

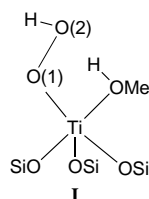
Elucidation of the mechanism of alkene epoxidation by hydrogen peroxide catalysed by titanosilicates: a computational study

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Calculated transition states for alkene epoxidation by hydrogen peroxide, catalysed by titanosilicates, predict that it is the oxygen atom of the titanium(IV)-hydroperoxide intermediate closer to the metal centre which attacks the alkene.

Zeolite-based metal oxide systems are effective catalysts for a variety of oxidation reactions, many of considerable industrial importance.¹ Of particular interest are titanium containing zeolites such as TS-1, TS-2 and Ti-MCM-41, which involve framework Ti^{IV} species, and which catalyse, under mild conditions, many useful oxidations with hydrogen peroxide, such as alkene epoxidation.² EXAFS studies³ suggest that in these catalysts the titanium is 4-coordinate, but may expand its coordination sphere on interaction with adsorbates. The active species for oxidation *via* hydrogen peroxide is generally considered to be a hydroperoxide species accommodated in the titanium coordination sphere, and possibly hydrogen bonded to a water or alcohol molecule, as in structure **I**.¹



The mechanism of the subsequent epoxidation reaction involving structure **I** is far from clear at present, particularly with regards to which oxygen atom [O(1) or O(2)] attacks the carbon-carbon double bond of the alkene. On the basis of stereoselectivity Adam *et al.*⁴ propose a mechanism for the epoxidation of chiral allylic alcohols involving attack of O(2), the oxygen atom closer to the hydrogen atom. Using steric arguments, Clerici and Ingallina⁵ also suggest that it is this oxygen atom [O(2)] that attacks the alkene. However, there is no real evidence that rules out attack of the oxygen atom [O(1)] directly bonded to the titanium centre. There is thus a need for a more complete understanding of the catalytic mechanism, which will be aided by an investigation of the potential energy surface, particularly of the structure and energetics of the transition states corresponding to attack by either O(1) or O(2). We here describe high level *ab initio* calculations which address this question.

As is common practice,⁶ we have used a finite molecular cluster to model the active site of **I**, in which the silicon atoms are terminated by hydrogen atoms. A more complete treatment would naturally take proper account of the effect of the infinite lattice,⁷ but finite clusters are taken to be a good initial approximation. Stationary structures on the potential energy surface involving the interaction of the cluster with ethene were located using a 3-21G* basis, electron correlation being included using density functional theory employing a B3LYP functional. The calculations were carried out using GAUSSIAN94.⁸

The minimum energy structures of the cluster with ethene close by are shown in Fig. 1. The structures shown in Fig. 1(a) and (b), which are close in energy, are on the reaction pathway leading to the two transition states involving attack on ethene by O(1) and O(2), respectively. Of particular note is the sideways coordination of the peroxy group, with both Ti-O distances [1.95 and 2.23 Å in the lowest energy structure, Fig. 1(a)] being significantly longer compared to the three Ti-O(Si) distances. Of these two distances, one is considerably shorter, implying preferential interaction of O(1) with the Ti^{IV} centre, and a corresponding weaker interaction of O(2). A previous calculation⁹ of the related system, Ti(OH)₃OOH, gave one longer (2.59 Å) and one shorter (1.87 Å) Ti-O length, compared to our structure, suggesting a somewhat different coordination mode. Our reactant structures are however similar to that found in the crystal structure of {[(η²-*tert*-butylperoxy)titanatranne]₂·3 dichloromethane},¹⁰ when Ti-O lengths of 1.91 and 2.27 Å were found, although the O-O distance (1.47 Å) is a little shorter than our calculated value (1.54 Å). We have located a third minimum energy structure [Fig. 1(c)] with a considerably longer Ti-O(2) length, which is best described as having the O₂H group bonded end-on. We find this structure, which resembles the one calculated by Neurock and Manzer,¹¹ to be 2.6 kcal mol⁻¹ higher in energy than our lower energy structure.

