

The mechanism of decomposition cyclohexyl phenyl sulfide in the process of aquathermolysis

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Abstract

This paper presents results of a theoretical study of the mechanism of aquathermolysis cyclohexyl phenyl sulfide (**I**), for which there are experimental data on aquathermolysis products such as clean water, and with the use of various additives, which have different effects on the depth conversion of the starting material. The calculations were carried out using semi-empirical method QM_N3 density functional in the 15th version of the Priroda program developed by D.N. Laikov. P-AutoEkstremum shell was used to search for the extreme points of the potential energy surface (the transition states and lows corresponding to the reactants and products). This shell allows calculating an elementary stage of a chemical reaction in a single launch. The conformation of compounds have been identified for rotation relative to the cyclohexyl radical SPh-bond. The results were compared with those obtained previously, R.M. Aminova, Y.V. Lysogorsky and D.A. Tayursky investigated the compound density functional method GGA PBE, B3LYP, wB97XD by using GAUSSIAN 03 and VASP quantum chemistry computer codes. For the two conformers in processes aquathermolysis involving water molecules in a transient state result were obtained similar to the article mentioned above, but for a third conformer the most advantageous proved to be one-step synchronous process in which the reaction products were cyclohexene and thiophenol. It should be noted that the enthalpy of activation of this process is much smaller than any of its alternatives. Even more advantageous proved to be the autocatalytic process involving two molecules of water, which also leads to the formation of cyclohexene. According to Katritzky and et al, cyclohexene and 1-methylcyclopentene were found among aquathermolysis **I** products, that is, our results are in agreement with experiment. In the article Tayurskii and et al, that the most favorable mechanism of aquathermolysis **I** concluded to be the C-S bond cleavage catalyzed ion hydronium. This is a wrong conclusion, since the authors of the said article did not take into account the energy costs for the formation of hydronium ion.