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Thematic course: Quantum-chemical study of the transformation of triglycerides. Part 4.

Elementary acts of supercritical water oxidation (SCWO) model analogs fatty acid triglycerides in supercritical fluid media

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Content

Abstract

Quantum-chemical, using DFT method with the functional density of PBE and extension-indigenous sets effective spanning capabilities, elementary acts of SCWO of hydrogen hydroper-oxide were investigated, as well as various triglycerides reactions that occur when exposed to aqueous solutions of hydrogen hydroperoxide in the supercritical fluid environments.

It is shown that hydrogen hydroperoxide can form associates with various governmental hydrogen-bonds – between two molecules of hydrogen hydroperoxide and between molecules hydroperoxide in various combinations of hydrogen and water. For each associate form described singlet radical and non-radical transformation resulting from the exchange between hydrogen relevant molecules in the associate. The equilibrium shape of the hydrogen exchange are singlet radical pairs $OH^{\cdot}$ and $HOO^{\cdot}$, separated by water molecules. For some associate forms singlet molecular oxygen is the product.

It is proved that the hydroxyl radical is able to engage in initial formation of recombination with hydrogen peroxide forms a triplet with loosened O-O bond. This triplet dimer of 2 hydroxyl radicals molecules through the proton exchange reaction is in thermodynamic equilibrium with the-triplet form of atomic oxygen. It is shown that the hydroxyl radical in the aqueous solution has a unique feature that allows almost instantly migrate to the potential reaction partner not on the basis of physical diffusion and to chemical interaction with the proton of water, thus translating itself in micro- and possibly macro-volume.

On the other hand, the fatty acids resulting from the autocatalytic hydrolease acid triglycerides with low activation barriers enter into exchange reactions with the hydrogen hydroperoxide associate form and water. This two-stage transformation comes with closed electron shells of the reactants, ie, incompletely, and its product is the first-initial are peroxide forms fatty acids which, in turn, interact with each other and with fatty acids to form water and carboxylic fatty acid radicals which decompose to CO_2 and alkyl radicals.

Hydroxyl radical with minimal activation barriers able to tear off a proton from C-H bonds of hydrocarbons or alkyl radicals indiscriminately biradical generating centers, which are able to migrate through

the carbon skeleton with the assistance of the promoter of one water molecule or its dimer associate. In the case of 1,4-valence radical localization takes place β-limination of ethylene, which is the main mechanism alkyl defragmentation large molecules in GFR and pyrolysis conditions.

For soft and hard physical conditions characterized by its own set of *soft*- and *hard*-peroxil interactions, past and determine the specificity of the chemical decomposition of triglycerides under the influence of hydrogen peroxide in the supercritical fluid conditions.