Atmospheric Acids as Catalyst for Gas Phase Reactions: CH_3O isomerization and SO_3 hydrolysis

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The catalytic ability atmospheric acids such as formic and sulfuric acid to facilitate the isomerization of the CH_3O radical to CH_2OH have been studied. It is shown that the activation energy for isomerization are respectively 30.2, 4.2 and 2.3 kcal mol^{-1} when carried out in isolation versus with formic acid and sulfuric acid as catalysts. The formation of a double hydrogen bonded transition state is central to lowering the activation energy and facilitating the intramolecular hydrogen atom transfer that is required for isomerization. The results demonstrate the feasibility of acids catalyzing a thermal gas phase reaction that would otherwise be forbidden.[1] In a second computational study we explore the changes in reaction barrier height for the gas phase hydrolysis of SO_3 to form H_2SO_4 in the presence of a single formic acid (FA) molecule. For comparison, we have also performed calculations for the reference reaction involving water assisted hydrolysis of SO_3 at the same level. Simple kinetic analysis of the relative rates suggests that the reduction in barrier height facilitated by FA, the greater stability of the pre-reactive $SO_3\cdots H_2O\cdots FA$ collision complex compared to $SO_3\cdots H_2O\cdots H_2O$ and the rather plentiful atmospheric abundance of FA, combine to make the formic acid mediated hydrolysis of SO_3 a potentially important pathway for gas phase atmospheric sulfuric acid production.[2]

References:

1. Buszek, R. J.; Sinha, A.; Francisco, J.S; J. Am. Chem. Soc.; **133 ,** 2013-2015 (2011).

2. Hazra, M.K.; Sinha, A.; J. Am. Chem. Soc.; **133 ,** 17444-17453 (2011).