SYNTHESIS OF ACETIC ANHYDRIDE FROM METHYL BISULFATE WITHOUT IODIDE PROMOTER

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The functionalization of methane is of significant practical interest, but methane is relatively unreactive. The first important homogeneous catalytic system for selective methane functionalization is Shilov system with aqueous solutions of Pt(II) salts to produce alcohol and alkyl chloride.[1] However, use of Pt(IV) as a stoichiometric oxidant in this system has been a problem. So Periana has developed an alternative system with $(bpym)_2PtCl_2$ (bpym=2,2'-bipyridine) in concentrated or fuming sulfuric acid (oleum) to oxidize methane to methyl bisulfate (MBS) using sulfur in the +6 oxidation state (SO_4^{2-} or SO_3) as the oxidant.[2] The limitation of this catalyst is the volumetric production of functionalized product < 1 M. Recently Schüth has shown that simple platinum salts are stable, selective, and unprecedently active, and under most conditions superior to Periana system.[3]

Hence we became interested in whether methyl bisulfate synthesized via selective oxidation of methane in oleum can be used in the production of acetic anhydride. By doing so methyl bisulfate can be transformed to a more valuable product than methanol which is formed via hydrolysis.

We have performed the hybrid density functional theory (DFT) calculations to gain molecular-level insight into the intricate features of catalytic behaviour of a simple soluble $[Rh(CO)_2(OSO_3H)_2]^-$ species towards acetic anhydride synthesis. We have determined the full potential energy profiles for plausible catalytic pathways along the major phases of the catalytic cycle. From the calculated results important insight is gained into the mechanism of the reaction.

References
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