intermolecular hydrogen bonds and opens the ways for the corresponding modification of polymers. In this regard, such polyurethanes sometimes turn out to be better than traditional ones obtained according to the classical scheme using isocyanates and hydroxyl-containing oligomers. The oligomers with terminal cyclocarbonate groups for new urethanes are usually obtained from epoxy or hydroxyl-containing precursors. It is also important for green chemistry of polyurethanes that such oligomers can be produced from renewable raw materials—vegetable oils via their preliminary oxidation with the formation of epoxy-containing triglycerides followed by the catalytic carbonization of the latter under the action of carbon dioxide [10].

The addition reaction of amines to cyclocarbonates has been known since the mid-fifties of the last century [11], but the mechanism and quantitative patterns of hydroxyurethane formation have come to be intensively studied only in recent years [12–22]. In our previous kinetic and quantum chemical works performed on the model objects [14–19], it has been found that aminolysis of cyclocarbonates proceeds by two parallel channels with the participation of one and two amine molecules (or its dimer). The



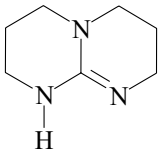
Scheme 1 Reaction of primary amines with cyclocarbonates

second amine molecule serves as a catalyst, taking part in the stage of the proton transfer from amine to carbonyl group of cyclocarbonate.

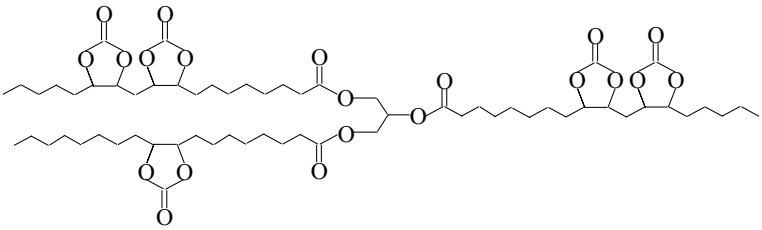
The relatively low rates of the cyclocarbonate ring-opening reaction at addition of the amine molecule (especially in the processes involving oligomers) actualize the search for suitable catalysts for this reaction. At the same time, the green chemistry assumes the application of the organic catalysts (organocatalysts), in contrast to the widespread and often quite active metal-containing compounds and complexes used in the classical polyurethane chemistry, based on the reaction of NCO and OH groups of monomers and growing chains.

About two dozens of compounds have been tested as the possible catalysts for the reactions of cyclocarbonates with amines in recent works [13, 23, 24]. Although Lewis acids, alcoholates, triflates, and salts of some metals exhibit a certain catalytic activity, but in most cases inhomogeneous colored products are formed in their presence even at 25 °C. Among the organic catalysts various tertiary amines and organophosphorous compounds have been proposed, which are used recently at the ionic polymerization reactions with the cycle opening of epoxides, lactones, lactides, carbonates, lactams and other monomers. The reviews [25, 26] show such catalysts for the ring-opening polymerization as trifluorophenylcyclohexylurea [27], which operates according to the principle of supramolecular recognition of atoms and groups, guanidines—1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and some others.

Among organocatalysts TBD has the highest catalytic activity in the reaction of cyclocarbonates with amines [13, 23, 24], the action mechanism of which is studied in the present work.



The subject of the experimental investigation was the reaction of *n*-butylaminolysis of cyclocarbonate-containing triglyceride based on soybean oil (CSBO) in dimethyl sulfoxide (DMSO). The studied oligomer of 95% conversion was obtained in our work [28] by a catalytic carbonization of epoxy-containing triglyceride by carbon dioxide. According to the mass spectrometry data [28], it represents a mixture of more than 20 triglycerides of different composition and functionality, the main component of which is the product of the generalized formula:



Such concept of the structure of triglycerides corresponds to the initial composition of soybean oil, in which the linoleic acid bifunctional by double bonds is about twice as many (~ 50%) as monofunctional oleic acid (~ 23%). The average functionality *f* of the oligomer by the cyclocarbonate groups is ~ 4.5, the molecular weight M_w according to the GPC data equals 1.319 [28].

Along with the kinetic study of non-catalytic and catalytic *n*-butylaminolysis of CSBO, the quantum chemical calculations by the DFT method of the catalysis mechanism under the action of TBD (using the reaction of methylamine with ethylene carbonate in DMSO as a model one) were carried out in the present work. Consideration of the solvent effects and calculation of all possible isomers/conformers for all reaction pathways allowed making more accurate quantitative calculation of reaction barriers and this distinguishes this study from gas-phase calculations by DFT, performed earlier by us [17] and others [29].

Experimental

Reagents

CSBO oligomer was obtained by the catalytic carbonization of the epoxy-containing soybean triglyceride. Its synthesis, MW, composition, and functionality were described earlier [28]. Normal butyl amine, catalyst TBD, solvent DMSO were purchased from Sigma-Aldrich and used without further purification.

Measurements

The reaction kinetics was studied in DMSO by a FTIR spectroscopy on a FTIR Tensor 27 spectrometer ("Bruker") by measurement of changing in time of optical densities near to the maximum of stretching vibrations of carbonyl groups of cyclocarbonates (1795–1803 cm^{-1}) and the final hydroxyurethanes (~ 1713 cm^{-1}). The reaction was carried out at 55 ± 0.1 °C directly in thermostatic CaF_2 cuvettes with a thickness of 0.1 and 0.4 mm. The reactions were described by the pseudo-first order law at concentrations of the cyclocarbonate groups (1.5–5.0) × 10^{-2} mol/L in an excess of amine in the concentration range of 0.1–0.75 mol/L. The observed rate

constants k_{obs} were calculated by non-linear least squares fitting of kinetic data to the equation:

$$D = Ae^{-k_{obs}t} + D_{\text{inf}}. \quad (1)$$

Here D is the optical density; A, k_{obs} and D_{inf} are various parameters [30]. The measurement procedure of the reaction kinetics of cyclocarbonates with amines is described in detail [16, 31].

