ISSN 1560-0904, Polymer Science, Series B, 2023, Vol. 65, No. 4, pp. 467–474. © Pleiades Publishing, Ltd., 2023.
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CHEMICAL TRANSFORMATIONS

Reactivity of New Monomers of the Polyurethanes Green Chemistry, the Reaction Mechanism, and the Medium Effect

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Received May 10, 2023; revised June 5, 2023; accepted June 9, 2023

Abstract—The influence of the substituents inductive effect and the proton-donor OH group in the substituted cyclocarbonates differing in the alkyl chain length on the activation barrier of their aminolysis reaction, which underlies the process of urethane formation without the participation of isocyanates, has been studied. Account for the solvent molecules has allowed quantitative interpretation of the process regularities. Kinetics of the model aminolysis reaction of a series of monomers in DMSO has been investigated.

DOI: 10.1134/S1560090423701063

INTRODUCTION

The process of polyurethanes preparation from hydroxyl-containing oligomers and isocyanates leaves much to be desired from the environmental viewpoint. This fact is due to high toxicity of the isocyanates as well as their preparation via the phosgenation of primary amines [1]. Therefore, the studies on the development of alternative phosgene-free syntheses of isocyanates as well as production of the polyurethanes avoiding the use of isocyanates have been considered topical issues recently [2–20]. The reaction of primary amines with cyclocarbonates is among the most promising approach to new urethanes (see Scheme 1).

The oligomers bearing terminal cyclocarbonate groups are usually obtained from the epoxide- or hydroxyl-containing precursors. Regarding the polyurethanes green chemistry, it is important that such oligomers can be prepared from renewable sources [14, 18–20].

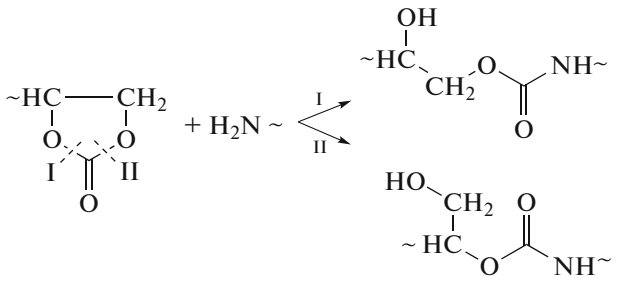
Practical application of this reaction demands elucidation of the factors affecting the reactivity of cyclocarbonate groups in the monomers depending on their structure. We have earlier found that the reactivity depends on the inductive effect of the substituent at the cyclocarbonate group, the substituents exhibiting negative inductive effect accelerating the reaction [21]. On the other hand, the presence of proton-donor groups in the substrates or in the reaction medium leads to further decrease in the activation energy and acceleration of the process. The proton donors can either solvate the reactive site to compensate for the excessive electron density at its heteroatoms or be involved in the cycle of the proton transfer from the amine to the alkoxy group; the latter effect is the most efficient in the process acceleration [22–29].

This study aimed at comparative investigation of the reactivity of the cyclocarbonate groups in the compounds modeling new oligomers for the synthesis of polyurethanes. The influence of the inductive effect of typical substituents as well as of the proton-donor OH groups in the cyclocarbonates differing in the length of the alkyl chain in the hydroxyalkyl substituents towards the model reaction with methylamine was investigated by means of quantum-chemical calculations. Kinetic features of the corresponding reactions were investigated for a series of the monomers.

EXPERIMENTAL

Chemicals and Experimental Methods

Ethylene carbonate (major component content 99.9%) (**1**), 4-(2-ethylhexyloxymethyl)cyclocarbonate (**2**) [21], 4-(hydroxymethyl)-1,3-dioxolan-2-one



Scheme 1.

(90%, ACROS) (**3**), and 4-ethyl-1,3-dioxolan-2-one (98%, ACROS) (**4**) were used.

Cyclocarbonates **1**–**4** as well as *n*-butylamine and DMSO used as solvent (both from Sigma-Aldrich) were used as received.

