Thematic Section: Quantum-Chemical Research. **Full Paper**
Subsection: Supercritical Fluids. *Registration Code of Publication:* 14-39-9-1
Publication is available for discussion in the framework of the on-line Internet conference "*Butlerov readings*".
http://butlerov.com/readings/ *(English Preprint)*
Contributed: November 30, 2014.

Thematic course: Quantum-chemical study of the transformations of triglycerides. Part 1.

Elementary acts of noncatalytic transesterification reaction of triglycerides and their analogs under the conditions of supercritical fluids

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Keywords: triglycerides of fatty acids, ethanol, methanol, methyl acetate, triacetin, associates, transesterification, reaction mechanism, elementary acts, quantum-chemical modeling, supercritical fluids, the method of DFT.

Abstract

Using quantum-chemical DFT method with density functional PBE in the basis 3z (comparable basis set cc-pVTZ) realizing the programs *Priroda 4.11* and B3LYP/6-311++g(df,p) applying the program *Gaussian09* we have studied the reactions of transesterification of triglycerides in methanol in the physical conditions of supercritical fluids, that is at T = 623 K and P = 30 MPa. Detailed consideration of the energy specificity of the following reaction systems was carried out: 1) The simplified gas phase reaction systems with triglyceride (or its analogues) and monomeric form of methanol in which the reaction proceeds by a one-step reaction mechanism involving alkoxycarbonyl bonds or two-step mechanism involving a carbonyl group in a first step of the alkoxy quaternary intermediate in the second step; 2) The reaction systems in which the elementary event involve carbonyl or alkoxy carbonyl group of triglyceride and dimer or trimer form of methanol and its substitution analogs.

It is shown that the simplified gas phase reaction systems involving methanol monomeric form are hypothetical and those with dimeric and trimeric forms of methanol are actually proceeding reaction directions, still not having a pronounced potential trap for target products – methyl esters of fatty acids and their substitution analogs that means equiprobable flow direction of most of the competitive transesterification of triglycerides, i.e., reaction systems described are in equilibrium with each other.

However, the presence of a few percent of water in in dry alcohol leads to the fact that for the associate pair glycerol-water at the interaction with alkoxy carbonyl bond of triglyceride there is observed a rather big potential trap (10.33 kkal/mol) for the forward direction reaction products, namely the hydrolysis products – aliphatic monocarboxylic acids with open chain that transfer the given transformation from a model category to the category of the real direction of the reaction.

It is concluded that in order to explain the experimental fact of the formation of the desired product - methyl ester of fatty acids in the transesterification reaction of triglycerides in the physical conditions of supercritical fluids it is required to conduct a detailed exploration of the potential promoter effect of fatty acids, which are the equilibrium products of a competitive hydrolysis reaction of triglycerides.