Theoretical

The quantum chemical calculations were performed within the density functional theory (DFT) using the nonempirical generalized gradient approximation and the PBE functional [32, 33] in the TZ2P basis set using the PRIRODA program [34, 35]. The geometries for all initial reagents, intermediates and transition states were optimized. The nature of the stationary points found (a minimum or a saddle point on the potential energy surface) was determined by calculating the eigenvalues of the matrix of second derivatives of the energy by the coordinates of the nuclei. The correspondence between the transition states and a given transformation has been established by the calculation of intrinsic reaction coordinate (IRC).

Results and discussion

Uncatalyzed reaction of urethane formation: kinetic regularities

The aminolysis kinetics was studied by IR-spectroscopy in a significant excess of amine compared to the concentration of the cyclocarbonate groups of the oligomer at 55 °C under pseudo-first order conditions (see experimental part and our recent articles) [16, 17, 31]. The observed rate constants were calculated by non-linear least squares fitting of kinetic data to the Eq. (1) [30]. Semi-logarithmic anamorphoses of the kinetic curves (anamorphose—transformation of the kinetic curve in the coordinates of the first order equation) were calculated to clarify the deviation from pseudo-first order law. The anamorphoses of the kinetic curves of *n*-butylaminolysis of model ethylene carbonate are linear throughout the reaction (in DMSO, dioxane and *n*-butanol [16]). In contrast the linear segment of the anamorphoses of the oligomer extends only to 30–40% conversion (Fig. 1). Under the above conditions, these reactions are very slow, usually proceeding more than 10 h, and they do not even reach the end in some cases especially in the absence of the catalyst.

The observed rate constants for non-catalytic and catalytic reactions with CSBO oligomer were calculated from the initial part of the kinetic curves till the deviation from the pseudo-first order law. The reasons for the deviation of the kinetic curves from the first order law are connected with the presence of cyclocarbonate groups of different nature in triglycerides and discussed in a special section at the end of this article.

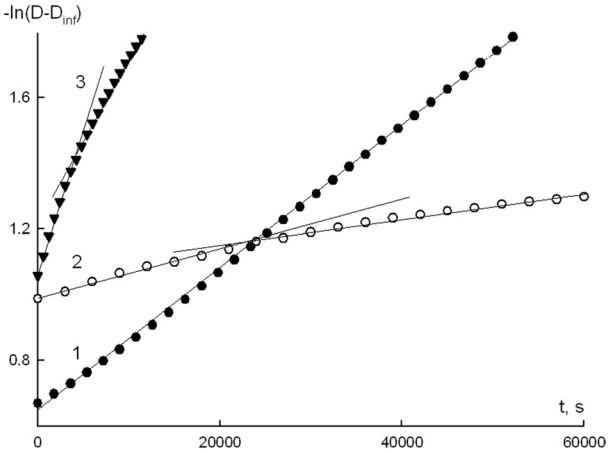


Fig. 1 Typical kinetic anamorphoses in semi-logarithmic coordinates for aminolysis reaction in DMSO: **1**—ethylene carbonate ([$BuNH_2$] = 0.4 mol/L), **2**—CSBO oligomer ([$BuNH_2$] = 0.5 mol/L), and **3**—CSBO oligomer in presence of 3.5×10^{-3} mol/L TBD ([$BuNH_2$] = 0.3 mol/L). T = 55°C

In our previous investigations [14, 16] performed on the model objects, it has been shown that the process proceeds by two parallel channels with the participation of one (rate constant k_1) and two (rate constant k_2) amine molecules. The observed rate constant of pseudo-first-order k_{obs} on $BuNH_2$ concentration obeys the following equation:

$$k_{obs} = k_1\left[BuNH_2\right] + k_2\left[BuNH_2\right]^2 \quad (2)$$

The experimental values of k_{obs} (s^{-1}) at various concentrations of *n*-butylamine under the conditions of the non-catalytic and TBD-catalyzed reaction are given in Table 1. A nonlinear relation between k_{obs} and the amine concentration at *n*-butylaminolysis of CSBO in DMSO in the absence of the catalyst (as well as in the reaction with the model ethylene carbonate [14, 16]) takes place (Fig. 2) and it is described by the Eq. (2) with the correlation coefficient $R^2 = 0.99$. At 55 °C $k_1 = 0.24 \times 10^{-5}$ L/mol s and $k_2 = 2.5 \times 10^{-5}$ L^2/mol^2 s, whence it follows that within the concentration range under investigation, the contribution of the channel with two amine molecules into the observed non-catalytic reaction rate is on average greater on order than the reaction with one amine molecule ($W_2/W_1 = (k_2/k_1)$ [$BuNH_2$]). A similar pattern was observed earlier in the model reactions with ethylene carbonate in different media, and it was shown that the second amine molecule by fitting into the cyclic structure of the transition state promotes the proton transfer from the amine to cyclocarbonate via the catalytic assistance mechanism [14–17].