Kinetic measurements were performed in DMSO by means of IR-Fourier spectroscopy using a FTIR Tensor 27 instrument (Bruker, Germany), monitoring the evolution of absorbance at the frequencies corresponding to stretching of the carbonyl groups of the starting cyclocarbonates (1794–1803 cm^{-1}). The experimental procedure has been described in detail in our earlier report [23], exemplified by aminolysis of compound **1**. The measurements were performed at temperature 55 ± 0.1°C in thermostated CaF_2 cells with constant thickness of 0.1 or 0.4 mm. At concentration of the cyclocarbonate groups (1.5–5.0) × 10^{-2} mol/L and excess of amine (0.2–0.7 mol/L), the reaction followed the pseudo first order up to the conversion of 95–100%. Under those conditions, the observed first-order rate constant was independent of the starting content of the cyclocarbonate in the solution. The reactions of compounds **2**–**4** were noticeably slower than that of ethylene carbonate **1**.

The Methodology of Quantum-Chemical Calculations

Quantum-chemical calculations were performed in the scope of the density functional theory (DFT) using the non-empirically generalized gradient approximation and the PBE functional [30, 31] in the TZ2P basis implemented in PRIRODA software [32, 33]. The geometry optimization to find the energy minimum was performed for the intermediates (I), pre-reaction complexes (RC), and the product complexes (PC); the saddle points search was performed for the transition states (TS). The character of the revealed stationary points (minimum or saddle point in the potential energy surface) was determined by calculation of the eigenvalues of the matrix of the energy second derivatives over the nuclei coordinates. Correspondence of the transition state to the considered transformation was verified by calculation of the intrinsic reaction coordinate (IRC). Since the difference in the conformers energy could exceed the activation energy of single stages, the activation barriers should be calculated for the reactions involving the structures with the lowest energy [28, 34]. To identify the structures with the minimal energy, conformational analysis was performed for the transition states and stable compounds simulated in the study. The reported Gibbs free energy values (kcal/mol) were sums of the electronic energy, heat corrections (298 K), and dispersion corrections (PBE-D4) [35–37].

RESULTS AND DISCUSSION

Aminolysis of cyclocarbonates can occur via two parallel pathways, involving one or two amine molecules [38, 39]. In either case, the reaction can occur via single-stage or multistage mechanism. In the transition states of the single-stage mechanism (TS3 and TS4 in Scheme 2), the addition of amine, ring opening, and the proton transfer occur in a single act. If the reaction occurs via the multistage mechanism, the amine molecule is first added at the carbonyl group of the cyclocarbonate, the proton being transferred to the carbonyl O atom (TS1 and TS5) and the amino alcohol being formed, and then the carbonate cycle is opened (TS2 and TS7). When two amine molecules are involved in the reaction, the additional stage is required, consisting in the rearrangement of the six-membered cycle in intermediate I2 to form intermediate I3 with the position of the hydrogen bonds demanded for further reaction progress [38, 39].

