*Mechanism of the Activation of Hydrogen Peroxide by Arsonic Acids and Fluorinated Alcohols: Theory and Experiment*

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Abstract:

In this thesis, the mechanisms of epoxidation reactions with hydrogen peroxide were elucidated by experimental and theoretical means. The catalytic activity of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in the olefin epoxidation could be attributed to the strong H-bond donor ability of this fluorinated alcohol solvent. A pronounced dependence of this property on conformation and self-aggregation was found to be decisive for the H-bond donor ability of HFIP in the liquid phase. A quantum chemical analysis of reaction pathways rendered a reaction model displaying a high degree of correlation with the experimental findings. On the basis of this model, the oxygen transfer was unambiguously identified as a concerted dipolar process.

For the catalytic activity of arsonic acids in the olefin epoxidation with $H_2O_2$, perarsonic acids and arsadioxiranes were identified as oxygen transferring species. Their formation proceeds via a nucleophilic addition-/elimination mechanism. The synergism of arsonic acids and HFIP as solvent could be attributed to the preferred formation of the corresponding perarsonic acid and its activation for subsequent oxygen transfer to the olefin.