

***Ab Initio* Calculations of Chemical Equilibria and Comparison with Experimental Data in the Vapor and the Liquid Phase Using the TAME-Synthesis Reaction as an Example**

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Quantum-mechanical *ab initio* calculations of the reactants of the tert-amyl-methyl-ether synthesis are presented. The chemical structure, electronic zero point energies, normal frequencies, and thermodynamic gas phase properties such as heat of formation and entropies of formation for TAME, methanol, and methylbutenes have been calculated using G2(MP2), G3(MP2), G3 and density functional methods. Predicted values of the equilibrium constant K_p , standard reaction enthalpies, and entropies as function of temperature are presented and compared with experimental data in the gaseous phase. The experimental data have been obtained using a gaseous phase flow reactor equipped with an ion-exchange resin in the H⁺-form as catalyst.

It is shown that remarkably good agreement of *ab initio* calculated values and experimental results have been obtained concerning the enthalpy of reaction. For K_p -values and reaction entropies, the agreement between predicted and experimental values is less satisfying. However, it can be shown that disagreement of calculated and experimental values of the reaction entropy is mainly caused by neglecting anharmonicity effects in torsional vibrations of the molecules, which have the character of a hindered internal rotation rather than a vibration. Accounting for this effect by an approximative method improves the agreement of theory and experiments for K_p and the entropy of reaction.

The important conclusion to be drawn from this study is that *ab initio* calculation of reactive equilibria in the real gas phase can be predicted today with an accuracy approaching to the quality of the experimental results even for chemical equilibria involving complex molecules such as TAME and methanol.