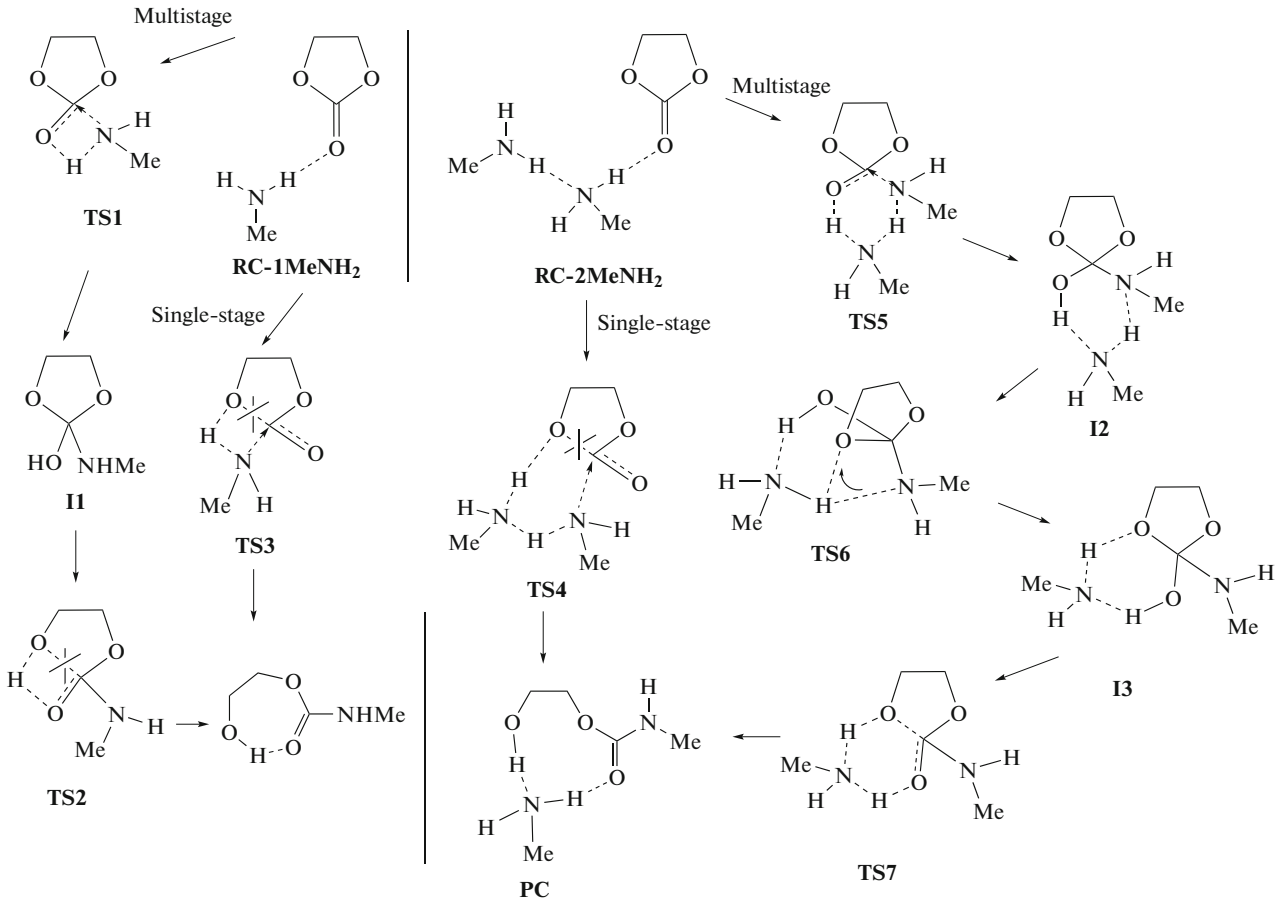
The mechanism is further complicated considering the molecules of solvent such as methanol [23, 25, 28] and DMSO [26] or when molecules of catalyst are involved, such as acetic acid [22] and 1,5,7-triazabicyclo[4.4.0]decene-5 [24, 26, 40]: the intermediates stability is increased and additional stages appear, for example, the proton transfer stage. The single-stage mechanism turns actually multistage, since the intermediate of the amine molecule addition at the carbonyl group becomes stable, due to the system stabilization. In this case, the ring opening occurs as the second or the third stage (if the proton transfer is a separate stage). The formation of certain transition states and intermediates is determined by the factors of the structures stabilization and can be different even for the reaction of the same compound, depending on the favorability of the conformations of the corresponding structures.

For comparison, it is often not needed to elucidate the complete mechanism for each compound. Due to the activation barriers, the reaction should mainly occur via the mechanism involving two amine molecules [38, 39]. That fact is confirmed by the earlier reported data [21–27, 41] as well as the kinetic and simulation data discussed below.

