Abstract Submitted
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Computational studies of the acid catalysts and solvent effects on Diels-Alder cycloaddition and dehydration reactions: Maleic anhydride and 2,5 dimethylfuran TAHA SALAVATI-FARD, STAVROS CARATZOULAS, DOUGLAS DOREN, University of Delaware — Using DFT calculations, we present a detailed gas-phase mechanism for the conversion of DMF and maleic anhydride to 3,6 dimethyl phthalic anhydride. The conversion includes Diels-Alder cycloaddition followed by dehydration of cycloadduct. In addition, we consider the effects of solvent by making use of the PCM. We provide free energies of uncatalyzed, Lewis acid and Brönsted acid catalyzed reactions in vacuum and in a broad range of solvents. Our calculations show that a Lewis acid catalyzes the reaction through decreasing HOMO-LUMO gap of the addends. Also, a Brönsted acid changes the mechanism of reaction and is able to lower the activation free energy of cycloaddition, effectively. Furthermore, we show that as Lewis acids lower the activation barrier of dehydration reaction which is originally too high, a Brönsted acid changes the mechanism and is extremely effective in catalyzing the dehydration. Also, increasing dielectric constant of solvent decreases the activation barrier of uncatalyzed and Lewis acid catalyzed Diels-Alder reaction. For both the Lewis and Brönsted acid catalyzed Diels-Alder reaction, the dependency of activation free energy to increasing dielectric constant is much stronger when the acid is coordinated to DMF.

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