

# On the Electronic Structure Origin of Mechanochemically Induced Selectivity in Acid Catalyzed Chitin Hydrolysis

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Recently, mechanical ball milling was applied to chitin depolymerization. The mechanical activation afforded higher selectivity toward glycosidic bond cleavage over amide bond breakage. Hence, the bioactive N-acetylglucosamine (GlcNAc) monomer was preferentially produced over glucosamine. In this regard, the force-dependent mechanochemical activation–deactivation process in the relaxed and pulled GlcNAc dimer undergoing deacetylation and depolymerization reactions was studied.[1-3] For the relaxed case, the activation energies of the rate-determining steps (RDS) proved that the two reactions could occur simultaneously. Mechanical forces associated with ball milling were approximated with linear pulling and were introduced explicitly in the RDS of both reactions through force-modified potential energy surface (FMPES) formalism. In general, as the applied pulling force increases, the activation energy of the RDS of deacetylation shows no meaningful change, while that of depolymerization decreases. This result is consistent with the selectivity exhibited in the experiment. Energy and structural analyses for the depolymerization showed that the activation can be attributed to a significant change in the glycosidic dihedral at the reactant state. A lone pair of the neighboring pyranose ring O adopts a syn-periplanar conformation relative to the glycosidic bond. This promotes electron donation to the  $\sigma^*$ -orbital of the glycosidic bond, leading to activation. Consequently, the Brønsted–Lowry basicity of the glycosidic oxygen also increases, which can facilitate acid catalysis.

## References

- [1] D. P. De Chavez, H. Kobayashi, A. Fukuoka, J. Hasegawa, *J. Phys. Chem. A*, **125**, 187-197 (2021).
- [2] D. P. De Chavez, J. Hasegawa, *SoftwareX*, 16, 100879 (8 pages). (2021).
- [3] D. P. De Chavez, M. Gao, H. Kobayashi, A. Fukuoka, J. Hasegawa, *Mol. Catal.*, **475**, 110459 (2019).