The dependence of the observed pseudo first-order rate constant k_{obs} of the cyclocarbonates **1**–**4** reaction with *n*-butylamine on the amine concentration $[BuNH_2]$ shown in Fig. 1 were described by the equation

$$k_{obs} = k_1[BuNH_2] + k_2[BuNH_2]^2$$

with the coefficient of determination $R^2 = 0.99$. The coefficients k_1 and k_2 were the effective second-order



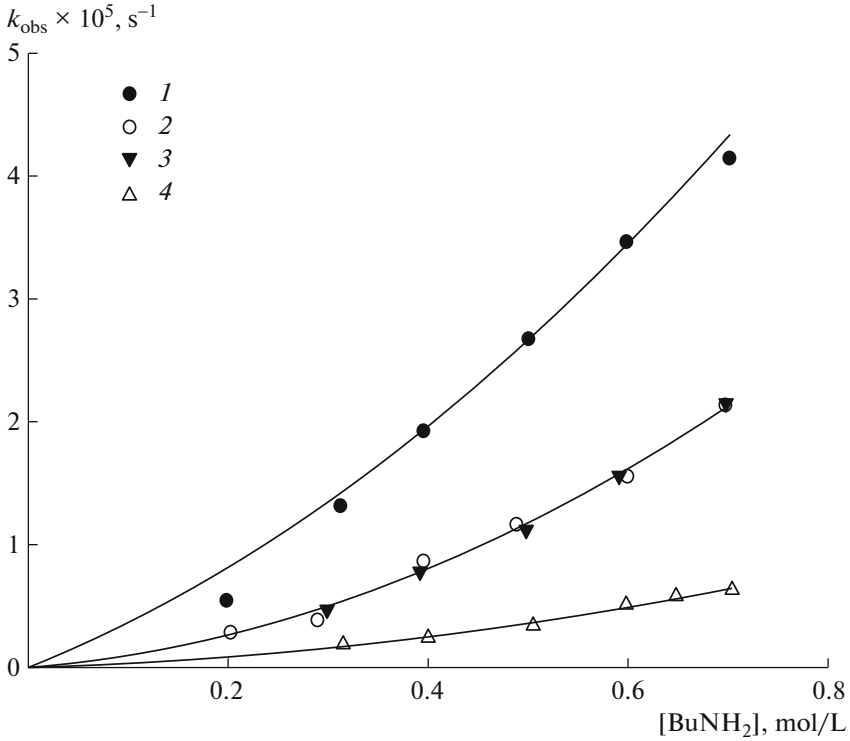
Scheme 2.

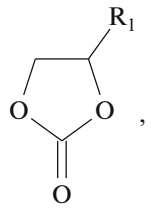
rate constants of the reaction involving one or two amine molecules (or its dimer), respectively. Their values (DMSO, 55°C) for the considered cyclocarbonates were as follows: $k_1 \times 10^5 = 2.8$ (**1**), 0.61 (**2**), 0.44 (**3**), and 0.24 L/(mol s) (**4**) and $k_2 \times 10^5 = 4.6$ (**1**), 3.5 (**2**), 3.7 (**3**), and 0.97 $L^2/(mol^2\ s)$ (**4**).

The rate constant of the reaction involving two amine molecules was always significantly higher in comparison with the reaction with the single molecule, even at low amine concentrations. According to the obtained data, rate of the reaction of the cyclocarbonates with the hydroxymethyl and 2-ethylhexyloxymethyl substituents were approximately equal, which evidenced no catalytic co-action of the OH group in the process in the presence of a short alkyl chain.

To investigate the influence of the substituents on the activation barriers of the reaction, in this study we limited the consideration to the single-stage pathway of aminolysis involving two amine molecules. The profiles of the free energy surfaces for the aminolysis reactions of a series of typical substituted cyclocarbonates bearing the substituents exhibiting the inductive effect as well as the proton-donor substituents are shown in Fig. 2. The reaction of hydroxypropyl-substituted ethylene carbonate is presented separately in Fig. 3, since, in contrast to the compounds with other substituents, it occurred through three stages (addition of amine, TS8; proton transfer, TS9; cyclocarbonate ring opening, TS10). The involvement of the hydroxyl group in the proton transfer cycle led to the stabilization of the intermediates and overall decrease in the activation barriers of the reaction.

