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Quantum-chemical studying of noncatalytic methanolysis of diethyl carbonate

© **Maxim V. Korshunov**, **Nikita I. Kurshev**, **Alexander Ya. Samuilov**,*+
Elena D. Prokhorova, and **Yakov D. Samuilov**
Kazan National Research Technological University. K. Marx St., 68. Kazan, 420015. Russia.
E-mail: ysamuilov@yandex.ru

*Supervising author; +Corresponding author

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Abstract

Mechanism and thermodynamical parameters of activation and reaction of model reaction underlying in the basisof chemical recycling of polycarbonates – noncatalytic transesterification of diethyl carbonate by methanol are studied by B3LYP/6-311++G(df,p) quantum-chemical method. Detailed description of two possible reaction mechanisms is carried out. They are: nucleophilic carbonyl atom substitution mechanism and "addition – elimination" mechanism including allogenic addition of methanol to diethyl carbonate's carbonyl group which leads to tetrahedral intermediate formation and its further decomposition which results in new molecule of carbonate and alcohol formation. The second way that is rate-limiting step characterizes by lower free energy barriers. Nevertheless, this way is problematical. It is explained by the fact that tetrahedral intermediates formation characterizes by low values of equilibrium constants.

Both monomers and dimers of methanol can be involved in reactions. Reactions with methanol dimers are more kinetically preferable than reaction with methanol monomer, both in nucleophilic carbonyl atom substitution mechanism and "addition – elimination" mechanism. It is provided by more higher donor-acceptor and acid-base properties of methanol dimer in comparison with methanol monomer. All reactions are carried out through cyclic approved transition states.

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