

## Summary of the PhD thesis entitled

*„Mechanisms of selected organic reactions catalyzed by Lewis-Brønsted superacids and the structure-acidity relationship of these systems”*

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Superacids are defined as acids stronger than sulfuric acid. Due to their extreme properties, they are widely used both in industry and science. The most important applications of these compounds include their use as catalysts in organic chemistry.

The main goal of my work was to perform theoretical evaluation of the possibility of application of selected Lewis-Brønsted superacids as catalysts for electrophilic addition of water and hydrogen sulfide to alkenes. Bearing in mind the experimental studies on the dependence of the rate of water addition to alkenes on the value of the Hammett function of the catalyst used available in the literature, I decided to investigate the possibility of using common Lewis-Brønsted superacids ( $\text{HSbF}_6$ ,  $\text{HAsF}_6$  and  $\text{HBF}_4$ ) to catalyze the hydration and hydrosulfurization of a representative alkene (isobutene). Since the use of superacids in catalysis is mostly related to their strong acidic properties, I investigated the series of compounds to recognize the factors affecting the strength of Lewis-Brønsted superacids.

In the first part of my research, I determined the mechanism of addition of water to isobutene, catalyzed by fluoroantimonic superacid, and compared it to the reaction mechanism of the same process catalyzed by sulfuric acid which is commonly used for this purpose. In addition, for the sake of comparison, I investigated the mechanism of the discussed reaction without the use of any catalyst. As shown by the obtained results, the latter reaction, due to the considerable height of the activation barrier, cannot proceed under standard conditions in the absence of a catalyst. The catalysis efficiency turned out to be strongly dependent on the strength of the acid used (the use of  $\text{HSbF}_6$  led to a more effective reduction of the activation barrier than  $\text{H}_2\text{SO}_4$ ).

In the second part of my work I investigated the possibility of catalyzing hydrogen sulfide addition (hydrosulfurization) to isobutene by the following superacids:  $\text{HBF}_4$ ,  $\text{HAsF}_6$  and  $\text{HSbF}_6$ . Analogously to the above-mentioned hydration, the hydrogen sulfide

addition process cannot proceed without the presence of a catalyst. As I have shown, the use of each of the mentioned catalysts leads to a significant reduction of the activation barrier. I also showed that the use of  $\text{HBF}_4$  as a catalyst leads to a reduction of the overall yield of the reaction due to the formation of an undesirable by-product. The use of  $\text{HAsF}_6$  and  $\text{HSbF}_6$  superacids as catalysts proved to be effective in reducing the activation barrier to the level of ca. 2kcal/mol.

In the third part of the research, I analyzed the effect of the stoichiometry of the molar ratio of Lewis and Brønsted acid, and more specifically the effect of the excess of the former on the strength of the resulting Lewis-Brønsted acid. I conducted the calculations on two types of systems, namely  $\text{HClO}_4/n(\text{AlF}_3)$  and  $\text{HClO}_4/n(\text{SbF}_5)$ . My calculations revealed that the solvation of the Brønsted acid molecule by Lewis acid molecules leads to an increase in the strength of the resulting acid. Saturation of the acidity of  $\text{HClO}_4/n(\text{AlF}_3)$  occurs for the  $n$  value of 2-3, while in the case of  $\text{HClO}_4/n(\text{SbF}_5)$  the value of  $n$  is larger than 3.

In the next part of my research, I determined the influence of the ability of electron-withdrawing substituents ( $X$ ) on the strength of Lewis-Brønsted acids  $\text{HF}/\text{AlX}_3$ . This research subject was motivated by the fact that withdrawal of the electron density from Brønsted acid to Lewis acid in the Lewis-Brønsted superacid unit is one of the most important factors determining the power of the latter. As I showed, the strength of Lewis-Brønsted acids strongly depends on the electron-accepting abilities (expressed in the values of electron affinity) of the substituent  $X$ .

In the final part of my research, I analyzed the strength of carborane acids composed of a carborane core and various substituents. I have demonstrated that a proton attached to the electronegative substituent can almost freely migrate between the ortho-belt substituents and the substituent attached to the antipodal boron atom of the carborane core. Moreover, by examining the effect of carborane acid dimerization on acid strength, I showed that it increases the strength of the resulting system.

The results of my research extend the range of organic reactions that can potentially be catalyzed by superacids to include hydration and hydrosulfurization reactions of alkenes. In addition, the obtained results shed some light on the problem of the dependence of acid strength (in particular Lewis-Brønsted acids) on their structure.