Platinum Catalyzed C-H Activation in Strong Acid.

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All of the most successful homogeneous catalysts for methane activation operate in highly acidic media. The most promising system to date is the Catalytica system developed by Periana and co-workers which uses a platinum(II) bipyrimidine catalyst in concentrated sulfuric acid. The sulfuric acid acts both as the solvent and the oxidizing agent. Despite high yields of up to 71% and selectivities around 80% the reaction does not quite qualify for industrial applications. The reason was that the catalyst was functioning only at very high acid concentrations, and since water is released during the course of the reaction the acidity inevitably is decreased as the product is formed.

The substitution of the possible leaving groups chloride, bisulfate and water by methane is thought to be the rate limiting step. Such substitution reactions at electrophilic centers are frequently accelerated by acid. The effect of protonation and neutralization of the leaving group on the methane uptake step will be presented. The initial protonation of the leaving groups was found to be endothermic in all cases. However, the substitution barriers were significantly reduced by up to 10 kcal/mol. Improved agreement with the experimentally determined barriers were also achieved compared to earlier computational studies.