TBD catalyzed reaction of urethane formation: kinetic regularities and DFT study of the reaction mechanism

Unlike a non-catalytic reaction, the presence of TBD (the experimental data on k_{obs} are in Table 1) in the same concentration range of $BuNH_2$ leads to disappearance

Table 1 The rate constants of pseudo-first order of aminolysis of CSBO in DMSO at 55 °C

$[BuNH_2]$, mol/L	$[TBD] \times 10^3$, mol/L	$k_{obs} \times 10^5$, s^{-1}
0.30	–	0.32 ± 0.01
0.41	–	0.54 ± 0.01
0.50	–	0.69 ± 0.03
0.60	–	1.12 ± 0.04
0.65	–	1.17 ± 0.05
0.71	–	1.45 ± 0.03
0.19	3.47	4.90 ± 0.24
0.30	3.48	7.19 ± 0.31
0.40	1.13	2.62 ± 0.05
0.40	3.51	8.78 ± 0.37
0.40	4.91	15.4 ± 0.28
0.40	8.56	24.8 ± 0.78
0.52	3.52	11.1 ± 0.57
0.60	3.52	14.1 ± 0.47
0.67	3.50	15.9 ± 0.28

The concentration of cyclocarbonate groups is (1.5–5.0) × 10^{-2} mol/L

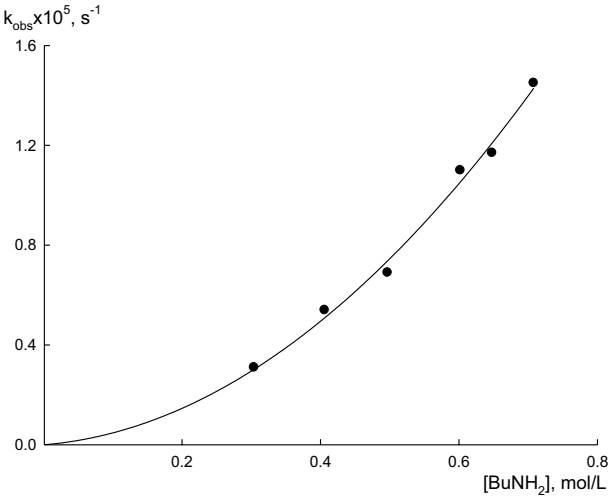


Fig. 2 Dependence of observed rate constant of pseudo-first order k_{obs} of CSBO non-catalytic reaction with *n*-butylamine in DMSO on amine concentration $[BuNH_2]$. T = 55°C

of the channel with participation of two amine molecules, that is resulted in almost linear dependence of k_{obs} on $[BuNH_2]$ (Fig. 3). The dependence of the catalytic rate constant on the TBD concentration (at $[BuNH_2]$ = Const) is also linear (Fig. 4).

As seen from Figs. 3 and 4, the patterns of the CSBO catalytic aminolysis are similar to those of the model ethylene carbonate. The reaction is the first order by

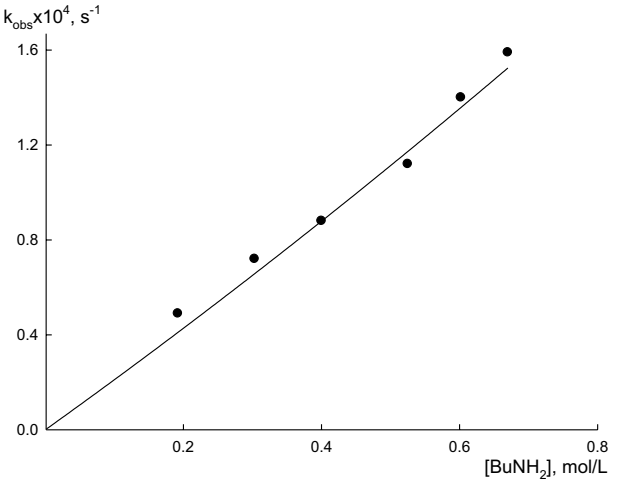


Fig. 3 Dependence of observed rate constant of pseudo-first order of CSBO catalytic reaction with *n*-butylamine in DMSO on amine concentration [$BuNH_2$] in presence of 3.5×10^{-3} mol/L TBD, T = 55°C

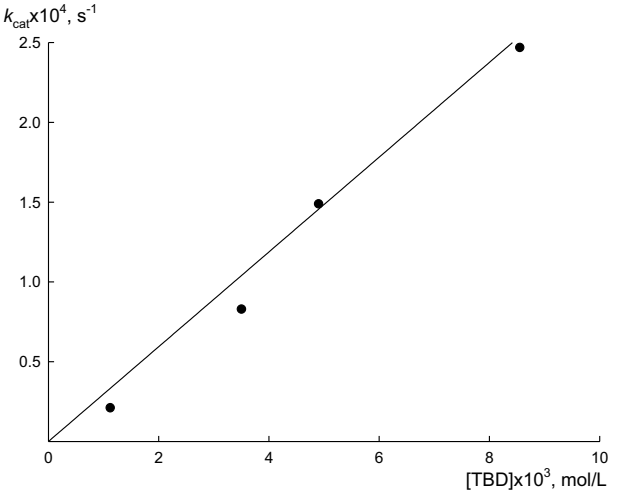


Fig. 4 Dependence of catalytic rate constant of pseudo-first order $k_{cat} = k_{obs} - k_0$ (k_0 is the rate constant of non-catalytic reaction) of CSBO reaction with *n*-butylamine in DMSO on TBD concentration at [$BuNH_2$] = 0.4 mol/L, T = 55°C

amine and catalyst, which was used as a basis in the present work for the quantum chemical description of the catalysis mechanism of the studied reaction under action of TBD in DMSO.

