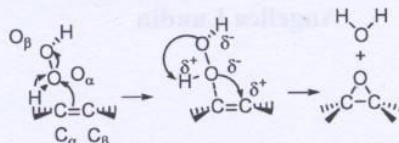


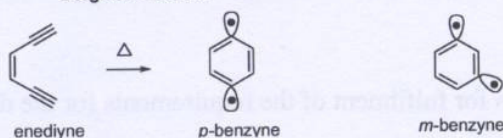
ABSTRACT

Density Functional Theory, DFT, has successfully been applied to two different chemical problems. The hybrid functional, B3LYP, was shown to be reliable in: 1) heterolytic bond breaking systems with hydrogen bonds such as the water micro-solvated epoxidation reaction, 2) the description of multi-reference character molecules, such as the benzyne biradicals, if broken-symmetry unrestricted description, UB3LYP, is used.



The mechanism of the epoxidation of ethene with hydrogen peroxide was shown to proceed via a concerted displacement of electron pairs. Micro-solvation with water was shown to decrease the activation enthalpy with $\sim 45 \text{ kJ mol}^{-1}$. Further decrease of the activation barrier by $\sim 20 \text{ kJ mol}^{-1}$ was obtained for a binuclear hydroxide active site, thus making the epoxidation reaction feasible both via a *direct* and an *indirect* pathway in a confined environment. The *direct* pathway is a one-step reaction where hydrogen peroxide is hydrogen bonded to the surface hydroxide and the dependence on the M ion is insignificant. The *indirect* pathway involves a two-step reaction where hydrogen peroxide first forms a hydroperoxy group on the active site before the epoxidation reaction takes place. Hydrolysis of ethylene oxide to the corresponding diol was shown to follow an $\text{S}_{\text{N}}2$ mechanism. Under neutral conditions the ring-opening reaction involves only one water molecule which is protolysed and the activation enthalpy is high. In acidic and alkaline conditions water and hydroxide ions act as nucleophiles, and oxonium ions and water as electrophiles, respectively. The activation enthalpies in acidic and alkaline environment are lower than in neutral environment, in agreement with experiment

Bergman reaction



Investigations of the Bergman reaction in connection with enediyne anti-tumour agents show good agreement with experimental data when using UB3LYP and therefore this method is feasible also for the larger enediyne systems. IR-spectra measured in a low-temperature matrix reveals, in agreement with high-level ab initio and UB3LYP calculations, a monocyclic structure of *m*-benzyne. *m*-benzyne can rearrange to enediyne without preceding [1,2] hydrogen migration to *p*-benzyne.

Keywords: DFT, hybrid functional, mechanism, epoxidation, micro-solvation, hydrogen bonds, active site, hydrolysis, benzyne biradicals, Bergman reaction, broken symmetry