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Thematic course: Quantum-chemical study of the transformation of triglycerides. Part 5.

A recessed analysis of the quantum-chemical thermochemistry of the alcoholysis and hydrolysis of fatty acid triglycerides, carried out under supercritical conditions in the presence of and in the absence of authentic carboxylic acids and their analogues

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Abstract

Quantum-chemically, using DFT method with the functional density of PBE with 3z basis (comparable basis set cc-pVTZ) in the implementation of the program *Priroda 4.11* and B3LYP/6-311++g(df,p) in the implementation of the program *Gaussian09* investigated transesterification of triglycerides in the methanol medium in physical conditions of supercritical fluids, i.e., at T = 623 K and P = 30 MPa. We discuss the energy specificity of the following reaction systems: 1) the simplified gas phase reaction systems involving triglyceride (or analogues thereof) and the monomeric form methanol which the reaction proceeds according to a one-step mechanism involving alkoxycarbonyl communication or two-step mechanism involving the carbonyl group in the first stage and quaternary alkoxy a second intermediate stage; 2) The reaction system in which the elementary event involving carbonyl, or alkoxycarbonyl group and triglyceride dimeric or trimeric form methanol and its substitution analogs.

It is shown that the simplified gas phase reaction systems involving monomeric form of methanol are hypothetical, and with dimeric and trimeric forms of methanol are actually flowing reactive lines, however, don't have a pronounced potential traps for the desired products – the methyl esters of fatty acids and their substitution analogs that mean the equiprobable flow directions most competitive transesterification of triglycerides, i.e., reaction systems described are in equilibrium with each other.

However, the presence in the crude alcohol, a few percent of water, leads to the fact that for associated pair glycerol-water interaction with alkoxycarbonyl bond triglyceride, a fairly large potential trap (as 10.33 kcal/mol) for the products of forward direction reaction, in this case the hydrolysis products – aliphatic monocarboxylic acids, open-chain, that carries out this transformation model category in the category of the real direction of the reaction.

It was concluded that in order to explain the experimental fact of the formation of the target product – methyl ester of fatty acids in the transesterification of triglycerides in the physical conditions of supercritical fluids, the potential promoter effect of fatty acids, which are the product of a competitive equilibrium of the reaction of hydrolysis of the triglycerides should be investigated in detail.