In the present work, the effect of the solvent on the catalysis mechanism of the aminolysis reaction under the action of TBD was first taken into account. The non-catalytic reaction of aminolysis of cyclocarbonates in such solvents as dioxane and methanol has been previously studied by the DFT method in a supermolecule

approximation [18, 19]. The theoretical description of the mechanisms of the liquid-phase reactions by the supermolecule method allows taking into account specific interactions between the molecules of reactants, catalyst and solvent, such as hydrogen bonds, which affect the chemical transformation. This effect cannot be taken into account when using other methods of modeling the reaction in solution.

In our case, DMSO is a highly dipolar aprotic solvent and, it cannot explicitly form chains or networks of hydrogen bonds like water or alcohols. However there are weak hydrogen bonds between the hydrogen atoms of the methyl groups and the oxygen atoms in this solvent, and this is sufficient for the formation of linear chains and small clusters from the DMSO molecules [36, 37]. Hydrogen bonds of the same type are formed with both reagents and co-solvent molecules [38–49]. Thanks to the cooperativity effect, the formation of even such weak hydrogen bonds can affect the chemical reactions in DMSO or its mixtures with other solvents and reagents, for example, with water, alcohols, amines [36, 37, 50, 51].

The structure of clusters consisting of the DMSO molecules has been recently studied by the quantum chemical methods [50]. The most stable isomers were mainly studied. In order to construct the correct solvated structures by the supermolecule method, it is necessary to study all possible ways of coordinating the DMSO molecules and compare the energy gain from the formation of such structures. It was carried out on the example of the DMSO dimer complexes (Fig. 5).

All five isomers of the DMSO dimer have already been calculated in different sources (**1a** [36, 37, 51], **1b** [52], **1c** [52, 53], **1d** [36, 52], **1e** [36]), and our data are in agreement with them. The most stable is the symmetric isomer **1a** with four hydrogen bonds, its energy is taken as the reference level for other isomers. Reducing the number of the hydrogen bonds up to three in **1b** increased the energy of the complex by 1 kcal/mol, and reducing the number of the hydrogen bonds to two in **1c**—by 2.4 kcal/mol. The complexes **1d** and **1e** differ in the symmetry of the arrangement of two DMSO molecules relative to each other and have

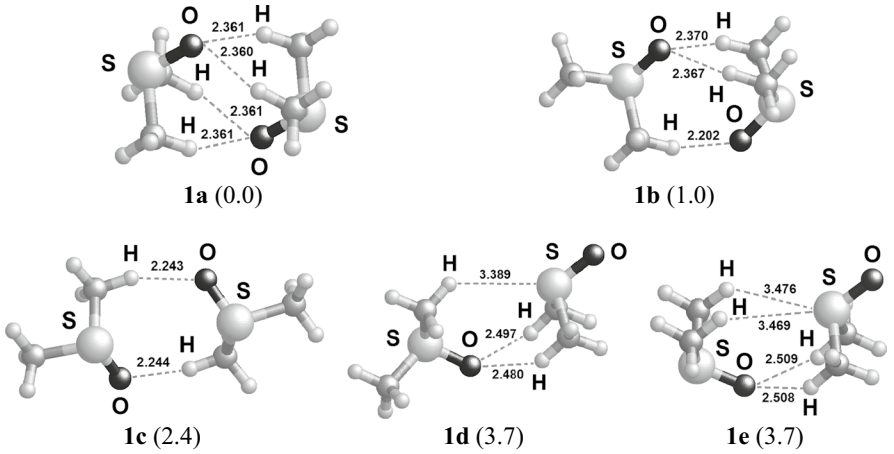


Fig. 5 Structures of stable isomers of DMSO dimer (relative energies (kcal/mol) are shown in brackets)

the additional possibility of binding due to a σ–hole effect. However, this effect does not give a sufficient energy gain, and because of the presence of the oxygen atom unbound by the hydrogen bonds, the **1d** and **1e** complexes turned out to be energetically the least beneficial.

Thus, the construction of supermolecules with the participation of DMSO should take into account the number of the hydrogen bonds formed and the presence of unsolvated unsaturated oxygen atoms. A certain role in the structure stabilization is played by the formation of cycles from hydrogen bonds with the oxygen and hydrogen atoms of the methyl groups of the DMSO molecules.

As was shown before, the main contribution into the process is made by the concert and stepwise reaction pathways at the calculation of the mechanism of non-catalytic and TBD-catalyzed aminolysis of ethylene carbonate in the gas phase [14, 15, 18, 19]. Other variants of mechanism have higher transformation barriers. Therefore, these two pathways were considered in the present work. An important role in the catalysis of aminolysis is also played by the process of the proton transfer, in which the solvent molecules can participate. This is typical for the reaction in the alcoholic solutions [18]. When the reaction takes place in DMSO, the solvent molecules can only stabilize the transition states, screening the forming excess charges, and cannot participate in the proton transfer.

When using the supermolecule method for the quantum chemical calculation of the reaction mechanisms in a solution, it is important to choose the optimal number of solvent molecules for correct modeling of the near solvation shell. It can be sufficient to take into account only one solvent molecule [19], and for another solvent it is necessary to consider, for example, five molecules [18]. This depends on the number and type of the specific interactions between the reagent and solvent molecules, as well as between the solvent molecules. The bonds caused by the specific interactions, which are not breaking and forming during the chemical reaction, should be maintained in all transition states, intermediates, pre-reaction complexes, and solvated reagents, so that the energies of such interactions do not introduce an error into the calculation of the complexation and activation energies.

