

Summary of the PhD thesis entitled
„Mechanism of the selected hydrogenation reactions catalyzed by superacids”

Olimpia Ciepla

Superacids are compounds exhibiting larger acidity than that of concentrated sulfuric acid, which means that in the liquid phase their Hammett acidity function (H_0) is lower than -12. On the other hand, superacids are commonly characterized as systems having their Gibbs free deprotonation energy (ΔG_{acid}^{298}) smaller than ca. 303 kcal/mol (i.e., the value corresponding to H_2SO_4). Many scientific reports concerning the use of superacids as catalysts in various chemical reactions have been published to date. Moreover, it was recognized that such compounds allow to generate highly acidic environment, in which even the carbocations are rendered stable.

The main goal of my research was to characterize mechanisms of selected hydrogenation reactions in which binary Lewis-Brønsted superacids act as catalysts and to determine the performance of catalysts exhibiting various acid strength. The additional goal was to explore the possibility of designing binary Lewis-Brønsted superacids by combining a strong Lewis acid molecule and a molecule exhibiting weak acidity but formally capable of acting as Brønsted acid (due to the presence of at least one hydrogen atom in its structure). All the calculations have been performed using quantum chemistry *ab initio* computational methods. The basicities and acidities of examined systems were evaluated by calculating the Gibbs free energy of deprotonation reaction (ΔG_{acid}^{298}) and gas-phase basicity (ΔG_{base}^{298}), whereas the thermodynamic stability of the systems studied (described by the X/AlF₃ formula, where X=HF, HCl, H₂S, AsH₃, PH₃, NF₂H, NFH₂, NH₃ and H₂O) were verified by calculating the Gibbs free fragmentation energy (ΔG_{frag}^{298}) for the most probable fragmentation paths.

During my research I have determined the mechanisms of two various hydrogenation reactions: (i) carbon monoxide hydrogenation yielding formaldehyde in which sulfuric acid and two superacids (HAlF₄ and HSbF₆) were used as the catalysts and (ii) acetaldehyde hydrogenation yielding ethanol catalyzed by HSbF₆ superacid. Mechanisms of these processes turned out to be different than the mechanisms of typical hydrogenation reactions catalyzed by transition metals. Namely, during the initial state of the reaction, there is no activation of hydrogen molecule (as it is the case in heterogeneous catalysis) but the carbon monoxide or acetaldehyde molecule are activated instead. Next, the heterolytic cleavage of the H-H bond takes place and

the resulting H^- and H^+ ions are attached to cation generated during initial protonation (CH_3CHOH^+ or HCO^+) and to deprotonated acid, respectively. Such a mechanism might be termed the ionic reversed-activation.

Moreover, I estimated the acidity of binary complexes composed of AlF_3 molecule (typical Lewis acid) and molecule containing at least one hydrogen atom and lone electron pair in its structure. In particular, I verified how the choice of Brønsted acid (X) affects the acidity of the complex characterized by the $\text{X} \rightarrow \text{AlF}_3$ formula.

On the basis of my investigations it can be stated that utilizing sulfuric acid and selected superacids (HAlF_4 and HSbF_6) as catalysts in carbon monoxide hydrogenation reaction yielding formaldehyde allows for effective reduction of the activation barriers in comparison to the uncatalyzed reaction. Furthermore, the use of HSbF_6 superacid as a catalyst in the formation of ethanol by acetaldehyde hydrogenation also leads to significant reduction of the activation barrier. Finally, it was found that the complexes characterized by X/AlF_3 formula exhibit strongly acidic properties, regardless the acid strength of the component X.