

The Malaprade reaction mechanism for ethylene glycol oxidation by periodic acid based on density functional theory (DFT)

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Artykuł

A general mechanism of the Malaprade oxidative carbon–carbon bond cleavage reaction of α -glycol in the presence of periodic acid has been proposed on the basis of density functional theory (DFT) computations. Ethylene glycol and periodic acid, both in their neutral forms, have been studied as noble substrate representatives in model reactions. The proposed reaction mechanism has been constructed based on and compared with previously published experimental kinetic, spectroscopic and temperature and pH-dependent studies. In the presented theoretical mechanistic considerations, four alternative molecular transformations have been analyzed from thermodynamic and kinetic points of view. Theoretically, the predicted activation energy barriers have been compared with experimental ones published elsewhere. The presented minimum energy pathway (MEP) unveiled the shape and conformation of the intermediate and transition state structures. The three-step reaction process involves the formation of a seven-membered quasi-ring assisted by an intramolecular hydrogen-bond intermediate structure forming one I–O bond (IC1_B), a cyclic ester intermediate forming two I–O bonds (IC2_C) and the final products formed at the two very last stages (HIO₃, water and two formaldehyde molecules). The computed and energetically the most favourable reaction landscape proposed in this work uniforms and refines the mechanistic proposition given by Criegee for Malaprade type of reactions and further gives a detailed molecular understanding of the reaction rate and atomic connections *en route* the transformation. The molecular geometries of all stationary points (intermediate and transition state structures) lying on the potential energy hypersurface have been optimized at the four alternative DFT levels under the solvation model based on the density approximation: B3PW91, CAM-B3LYP, BMK, ω B97XD. The 6-311+G(2d,p) basis set for C, O, and H atoms and both the full (DGDZVP) and Ahlrichs-Weigend¹ (def2-TZVP) basis sets for iodine atoms were used during the computations.

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