Computational study of the glycolitic degradation of poly(ethylene terephthalate) catalized by N^1,N^2-bis(2-aminobenzyl)-1,2-diaminoethane zinc(II)

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Abstract

A possible reaction mechanism of the glycolytic degradation of poly-ethylenetherephtalate catalyzed with N^1,N^2-bis(2-aminobenzyl)-1,2-diaminoethane zinc(II) (ABEN) was determined using KS-DFT using the meta-NGA hybrid functional, MN15-L up to def2-SVP level of theory making use of an energy-weighted climbing image nudged elastic band (EW-CI-NEB) algorithm to determine the minimum energy path (MEP) and then optimizing the converged climbing image (CI) using eigenvector-following partitioned rational function optimization (EF P-RFO) to obtain the transition state (TS)

Methods

The starting configurations for EG and ABEN where proposed and optimized using XTB[1] with the force field GFN2-xTB.[2] The staring configuration for DBHET was proposed using crystallographic data.[3]

The software ORCA (5.0.1)[4] was used to perform the geometrical optimization of the species involved in the depolymerization; PET dimer (DBHET), ABEN and EG in KS-DFT using a meta-NGA functional, MN15-L[5] with the def2-TZVP BS and employing the option to use automatic auxiliary basis set generation.[6]

The optimized structures where then merged onto the same Cartesian coordinates and then re-optimized in MN15-L/def2-SVP Then, a multidimensional relaxed surface scan was performed keeping constrained, and varying the bond distances in 5 steps to obtain the products of this reaction. The optimized product and the starting geometry of the relaxed surface scan where the input for an Energy-Weighted Nudged Elastic Band (EW-NEB)[7] algorithm to find the path of minimum energy connecting both ends, followed by a P-RFO optimization to find a TS was performed onto the image with the highest energy alongside the MEP.

In order to determine interactions regions between the molecules, an IRI algorithm within multiwfn was utilized[8] with the wavefunctions generated in the previous step.

Using JANPA,[9] CLPOs and the bond orders for the reactants, products and transition states where obtained from the wavefunction generated by ORCA.

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