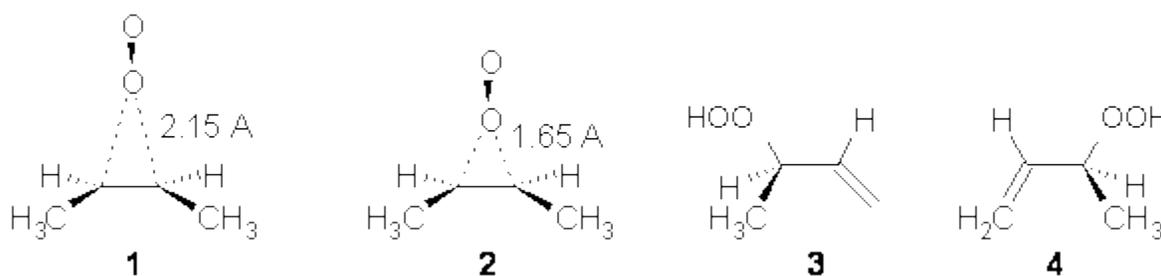


SINGLET OXYGEN ENE REACTION REVISITED

Sheppard and Acevedo¹ have reported a careful re-examination of the ene reaction of singlet oxygen with alkenes that points out inherent difficulties in examining high-dimension potential energy surfaces by reducing the dimensionality.

Their work begins by careful reassessment of the computational study of Singleton, Foote and Houk.² These authors looked at the reaction of singlet oxygen with *cis*-2-butene by creating a 15×15 grid of optimized geometries holding the C-O distance fixed to specific values while letting the other geometric variables completely relax (see **1**). These geometries were obtained at B3LYP/6-31G* and single-point energies were then obtained at CCSD(T)/6-31G*. They find two transition states, one corresponding to symmetric addition of oxygen to the alkene **2** which leads to the pereperoxide **3**. However, this pereperoxide **3** is not an intermediate, but rather a transition state for interconversion of the ene products **4** and **5**. These structures and mechanism appear consistent with the experimental kinetic isotope effects. The authors characterize the reaction as “two-step no-intermediate”.

Essentially, the reactants would cross the first transition state **1**, encounter a valley-ridge inflection point that bifurcates reaction paths that go to either **3** or **4** and avoid ever reaching the second transition state **2**.



Sheppard and Acevedo¹ tackle two major issues with this work. First, they are concerned about the role of solvent and so perform QM/MM computations with either DMSO, water or cyclohexane as solvent. The second factor is the choice of scanning just a 2-D grid as a projection of the multidimensional potential energy surface. Sheppard and Acevedo point out that since all other variables are optimized in this process, the hydrogen atom that is involved in the ene process must be bonded to either C or O and is therefore removed from the reaction coordinate. So they have performed a 3-D grid search where in addition to the two C-O distances they use the O-C-C angle as a variable.

They find that this PES provides the more traditional stepwise pathway: a transition state that leads to formation of the pereperoxide intermediate and then a second transition state that leads to the ene product. In addition, solvent effects are significant, a not unexpected result given the large dipole of the pereperoxide.

But the main point here is that one must be very careful in reducing the dimensionality of the hypersurface and drawing conclusions from this reduced surface. It appears that the valley-ridge inflection point in the single oxygen ene reaction is an artifact of just this reduced dimensionality.

Source: <http://comporgchem.com/blog/?p=5>