

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

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### Introduction

Biomass and biomass-derived sugar molecules have received considerable attention to replace fossil resources for the production of chemicals and fuels [1,2]. Strategies for the conversion of biomass solely based upon chemical or biological methods have been studied extensively in the past [1,3] with their limits in achieving high conversion to a desired product. In contrast, more recently a new strategy has been proposed to integrate fermentation and chemical catalysis to achieve high conversion and product selectivity [4,5]. Dumesic and co-workers have suggested 2-pyrones as a potential platform molecules and have shown that triacetic acid lactone (TAL) can undergo ring-opening and decarboxylation to 2,4-pentanedione at relatively mild conditions ( $T < 100$  °C), even without requirement of an acid catalyst [2,6]. It was proposed that key structural features of the 2-pyrone such as the position of the double bond and the substituents at C<sub>3</sub> and C<sub>5</sub> in the ring can significantly effect the reactivity of the 2-pyrene molecules.

Motivated from aforesaid studies, we have undertaken a detailed density functional theory (DFT) based mechanistic study to unravel the mechanism of the ring-opening of 2-pyrones. In order to study the effect of substituents at C<sub>3</sub> and C<sub>5</sub>, four different 2-pyrene molecules were thoughtfully selected. These selected 2-pyrene molecules, can be derived from polyketide biosynthetic routes via direct fermentation of biomass or the fermentation of biomass derived aqueous sugars by an appropriate microorganism. They differ from each other in terms of the substituent at C<sub>3</sub> and C<sub>5</sub> and are listed as; 6-propenyl-pyran-2-one (PPO), 6-(4-oxopentyl)-pyran-2-one (OPO), 4-hydroxy-3,6-dimethyl-2H-pyran-2-one (HMP) and 4-hydroxy-6-(2-oxopropyl)-pyran-2-one (HPP). DFT was utilized to suggest routes for possible ring-opening and decarboxylation for conversion into valuable chemicals like hepta-2,5-diene-4-one, non-7-ene-2,6-dione, hexane-2,4-dione etc. In order to experimentally demonstrate the integration of fermentation and catalytic processing, an attempt has been made to synthesize a 2-pyrene molecule by fermentation and to purify it by centrifugation and/or solvent extraction method. The molecule thus obtained was subjected to catalytic processing via ring-opening, decarboxylation and/or dehydration reaction to produce a high value chemical.

### Materials and Methods

All geometry optimization calculations were done using density functional theory (DFT) code implemented in DMol<sup>3</sup> 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 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Reactant, product and intermediates were characterized using GC, GC-MS and <sup>1</sup>H NMR.

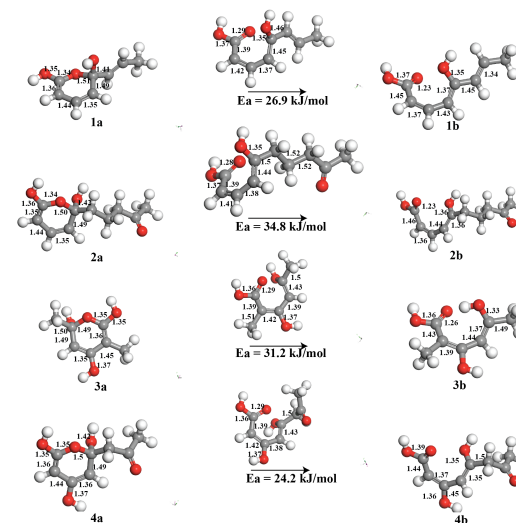


Figure 1: Ring opening step for the 2-pyrene molecules.

### 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 C<sub>5</sub>, which is followed by the dissociation of C<sub>5</sub>-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 suggest 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.

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