We studied the effect of one, two, and three DMSO molecules on the transformation barriers. The activation energies counted from the complexes of the solvated reagents **SR** are listed in Tables 2 and 3 for the concert and stepwise pathways, respectively. The general scheme of transformation is shown in Fig. 6. Because of the stabilizing effect of the DMSO molecules, the number of stages in both pathways increased, as compared with the gas-phase process [17], and even the proton transfers inside the cycle were broken down into separate stages.

The reaction by both pathways begins with the addition of amine to carbonyl group via **TS1** or **TS4**. The difference is in coordination of TBD proton to different O atoms, alkoxy or carbonyl O, respectively. The proton transfer between amine and TBD occurs in **TS2** and **TS5**, resulting in the TBD cation formation. Further, everything is ready for the cycle opening through **TS3** in the concerted pathway, but at the stepwise pathway the TBD molecule must be rotated by ~ 40° with the reorientation of the proton associated with TBD from N atom on amino group to O atom of the alkoxy group (**TS6**). The breaking of the C-O bond in the cycle occurs in **TS3** and

Table 2 Energies of transition states (**TS1**–**TS3**), intermediates (**I1**, **I2**), pre-reaction complexes (**RC**) and product complexes (**PC**) found for the concert pathway of ethylene carbonate aminolysis reaction at TBD catalysis in DMSO (in kcal/mol)

Number of DMSO	Isomer[a]	RC	TS1	I1	TS2	I2	TS3	PC	Maximal barrier
0	1	0.5[b]	–	–	–	–	14.9[b]	− 13.1[b]	14.9[b]
0	2	0.0[b]	–	–	–	–	15.5[b]	− 9.7[b]	15.5[b]
0	3	0.0[b]	–	–	–	–	17.6[b]	− 11.1[b]	17.6[b]
0	4	0.3[b]	–	–	–	–	18.2[b]	− 8.2[b]	18.2[b]
1	1	− 2.6	7.8	4.6	7.2	6.8	6.9	− 15.9	7.8
1	2	− 2.6	6.6	5.3	–	–	10.1	− 16.5	10.1
1	3	− 3.0	6.9	5.1	–	–	10.2	− 14.9	10.2
1	4	− 0.5	–	–	10.9	8.1	9.1	− 11.2	10.9
1	5	0.8	10.4	9.7	11.2	8.8	9.2	− 12.8	11.2
1	6	− 2.0	7.7	–	–	6.8	12.2	− 14.4	12.2
1	7	− 0.2	9.0	–	–	7.7	12.8	− 14.5	12.8
2	1	2.4	9.6	6.6	9.5	9.1	9.3	− 12.7	9.6
2	2	0.1	9.9	7.4	–	–	12.2	− 10.9	12.2
2	3	0.4	8.9	6.3	–	–	12.8	− 5.8	12.8
2	4	4.0	12.4	11.8	13.4	11.0	11.1	− 13.0	13.4
3	1	0.8	10.1	5.7	9.6	9.4	9.6	− 13.7	10.1
3	2	− 1.1	8.2	5.4	–	–	10.9	− 14.0	10.9
3	3	2.7	10.6	11.6	11.7	8.6	8.8	− 13.4	11.7
3	4	2.7	9.4	6.6	–	–	12.4	− 13.0	12.4
3	5	− 0.3	10.8	8.2	–	–	13.8	− 11.4	13.8

[a]Different isomers on potential energy surface

[b]Data from Ref. [17]

Table 3 Energies of transition states (**TS4**–**TS7**), intermediates (**I3**–**I5**), pre-reaction complexes (**RC**) and product complexes (**PC**) found for the stepwise pathway of ethylene carbonate aminolysis reaction at TBD catalysis in DMSO (in kcal/mol)

Number of DMSO	Isomer[a]	RC	TS4	I3	TS5	I4	TS6	I5	TS7	PC	Maximal barrier
0	1	0.8[b]	9.3[b]	9.1[b]	9.5[b]	4.2[b]	6.1[b]	5.7[b]	8.4[b]	− 12.9[b]	9.5[b]
0	2	1.1[b]	10.5[b]	9.9[b]	10.1[b]	3.8[b]	5.7[b]	5.1[b]	7.8[b]	− 11.9[b]	10.5[b]
2	1	2.4	9.7	4.5	6.4	4.9	6.8	6.2	7.4	− 13.4	9.7
2	2	− 0.2	10.0	8.2	–	–	8.7	5.7	10.4	− 6.9	10.4
3	1	1.1	10.1	4.6	–	–	8.4	7.0	7.5	− 13.4	8.4
3	2	− 0.9	8.3	6.2	–	–	9.7	9.6	11.8	− 12.5	11.8
3	3	1.1	8.2	6.0	–	–	8.0	7.9	12.3	− 10.8	12.3

[a]Different isomers on potential energy surface

[b]Data from Ref. [17]