The obtained data showed that the most efficient participation of the hydroxyl group in the catalysis of the proton transfer from the amine to the alkoxy group was possible only with the three-atom alkyl chain length, since in that case the non-strained 8-membered cycle of the proton transfer was formed, stabilizing the structures of TS8–TS10 (Fig. 3). In the system with the hydroxyethyl substituent (6 in Fig. 2), a strained 8-membered cycle of the proton transfer was formed, which did not give any energy gain (structure TS4(6a) is given in Fig. 4, $\Delta G = 28.6$ kcal/mol). The energy of that structure was practically equal to that of the transition state involving two amine molecules during the proton transfer with weak solvation of the O atom of the alkoxy group (structure TS4(6b) in Fig. 4, $\Delta G = 28.1$ kcal/mol).





where R1 = H (*1*), 2-ethylhexyloxymethy (*2*), CH_2OH (*3*) and Et (*4*).

Fig. 1. The observed rate constant k_{obs} of the cyclocarbonate-containing compounds **1**–**4** reaction with *n*-butylamine in DMSO as function of the amine concentration. $T = 55°C$.

In the case of the hydroxymethyl-substituted cyclocarbonate (3), the assisting of the hydroxyl group in the reaction proceeding was only possible via weak solvation of the carbonyl O atom due to the hydrogen bond formation (TS4(3) in Fig. 4). The hydroxyl group could not be incorporated in the proton transfer cycle. According to the calculations, the process of aminolysis of compound **3** was the least favorable, since it revealed the highest energy barrier (Fig. 2). Very weak intramolecular solvation of the hydroxyl group due to short alkyl chain of the substituent was among the main reasons for the so high energy barrier. The hydroxyl group in compound **3** could not form a favorable intramolecular bond with one of the heteroatoms, and the system energy was increased in comparison with the RC, in which the weakly bound amine molecules could be located in a favorable fashion, including the formation of the hydrogen bonds with the hydroxyl groups (i.e. forming the intermolecular hydrogen bond).

Since the kinetic features were studied for the reactions of the cyclocarbonates bearing the ethyl, hydroxymethyl, and 2-ethylhexyloxymethyl substituents in DMSO, we compared the experimental and theoretical series of the substituents according to their effect on the rate and activation energy of the reactions. The comparison revealed that the compounds with the hydroxymethyl (**3**) and alkoxymethyl (**2**, **5**) substituents stood out of the theoretical dependence, since higher reactivity was predicted for compounds **2** and **5**, whereas lower reactivity was predicted for compound **3**.

The reason for the discrepancy between the theory and the experiment could be solvation of the starting reagents and the transition states in the solution. We have earlier demonstrated strong dependence of the rate of aminolysis on the solvent polarity, the most prominent effect being observed for the proton-donor solvents, due to their ability to be incorporated in the

