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Submitted on June 18, 2018.

Quantum-chemical study methanolysis of diethyl carbonate catalyzed by bases and Lewis acids

© **Alexandr Ya. Samuilov**, **Maxim V. Korshunov**, **Nikita I. Kurshev**, **Alia R. Agliullina**, and **Yakov D. Samuilov***+
Kazan National Research Technological University. K. Marx St., 68. Kazan, 420015. Tatarstan Republic. Russia. Email: ysamuilov@yandex.ru

*Supervising author; +Corresponding author
Keywords: polycarbonates, alcoholysis, catalysis, mechanism.

Abstract

Mechanism of diethylcarbonate transesterification with methanol using sodium methylate and zinc acetate as catalysts resulting in dimethylcarbonate by means of density functional method has been investigated. Transesterification proceeds gradually and leads to methylethylcarbonate intermediate formation.

Reaction between methylethylcarbonate and sodium methylate proceeds according to "addition-elimination" mechanism and formation of prereaction complexes occurs. Sodium atom in these complexes is hold near carbonate fragment by Van der Waals and electrostatical forces. In these fragments, increase in nucleophilic and electron-donating properties of methoxy fragment and increase in electron-acceptor properties of carbonate fragment are observed. Prereaction complexes via low free energy barriers show transition to bipolar ions. In these ions, carbon's carbonyl atom of carbonates obtains tetraedrical structure. These intermediates due to beta-transformation result either in methylethylcarbonate or diethylcarbonate formation. When reaction catalyzes by sodium methylate, rate-limiting step is bipolar intermediate formation stage. Free energy barrier of this stage is fully depended on entropic part. Activation enthalpies of this stage has negative values.

Methanolysis reactions of diethyl- and methylethylcarbonates using zinc acetate as catalyst proceed according to mechanism of nucleophilic substitution near carbon's carbonyl atom. Reactions are accompanied by prereaction triple complexes formation; they show transition to methylethyl- or dimethylcarbonate through approved transition states. Comparison of thermodynamic parameters of activation shows that transesterification using sodium methylate as catalyst is more preferable than using zinc acetate as catalyst.

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