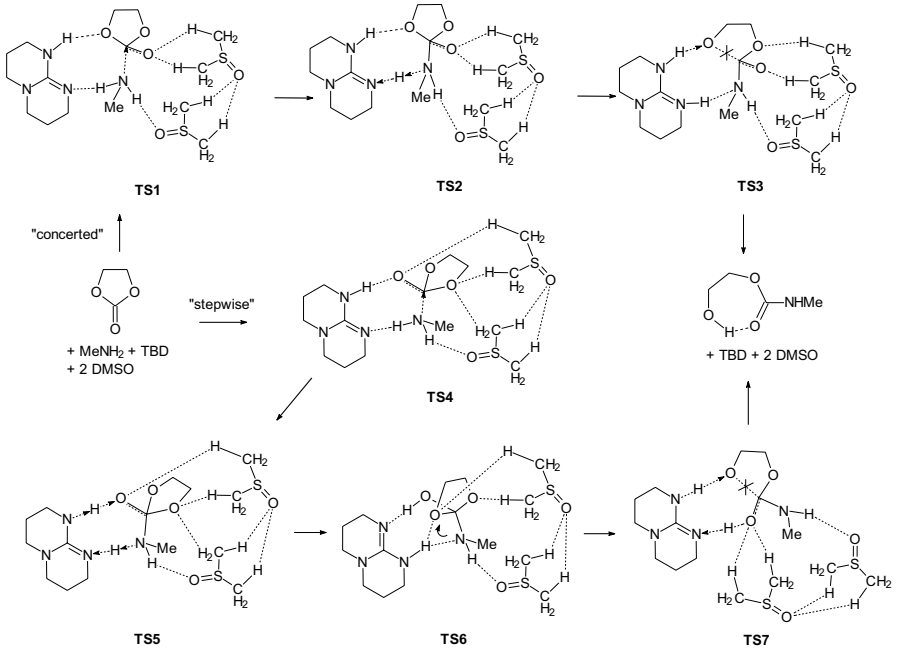


Fig. 6 Scheme of reaction and transition states of concert and stepwise pathways of TBD-catalyzed aminolysis of ethylene carbonate with participation of two DMSO molecules

TS7 with simultaneous proton transfer through TBD to the alkoxy O atom to form a hydroxy group.

There is a conformational isomerism of amine addition and also an isomerism of TBD connection from the front or back side of the cyclocarbonate cycle relative to the amine attachment [18]. Besides, the formation of several isomers with different arrangement of the DMSO molecules around the reagents is possible. In the most stable isomers of the transition states with the lowest transformation barrier, TBD is added from the reverse side of the cyclocarbonate, and the DMSO molecules close the cycle of the hydrogen bonds between proton of amino-group and carbonyl oxygen atom, as shown in the scheme (Fig. 6). Such cycles are similar to the so-called stabilization cycles formed by the methanol molecules described earlier [18]. Of importance is the formation of two hydrogen bonds with the hydrogen atoms of the methyl groups of each DMSO molecule. It is more efficient if these hydrogen bonds are formed by the same O atom (carbonyl O or atom O from DMSO), forming a six-membered cycle. Different stages can be limiting in the different isomeric transformation pathways.

As for the choice of the optimal number of the DMSO molecules for the calculation, in this case two solvent molecules are sufficient. If only one DMSO molecule is used for calculations, it is bounded too strongly into a complex with reagents, which leads to an underestimation of the activation energy. In addition, it is not possible to construct the structure of the solvated reagents (**SR**) with one DMSO molecule with the complete elimination of the interaction between reagents. An increase in

the number of the DMSO molecules up to three does not lead to a significant change in the activation energies.

On the reasons of the anomalous kinetics of CSBO aminolysis: experimental and theoretical interpretation

The deviation of the kinetic curves from a simple first-order law in an excess of amine, characteristic for the aminolysis process of the studied CSBO oligomer (Fig. 1), can be caused by the following reasons:

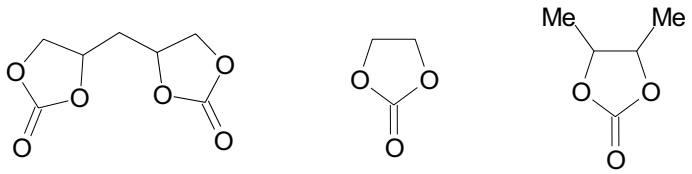
(a) increasing "blocking" of the cyclocarbonate groups, molecules of amine and catalyst as a result of inter-chain hydrogen bonds involving the hydroxyurethane fragments formed in the reaction and thereby change of the mobility and reactivity of reactants and catalyst,
(b) different reactivity of the cyclocarbonate groups of different types, contained in the initial triglyceride molecule and therefore reacting with the amine, each with its own rate constant.

The results on the inhibition of the interaction of cyclocarbonates with an oligomeric diamine (Jeffamine EDR-148) in chloroform, THF and DMF have been recently interpreted with regard to "blocking" of the reactants by the reaction products [22]. The authors accelerated the reaction by introducing into the system methanol, a solvent that breaks the interchain H-bonds with the participation of hydroxyurethane groups and increases the molecular mobility of oligomer chains. In the light of article [22], we also carried out the corresponding experiments, and it was established that there is a significant acceleration of the reaction of CSBO aminolysis in DMSO with the addition of *n*-butanol and in pure alcohol as in article [22]. So, at $[BuNH_2] = 0.4$ mol/L in DMSO, in the mixture of DMSO and *n*-butanol containing 51% *n*-butanol, and in 100% *n*-butanol, the rate constants, calculated from the initial part of the kinetic curves till the deviation from the pseudo-first order law, are 5.4×10^{-6}, 3.4×10^{-5} and 1.6×10^{-4} s^{-1}. However, there was no noticeable shift of the inflection point of the kinetic curve anamorphoses towards greater transformation depths. In fact, the acceleration of aminolysis in the presence of alcohol is previously well-studied phenomenon, observed not only in oligomeric, but also in monomeric systems. It is caused by the catalytic assistance of alcohol to the act of the proton transfer in the cyclic transition state of the limiting reaction stage [16, 18].