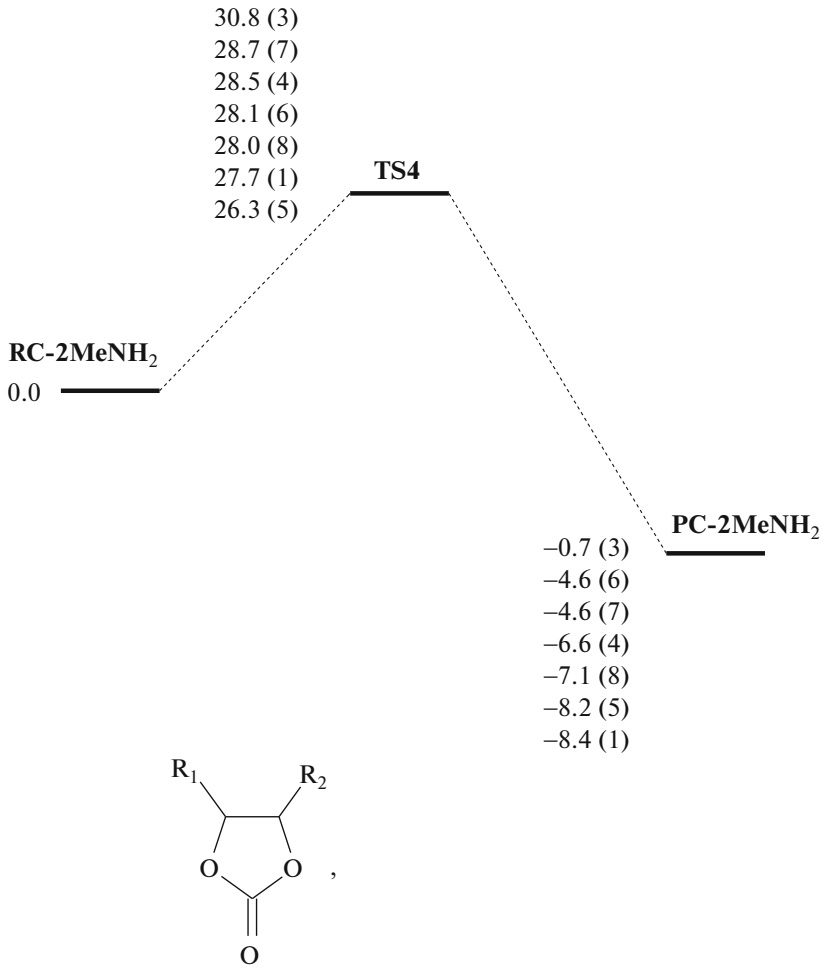


Fig. 2. Profiles of free energy surfaces of the aminolysis reactions of a series of substituted cyclocarbonates.

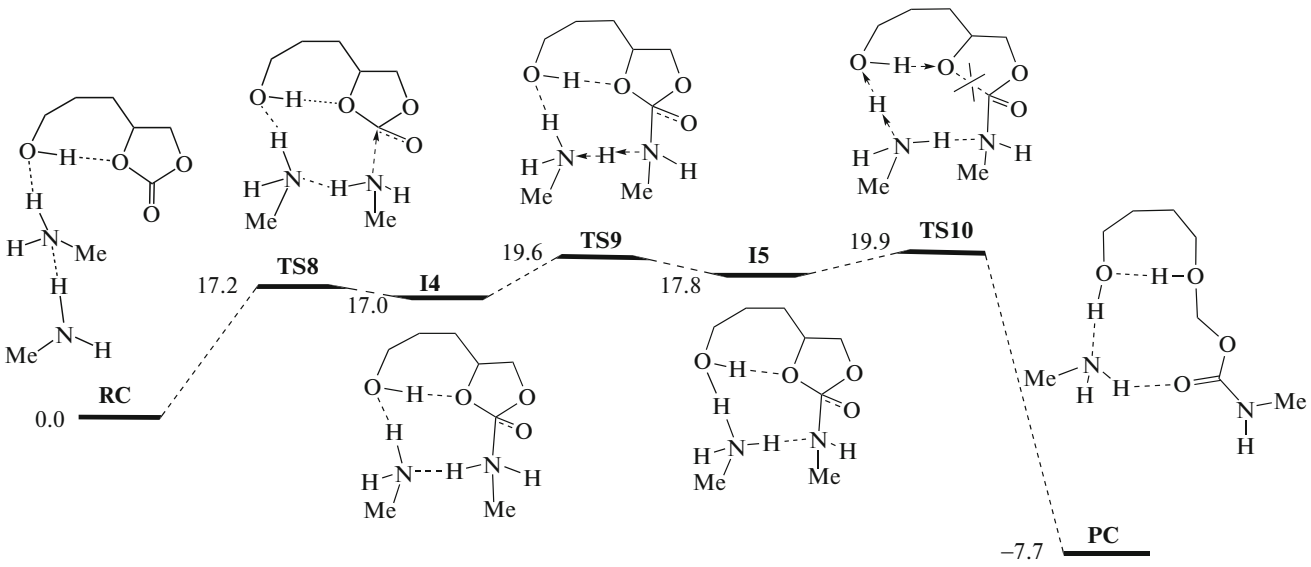
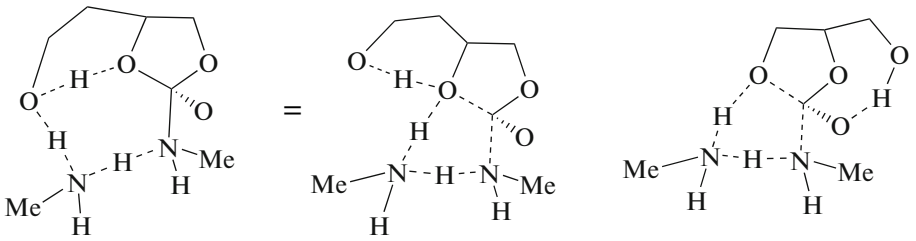


Fig. 3. Profile of the free energy surface of the reaction of aminolysis of 4-(3-hydroxypropyl)-1,3-dioxolane-2-one.



