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Application of Quantum Chemical Calculations on biobutanols as an Alternative Energy Resource

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Recent concern about environmental impact of fossil fuel, depletion of its reserves, and increase demand and cost have driven serious search for alternative fuel. Biofuel has been suggested as a good surrogate and can be used by its own or as a blend with fossil fuel. The second generation biofules are those produced from biomass comprised of the non-food crops as well as residues of non-food parts of current crops. Bioalcohols represent an important class of biofuel. However, biomethanol is toxic and corrosive, while bioethanol is hygroscopic and has low energy content but still in use. On the other hand, higher alcohols offer some advantages as gasoline substitutes because of their low toxicity, higher energy density, and lower hygroscopicity. Consequently, butanols have been recently suggested as alternatives. Accurate thermodynamic and kinetic parameters are needed for detailed mechanism of combustion of biobutanols.

In this study, quantum chemical calculations of thermochemistry and kinetics of unimolecular dissociation of 2-butanol have been conducted using ab initio (CBS-QB3) and density functional theory (DFT). Hybrid and hybrid meta functionals have been used in this work. Several pathways have been examined including simple and complex decompositions. The results indicate that the dehydration reactions to form 1- and 2-butene through four-center transition states are the most favorable channels. Among all the investigated dissociations, the formation of butenes, methyl ethyl ketone, and methyl ethyl carbene are kinetically and thermodynamically the most favorable decomposition reactions. The production of stained methyl cyclopropane is less preferable kinetically compared to CC and C_α-H bond breaking.

Reactions leading to ethanol and vinyl alcohol demand more energy than needed for simple bond fissions and only occur at elevated temperatures. The accuracy of long-range corrected DFT and functionals developed for kinetic studies compete with expensive ab initio CBS-QB3 method. The enthalpies of formation and bond dissociation energies of 2-buatnol and its radicals have been calculated with high accuracy. Analysis of the intrinsic reaction coordinate (IRC) allows us to follow structural changes with the progress of reactions.
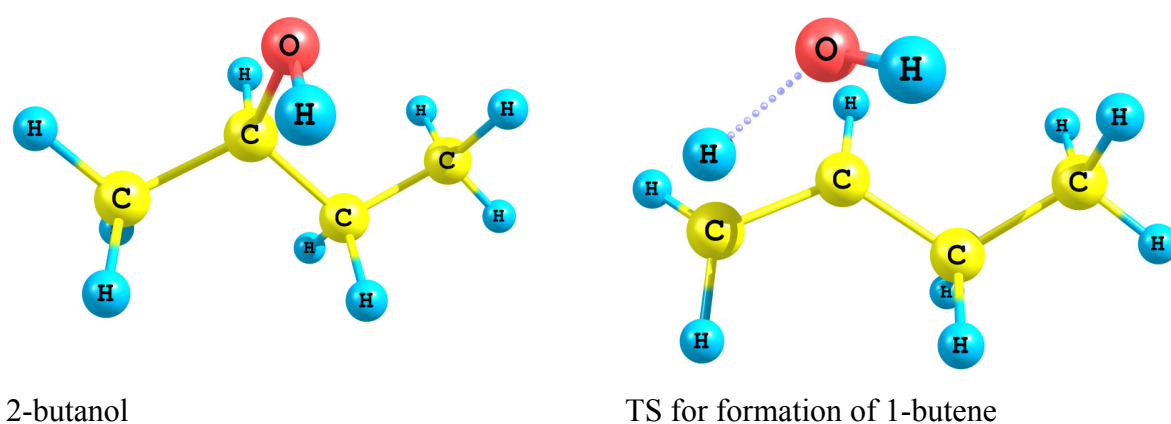

2-butanol   TS for formation of 1-butene

Figure 1. Optimized structures of 2-butanol and TS for formation of 1-butene at CBS-QB3.

Table 1. Calculated barrier heights (kcal/mol) for unimolecular decomposition of 2-butanol at CBS-QB3.

1-butene	Trans-2-butene	Me-cyclopr.	carbene	ketone	cis-2-butene	vinyloh	ethanol
65.97	67.16	94.89	77.98	81.40	67.90	109.55	111.91

Table 2. Calculated barrier heights (kcal/mol) for formation of 1-butene from 2-butanol at DFT/6-311++G(2d,2p).

B3LYP	BMK	BB1K	LC-ωPBE	MPW1B95	MPWB1K	MPW1K	BH&HLYP
59.25	66.11	65.93	67.03	62.49	66.47	67.47	68.30