There was also an attempt to understand the experimentally observed change in the activity of the functional groups of the oligomer during transformation, as a result of the presence in it of the cyclocarbonate fragments of linoleic (L) and oleic (O) nature (as main components) under the assumption of their different reactivity. These are not the only fatty acid residues in CSBO, linolenic (Ln) residues are presented in less amount, as well as nonfunctional unsaturated fatty acid residues—stearin (S), palmitic (P) and some others. The content of L-type triglycerides in the oligomer under study (LLL, LLO, PLL, LLS, etc.) according to the

mass spectrometry data [28] comprises ~ 55%, O-type (OOO, OLO, POO, OLS, etc.) ~ 22%, Ln-type (PLnL, LLnL, Ln, Ln, O, etc.) ~ 7%.

First of all, it was assumed the possibility to change the reactivity of the cyclocarbonate group of the L-fragment at the expense of the forming of the H-bond between the product of aminolysis (the hydroxyurethane group) and the unreacted by this time cyclocarbonate group located on the same chain. For this purpose, the quantum chemical calculation of the energy barriers of the sequential opening of the model bicyclocarbonate cycles (**a**) during its attack with methylamine and the activation energies for transformation of the monofunctional cyclocarbonates (**b**) and (**c**) in the same reaction was made.



a **b** **c**

Bicyclocarbonate **a** is the model of the L-fragment, and monocyclocarbonates **b** and **c** are the models of the O-fragment of the oligomeric chains.

For bicyclocarbonate **a**, the investigation was carried out on a single potential surface with the participation of two amine molecules. In the case of compounds **b** and **c**, the corresponding isomers of the pre-reaction complexes (**RC**) with the minimum energy were used as the reference level of all relative energies. For compound **a**, the **RC** isomer with the minimum energy among the isomers with excluding the interaction of two amine molecules was used as the reference level. It is necessary to correctly compare the barriers of three reactions proceeding on the different potential surfaces, since the interaction of amine molecules is not taken into account for **b** and **c**. To simplify the calculations, only concert non-catalytic reaction pathway in the gas phase was considered. The calculation results are presented in Fig. 7.

The activation barriers of the calculated transformations shown in the diagram have intervals due to the isomerism of transition states (see below). In our case, the minimum values of the barriers are important, because the path of reaction passes through them. The point to note during analysis of the potential curves (Fig. 7) is the lowest transformation barrier of the first (**TS8a**), and especially the second (**TS9a**) cyclocarbonate group of the linoleic fragment compared to O-fragment models (**TS8b**, **TS8c**). Fig. 8 shows the characteristic structures of the transition states and intermediates on the potential surface of transformation of bicyclocarbonate **a**, modeling the L-fragments of CBSO.

From the geometric structure of the most profitable transition state of bicyclocarbonate aminolysis (**TS9a**), it follows that the decrease in activation barrier of the second stage of L-unit transformation is the result of the solvation effect of the hydroxyl group (H bond) rather than the expected autocatalytic assistance. But in

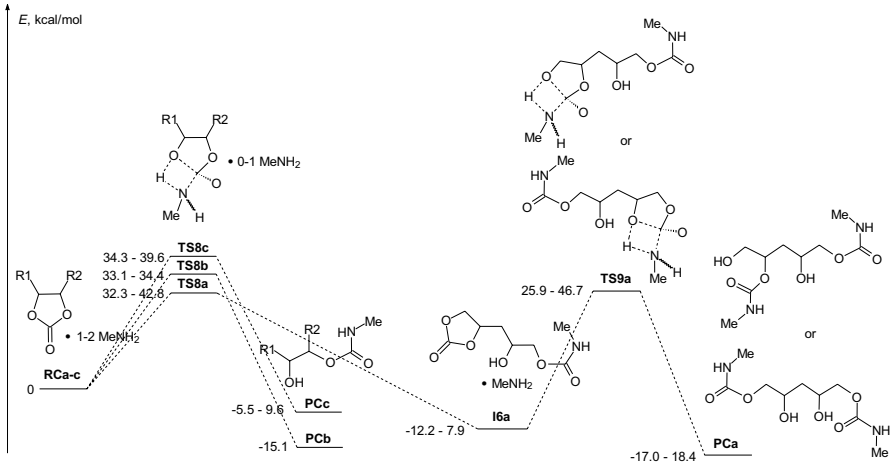


Fig. 7 Potential energy surfaces of opening reactions of cyclocarbonate groups under action of methylamine in model compounds **a–c**. Substituents in cyclocarbonates: **a**—$R_1 = H$, $R_2 =$ (2-oxo-1,3-dioxolan-4-yl)methyl; **b**—$R_1 = R_2 = H$; **c**—$R_1 = R_2 = Me$

this case, the reason for the decrease in the activation energy is of no significance. The main and doubtless fact is that the cyclocarbonate groups of the linoleic nature are more active than the cyclocarbonate groups of the oleic type, and this circumstance is the reason for the abnormal kinetics of the urethane formation with the CBSO participation.

Under the examination of such large molecules as bicyclocarbonate **a** for models, the problem of consideration of all possible isomers and conformers for the transition states, intermediates and pre-reaction complexes arises. As a rule, it is difficult to predict in advance, which of the isomers will be more profitable. If there is a possibility for the specific interactions in a molecule, the energy spread of isomers can be very large [18]. Therefore, it is necessary to calculate all isomers to find the reaction pathway with the minimum energy.

In our case, it was possible to reduce the number of the isomers under consideration to 39 for **TS8a**, since it was shown [30] that the inductive effect (2-oxo-1,3-dioxolan-4-yl)methyl substituent promotes the opening of the C(2)-O(1) bond in cyclocarbonate, and isomers with the opening C(2)-O(3) bond are less beneficial. In addition, the isomers with a possible effect of the second methylamine molecule on the transition state were excluded from consideration. The energy spread of the **TS8a** isomers is 10.5 kcal/mol.

