On the mechanism of the ring-opening of biomass derived 2-pyrones to produce high value chemicals

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Materials and Methods

All geometry optimization calculations were done using density functional theory (DFT) code implemented in DMol3 of Material Studio (Accelrys Inc., USA). The generalized gradient approximation (GGA) functional by Perdew and Wang (PW91) was used for all geometry optimization studies. Transition state search was done by using integrated linear synchronous transit and/or quadratic synchronous transit (LST/QST). For finding the transition state intrinsic reaction path studies were done in which reactant, transition state and product are connected via a path. One imaginary frequency was exhibited by all the transition state geometries in the reaction coordinate. Catalytic reactions in batch mode were carried out in a high-pressure 10 ml (Agilent, USA) glass vial reactor at a temperature range of 100 to 150 °C using a variety of acid catalyst such as Amberlyst-35, H-ZSM5 and/or SiO₂/Al₂O₃. Reactant, product and intermediates were characterized using GC, GC-MS and ¹H NMR.

Results and Discussion:

In all the 2-pyrones selected for this study, the most favorable mechanism was found to be a proton attack on the carbonyl oxygen and OH addition at C₅, which is followed by the dissociation of C₅-O bond leading to ring opening. The intrinsic activation barriers for the ring-opening step were estimated to be in the range 24 to 27 kJ/mol. The substituents were observed to have no significant effect on the ring opening of these molecules. The reactant, transition state and product geometry of the ring-opening step is shown in Figure 1.

Significance:

DFT study suggests routes for possible ring-opening and decarboxylation of these 2-pyrones for conversion into valuable chemicals like hepta-2,5-diene-4-one, non-7-ene-2,6-dione, hexane-2,4-dione etc. that were derived from petroleum and fossil fuels. These chemicals are used as precursors, additives in gasoline and diesel, flavoring agent etc.