QM study of energy barriers of breaking networks: hydrolysis of borate glasses

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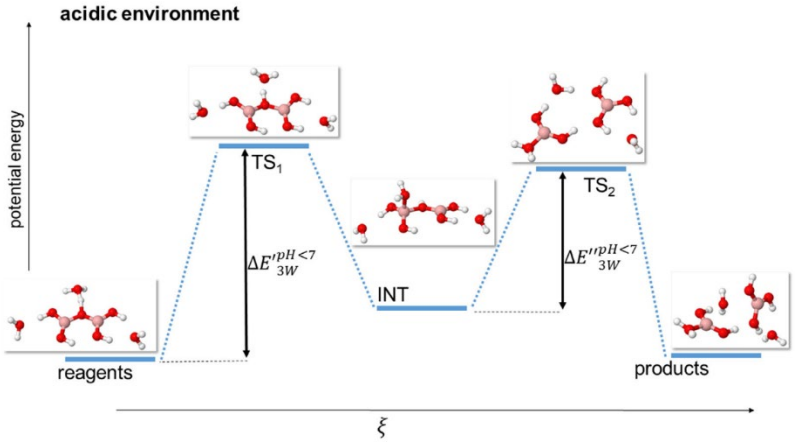
We investigated the mechanism and energy involved in the hydrolysis of borate networks, focusing on the role of water molecules. We simulated the borate network's interaction with water under various conditions, including acidic and basic environments, by modeling a system with two boron atoms, bridging oxygen atoms, and water molecules. The study applied ab initio calculations at the MP2 and CCSD(T) levels and DFT with several exchange-correlation functionals.



The findings suggest that borate networks are more prone to hydrolysis in basic conditions than in acidic or neutral ones. The presence of water molecules, especially in certain transition states with closed-ring structures involving the boron-oxygen-boron network, significantly influences the hydrolysis reaction, lowering the energy barriers. Some computational approaches, particularly the B3LYP, PBE0, and wB97Xd functionals (and also CAM-B3LYP in most cases)[1], provided results close to the reference MP2 and CCSD(T) calculations and in line with what expected with more studied silicate networks[2], both in describing the mechanism and in estimating the reaction barriers. The study highlights the importance of including water molecules in simulations and shed light on a reaction mechanism of paramount importance for the application of borate glasses.

References

[1] Peverati, R.; Truhlar, D.G., *Phil. Trans. R. Soc. A* **2014**, *372*, 20120476.

[2] James, T.D.; Phillips, M.D.; Shinkai, S. Boronic Acids in Saccharide Recognition; Rowan, A.E., Rowan, S.J., Aida, T., Fraser Stoddart, J., Eds.; RSC Publishing: Cambridge, UK, 2006; ISBN 978-0-85404-537-2