The energy spread of intermediate **I6a** and **TS9a** is even larger and comprises ~ 20 kcal/mol, since apart from the conformational isomers, the formation of cycles with hydrogen bonds is possible. In the most stable isomer **I6a**, the methylamine molecule participates in the formation of such a 10-membered ring. Only the most characteristic manners of the hydroxyl coordination with the rest of the molecule and all possible conformations at such coordination manners were considered for **TS9a**. Namely, the formation of the most stable complex of the first-stage

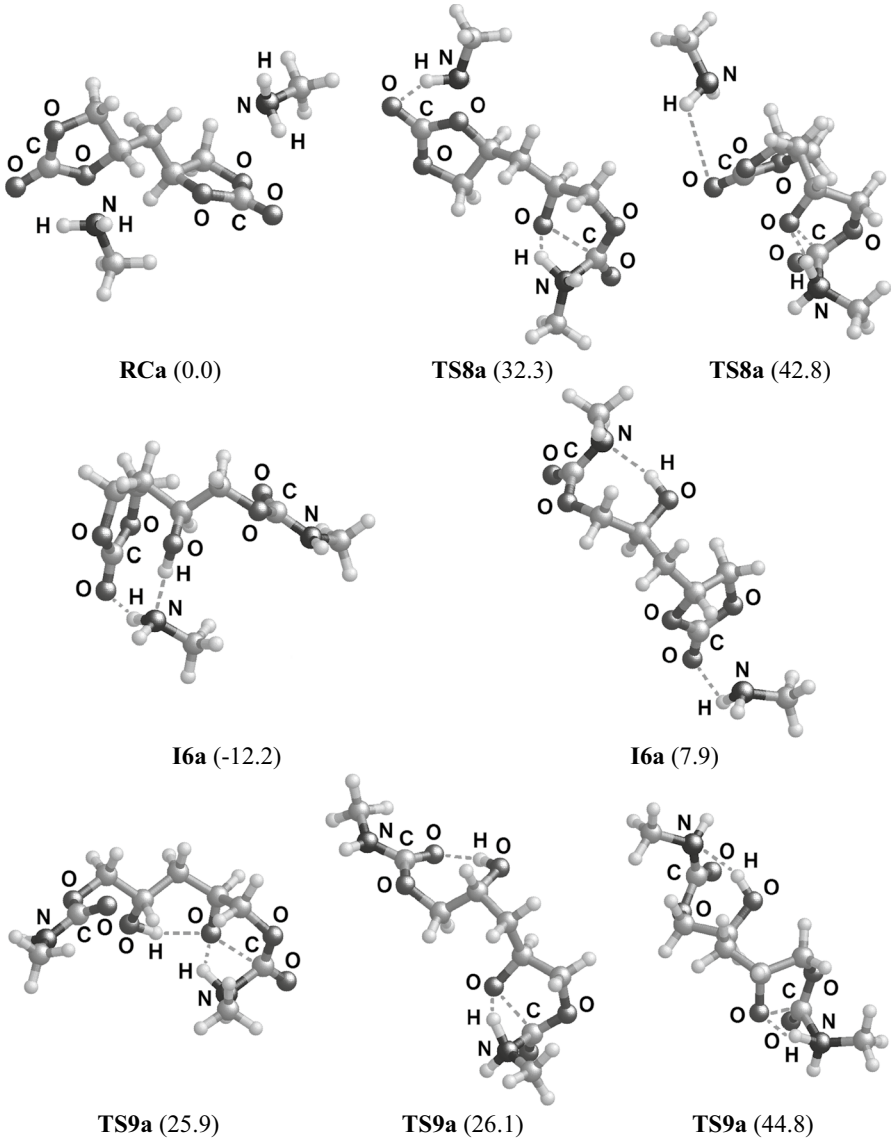


Fig. 8 Characteristic structures of transition states and intermediates on potential surface of aminolysis of bicyclocarbonate **a**, simulating the L-fragments of oligomer. Relative energies are given in the brackets (kcal/mol)

reaction product with the hydroxyl coordination by the O atom of the carbonyl group of the carbamate; the solvation promotion of the hydroxyl group to the reaction; the formation of less stable complexes of the hydroxyl group with the hydrogen bond to other heteroatoms; as well as structures without any interaction of hydroxyl with the environment (such **TS9a** are the least profitable energetically). It should be

noted that the assistance of the hydroxyl to proceeding of the reaction is equivalent in energy to the formation of the most stable hydroxyl complex with the carbonyl group of the carbamate, while other **TS9a** configurations are less beneficial.

Conclusions

The decrease in the activation energy of the reaction in DMSO compared to the gas-phase approximation is ~ 5 kcal/mol for the concert pathway and only ~ 1 kcal/mol for the stepwise pathway, if the structures with one DMSO molecule are not considered. The last difference is connected with the fact that in the stepwise pathway the carbonyl O atom participates in the reaction and its additional screening by solvent is not required. As a result, the energy barriers along two pathways were almost equal for the reaction in the DMSO solution. The TBD role in the aminolysis reaction consists in the proton transfer between the amine and the hydroxyl group formed, and the DMSO role is in the screening of the excess charges formed on the oxygen atoms of the cyclocarbonate group upon the amine addition.

Due to the weak negative inductive effect of the neighboring cyclocarbonate group, the reactivity of the linoleic acid residue is higher than that of oleic acid. In this connection at first the linoleic fragments react mainly on both cyclocarbonate groups, with the second cyclocarbonate group reacting faster. This contributes to an increase in the observed reaction rate and explains the deviation of the kinetic curves for aminolysis of CSBO from the first order law.

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