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DFT study of triplet and singlet elementary acts of acyclic and cyclic alkanes oxidation initiated by primary interaction with $^3O_2$

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Abstract

The primary oxidation stages of $^3O_2$ model acyclic and cyclic alkanes and their subsequent triplet and singlet elementary events were studied for the first time by the DFT method with the density functional B3LYP and basis set 6-311++g(df,p).

According to quantum chemical DFT calculations the C–H radical cleavage of the bonds of acyclic and cyclic alkanes upon interaction with $^3O_2$ is almost completely thermodynamically shifted toward the initial state of the reaction system. This energy of primary oxidizing events explains the extremely low reactivity of saturated alkanes in comparison with asphaltene structural fragments under the conditions of SCF technology for the extraction of heavy oils and asphaltenes by a propane-butane mixture.

It has been demonstrated that for all elementary acts of primary alkane oxidation the product of the direct reaction direction is not a free pair of radicals but a triplet hydrogen complex with a pronounced hydrogen bond between the hydroperoxyl radical and the radical form of the corresponding hydrocarbon.

A new, previously not taken into account very exothermic ($\Delta\Delta H$ = -29.25 – -30.77 kcal/mol) reaction direction is described which corresponds to triplet recombination of alkyl radicals and a hydroperoxyl radical in its oxygen-concentrated part. The products of this recombination are triplet forms of alkane hydroperoxides in which there is a fairly loosened triplet O---O bond with a length of 2.20-2.23 Å, which is ~0.72-0.77 Å more than bond length in the singlet state.

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