Two transition structures, both leading to the formation of the epoxide, were located (Fig. 2). The lower energy one involves attack on the ethene π-bond by the oxygen atom, O(1) [Fig. 2(a)], closest to the titanium centre, with a lengthening of the Ti-O(1) bond compared to the reactant, and an associated shortening of the Ti-O(2) bond. The developing negative charge on the O(2)-H group leads to the formation of a Ti-OH

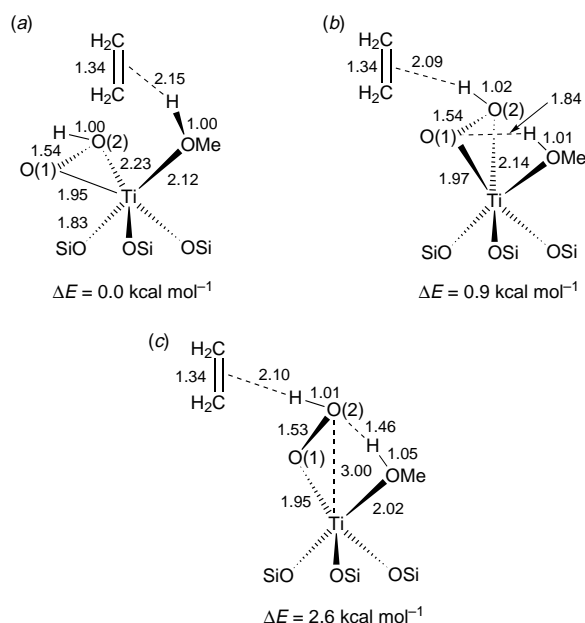


Fig. 1 Structures of ethene-cluster reactants

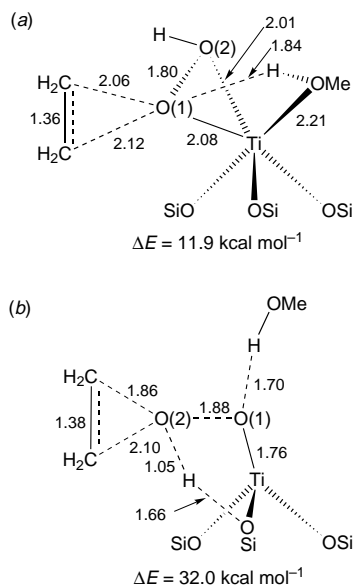


Fig. 2 Transition structures for attack of each hydroperoxide oxygen atom on ethene. ΔE is the calculated barrier.

bond in the product. When compared to this transition state, the second one involving the attack by O(2) [Fig. 2(b)] is of higher energy and has both O–C distances shorter and the O–O distance longer, so that the second mechanism, attack by O(2), proceeds *via* a later transition state. This second mechanism is significantly different from the first, involving a developing Ti–O double bond [Fig. 2(b)] (of length 1.76 Å in the transition state) and proton transfer to a siloxy group. Such a product involving a Ti–O double bond has been found to be less stable than the corresponding species with Ti–O single bonds.¹²

The two transition states that we have identified correspond to barriers that differ in energy by 20.1 kcal mol⁻¹. The relative ordering of these barriers is unlikely to change if more accurate calculations employing a larger basis and a better treatment of electron correlation were to be carried out. We have also used a continuum treatment¹³ to estimate the effect of a polar solvent on the calculated barriers. We find that using a relative permittivity of 78.3 to model solvation by water, the barrier for

attack of O(1) is unaltered, whilst the barrier for attack of O(2) is reduced to 25.8 kcal mol⁻¹. We are thus confident that the preferred route for attack involves O(1), and that inclusion of solvent does not affect this conclusion.

We have thus identified the mechanism of the epoxidation reaction, and obtained a transition state structure that may be of value in designing related enantioselective catalysts.¹⁴

This work was supported by the EPSRC and by a Royal Thai Government Scholarship to Duangkamol Tantanak.

Notes and References

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Received in Exeter, UK, 7th February 1998; 8/01164H