

# A theoretical study on etherification of 4,5-dihydroxy-1,3-bis (hydroxymethyl) imidazolidin-2-one with the primary alcohols and the hydroxyl groups of cellulose chain (n=1-2) in acidic condition

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October 15, 2020

## Abstract

Etherification mechanism of 4,5-dihydroxy-1,3-bis (hydroxymethyl) imidazolidin-2-one (DMDHEU) with the primary alcohols and the -OH hydroxyl groups of cellulose chain (n=1-2) in acidic condition were investigated by using density functional theory (DFT) method and a two-layer ONIOM approach. Geometry and energy of reactants, products, intermediate complexes, carbocation intermediate, and transition states were optimized at B3LYP/6-311g(d,p) level and ONIOM (B3LYP/6-311g(d,p):PM3MM) level. Computational results indicate that the etherification adheres to unimolecular nucleophilic substitution ( $S_N1$ ) mechanism; the reactant and product can form the activated complexes with  $H^+$  ions in which  $H^+$  ions are occupied by the O-atom of C=O group in the reactant complex and the product complex. Potential energy surface (PES) of the reaction has the triple-well shape. Effect of substituent R in primary alcohol R-CH<sub>2</sub>OH (R = H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>OCH<sub>3</sub>, CH<sub>2</sub>F) and cellulose chain on the reactivity is significant. The energy barrier of  $H^+$  ions releasing step is much higher than those of the activation steps. The calculational data is in the good agreement with the experimental data in the literature.