TS4(6a) **TS4(6b)** **TS4(3)**

Fig. 4. Characteristic structures of transitions states of aminolysis of the substituted cyclocarbonates **3** and **6**.

transition state structure with the formation of less strained and hence more favorable proton transfer cycles [23–26, 28].

Investigation of the properties of DMSO as solvent has been considered in many experimental [42–47] and theoretical studies [48–52]. According to these reports, the protons of the methyl groups of DMSO can form the so called "blue-shifted" hydrogen bonds with different heteroatoms [53, 54]. Such single interactions are very weak, but due to the possibility of the formation of multiple bonds contributing to the collective effect, the overall interaction can become noticeable.

We have earlier investigated the influence of the DMSO molecules on the activation parameters of the aminolysis reaction, but only in the presence of the catalyst (1,5,7-triazabicyclo[4.4.0]decene-5) and considering participation of a single amine molecule in the process [26]. Relatively small decrease in the activation energy in comparison with the gas phase, 5 kcal/mol for the single-stage path and only 1 kcal/mol for the multistage path, has been revealed. The barriers of the reactions via the single-stage and the multistage paths have become almost equal. It has been stated that the DMSO molecules could form weak yet efficient (due to the collective effect and the formation of six- and eight-membered cycles) hydrogen bonds between the protons of two different methyl groups and the heteroatom, for example, with the O atom of the carbonyl group of the cyclocarbonate. Due to this, the electron density appearing at the oxygen atoms of the cyclocarbonate upon addition of amine at the carbonyl group is shielded and, hence, the solvent molecules stabilize the structures of the transition states and intermediates and reduced their energy. Furthermore, the oxygen atom of DMSO can be coordinated with the acidic protons of the reacting molecules, contributing to the structures stabilization [26].

The most favorable transition state structures have been formed via the formation of a chain linking the amino group proton not involved in the reaction and one or two O atoms of the cyclocarbonate by two molecules of DMSO. Those structures were primarily considered in the present study, but for the sake of completeness the conformational analysis was performed, during which two or three DMSO molecules were attached to the structure of the transition state at different positions, and then the geometry was optimized to find the optimal interaction of the solvent molecules with the substrate. It has been earlier stated [26] that two DMSO molecules are enough for comprehensive modeling of such reaction; introduction of two DMSO molecules in the model was also found sufficient in the considered catalyst-free case.

The reaction mechanism was sophisticated when the solvent was considered. Due to the overall system stabilization with DMSO molecules, additional intermediates turned stable, and the single-stage path was divided into two separate stages: addition of the amine molecule at the carbonyl group of the cyclocarbonate (TS11) and the ring opening in the cyclocarbonate (TS12, Fig. 5). The proton transfer stage was not separated.

The overall process was limited by the ring opening stage. Despite noticeable lowering of the barriers in comparison with the gas-phase approximation (by 9.4–12 kcal/mol), the simulated series of the monomers reactivity depending on the substituent remained unchanged.

The most favorable structure of the transition state surrounding with the DMSO molecules was different from that found in the case of the catalysis with 1,5,7-triazabicyclo[4.4.0]decene-5 [26], when the DMSO molecules chain was closed at the proton of the amino group attached to the carbonyl. Moreover, four hydrogen bonds with the carbonyl O atom and two DMSO molecules O could be formed in the considered reaction with two amine molecules. However, that difference was minor, and the reaction catalyzed by 1,5,7-triazabicyclo[4.4.0]decene-5 occurred with lower barriers anyway.

