Anomerization reaction of bare and microhydrated D-erythrose via explicitly correlated coupled cluster approach. Two water molecules are optimal.

Autorzy

Marek Szczepaniak

Jerzy Moc

Rok wydania

2017

Czasopismo

Journal of Computational Chemistry

Numer woluminu

38

Strony

288-303

DOI

10.1002/jcc.24680

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

We present a comprehensive benchmark computational study which has explored a complete path of the anomerization reaction of bare d-erythrose involving a pair of the low-energy α- and β-furanose anomers, the former of which was observed spectroscopically (Cabezas et al., Chem. Commun. 2013, 49, 10826). We find that the ring opening of the α-anomer yields the most stable open-chain tautomer which step is followed by the rotational interconversion of the open-chain rotamers and final ring closing to form the β-anomer. Our results indicate the flatness of the reaction's potential energy surface (PES) corresponding to the rotational interconversion path and its sensitivity to the computational level. By using the explicitly correlated coupled cluster CCSD(T)-F12/cc-pVTZ-F12 energies, we determine the free energy barrier for the α-furanose ring-opening (rate-determining) step as 170.3 kJ/mol. The question of the number of water molecules (n) needed for optimal stabilization of the erythrose anomerization reaction rate-determining transition state is addressed by a systematic exploration of the PES of the ring opening in the α-anomer-(H2 O)n and various β-anomer-(H2 O)n (n = 1-3) clusters using density functional and CCSD(T)-F12 computations. These computations suggest the lowest free energy barrier of the ring opening for doubly hydrated α-anomer, achieved by a mechanism that involves water-mediated multiple proton transfer coupled with the furanose C□O bond breakage. Among the methods used, the G4 performed best against the CCSD(T)-F12 reference at estimating the ring-opening barrier heights for both the hydrated and bare erythrose conformers. Our results for the hydrated species are most relevant to an experimental study of the anomerization reaction of d-erythrose to be carried out in microsolvation environment.

Słowa kluczowe

CCSD(T)-F12 potential energy surface, carbohydrate microhydration, carbohydrate mutarotation, hydrogen bonding

Adres publiczny

http://dx.doi.org/10.1002/jcc.24680

Strona internetowa wydawcy

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