

Homogeneous Catalysis of the Gas-Phase Dehydration Kinetics of Several Tertiary Alcohols by Hydrogen Bromide: Density Functional Theory Calculation.

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The mechanism of the gas-phase thermal decomposition of tert-butanol, 2-methyl-2-butanol, 2-methyl-2-pentanol and 2,3-dimethyl-2-butanol under homogeneous catalysis conditions of hydrogen bromide was examined by Density Functional Theory (DFT) calculations with the hybrid functionals: M062X, CAMB3LYP and WB97XD. Reasonable agreements were found between theoretical and experimental enthalpy values at the CAMB3LYP/6-311++G(d,p) level. The dehydration mechanism of tert-butanol with and without the presence of the catalyst HBr gas was evaluated in order to examine the catalytic effect on the mechanism. The elimination reaction without catalysis involves a four-membered cyclic transition state, while the catalyzed reaction involves a six-membered cyclic transition state. The absence of the catalyst gives an activation enthalpy approximately 160 kJ/mol greater than the catalyzed reaction. These reactions are dominated by the leaving of O-H group in the water formation, and these processes were found to be non-synchronous ($S_y \approx 0.8$). No significant effect was originated when the alkyl chain is increased. In the Intrinsic Reaction Coordinate of these reactions illustrates the connection of the transition state with the Van-der Waals reactant and product complexes as well as the energy involved in the formation of these complexes