Accounting for the solvent in the quantum-chemical simulations allowed quantitative assessment of the difference in the reactivity of the substituted cyclocarbonates. The energy barriers of the reactions of differently substituted cyclocarbonates were decreased by 9.4–12 kcal/mol, but the position of the substituents in the series of their influence on the activation barri-

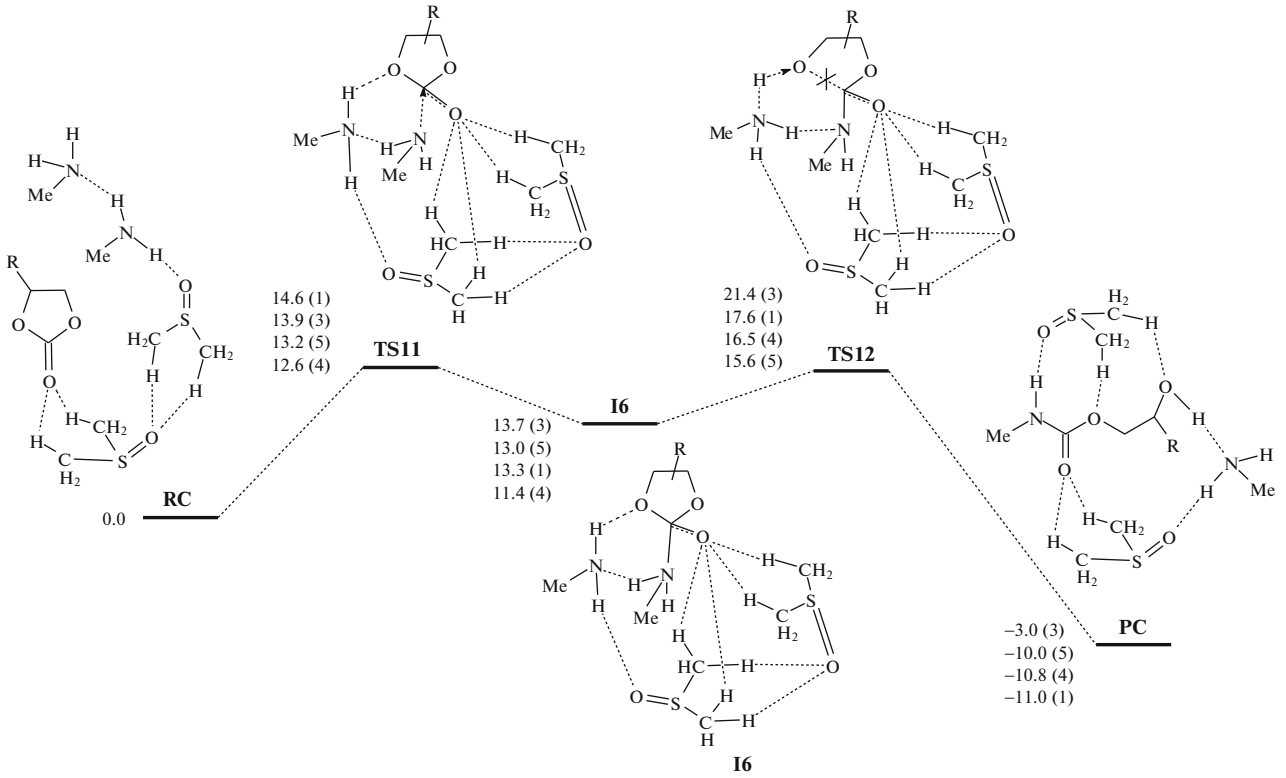


Fig. 5. Profiles of free energy surface of the reactions of aminolysis of a series of substituted cyclocarbonates involving two DMSO molecules.

ers was not changed. The difference in the calculated and experimental series of the substituents according to the effect on the rate and barrier of the limiting stage could be explained by additional processes, which have not been yet discovered by experimental and simulation methods. The presence of the proton-donor substituent in the cyclocarbonate gave the strongest contribution to the lowering in the energy barriers, the inductive effect being very weak and practically not affecting the activation barriers. The most efficient involvement of the proton-donor substituent as the intramolecular co-catalyst of aminolysis required the length chain between the cyclocarbonate and the donor group to be of at least three carbon atoms.

FUNDING

This study was performed in the scope of the State Task to Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences (no. FFZE-2022-0009).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Karpushkin