

Molecular structure and IR spectra of butyl nitrates

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Abstract

The article is devoted to the description of using of two density functional methods B3LYP/6-31+G(2df, p) and wB97X/Def2TZVPP, the geometric parameters and vibration frequencies of the CONO₂ group, as well as the enthalpy of formation and dissociation energy of the O-NO₂ bond in the molecules of isomeric butyl nitrates (butyl nitrate, 2-butyl nitrate, isobutyl nitrate, *tert*-butyl nitrate) are determined. The authors show that the observed changes in the geometric parameters of the CONO₂ group in the series of compounds studied are insignificant. According to the B3LYP method, they are 4.1 pm for the C–O bond, 0.7 pm for the O–NO₂ bond, and about 1 degree for the ONO angle. Another method used in this work (wB97X) predicts similar values of changes in the series. At the same time, the results of calculation make it possible to reliably distinguish, by the value of the geometric parameters, the nitrate groups attached to the primary secondary and tertiary carbon atoms, respectively. It is noted that the highest values of enthalpies of formation and energies (enthalpies) of dissociation are observed for compounds in which nitrate groups are attached to the primary carbon atom. The correlation dependences in the change in the enthalpies of formation of compounds and radicals, which are formed upon homolytic cleavage of the O-NO₂ bond, have been revealed. The tendencies of change in the series convey both methods used in the work in the same way. However, a comparison of the results with the available experimental data on the kinetics of thermal decomposition of the studied aliphatic nitrates shows that the most reliable estimates are the wB97X/Def2TZVPP method. The calculated values obtained on the basis of another B3LYP method used in the work are underestimated, by about 3-4 kcal/mol. It was found that of the stretching vibrations of the CONO₂ group, only asymmetric vibrations of N-O are characteristic.

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