

## Exploration of the Reaction Network of the Isobutenyl Radical + O<sub>2</sub> in PM6

During processes such as pyrolysis or oxidation of alkanes, alkenes are often produced and part of the initial products.<sup>1</sup> Therefore, it is important to understand the chemistry behind the different reactions that can occur with alkenes. Particularly, it has been shown that the isobutenyl radical plays a role in the mitigation of *n*-octane oxidation.<sup>1</sup> The goal of this project was to explore the reaction network of a system containing an isobutenyl radical and molecular oxygen using PM6 Hamiltonian in CP2K molecular dynamics (MD) engine. To increase the efficiency of the MD simulations, parallel bias metadynamics (PBMetaD) was employed to bias the social permutation invariant (SPRINT) coordinates of every atom in the system.

As reactions are considered rare events when operating with time steps on the order of 1 fs, standard molecular dynamics is an inefficient choice when exploring a reaction network. An effective solution is to implement an enhanced sampling method known as metadynamics (MetaD) wherein information about the reacting system can be accessed more efficiently by applying a potential bias to the collective variables (CVs) of the system. PBMetaD is a type of MetaD that can be used to increase enhanced sampling efficiency when dealing with a system of high dimensionality.<sup>2</sup> The isobutenyl radical and oxygen system contains 13 atoms and associated SPRINT coordinates; therefore, PBMetaD is a better choice due to the large number of CVs. SPRINT coordinates are used to uniquely describe any possible configuration of atoms by utilizing the contact matrix of the system.<sup>3</sup>

As mentioned previously, MD simulations were run using the CP2K engine and PBMetaD+SPRINT calculations were carried out using the PLUMED plugin. Three simulations were performed with varying Gaussian hill heights: 10 kJ/mol, 5 kJ/mol, and 0 kJ/mol (no PBMetaD, regular MD). The first two simulations were performed at 300 K and the regular MD run was performed at 1000 K. All simulations were performed with a 1 fs time step and a multiplicity of 2. Of the 3 simulations, only the 5 kJ/mol hill height run yielded physical results. A single reaction was observed where the O<sub>2</sub> molecule added to one of the CH<sub>2</sub> groups on the isobutenyl radical. This intermediate is known to be the first step of the reaction network, from which the network branches off into many different products.<sup>1</sup> Using Gaussian 09, the associated energy barrier for the reaction was quantified using the PM6 Hamiltonian.

The transition state (TS) connecting the reactants and product was optimized and verified to contain only one imaginary vibrational mode. An intrinsic reaction coordinate calculation was also performed to ensure that the optimized TS connected the reactants to the product. The electronic energies were calculated for the reactants, TS, and product and are tabulated in Table 1. It is noted that the reactants could not be optimized using PM6 with a multiplicity of 2; however, when the multiplicity was changed from 2 to 4 (accounting for triplet oxygen), the optimization converged. The energy difference between the TS and product was -4.344 kcal/mol, which is much smaller in magnitude than when compared with the work done by Chen et al.<sup>1</sup> However, Chen et al. performed calculations at much higher levels of theory (e.g. B3LYP, MP2, MP4, etc.) when compared to PM6, which is an entirely parameterized semi-empirical method.

Table 1: Calculated Electronic Energies

	Reactants	Transition State	Product
Electronic Energy (kcal/mol)	3.93*	9.79	5.45

\*Multiplicity = 4

Because the product of the O<sub>2</sub> addition to the isobutenyl radical is considered the first step from which all other reactions begin<sup>1</sup>, another simulation was performed with a 5 kJ/mol hill height at 1000 K to reduce computational time by skipping the time required for the initial reaction. It was seen that the starting structure was unstable and quickly decomposed (< 1 ps) into an O<sub>2</sub> molecule and an isobutenyl radical. The addition of O<sub>2</sub> is generally considered barrier-less and Chen et al. have shown that the energy required to decompose is approximately -21 kcal/mol. This result demonstrated that PM6 was an insufficient level of theory for simulating this reaction network.

To quantify the effectiveness of PM6, 4 optimizations were performed at different levels of theory: PM6, B3LYP, M062X, and MP2. The C-O and O-O bond distances were determined and can be seen in Figure 1. Clearly, PM6 over-predicts the C-O bond distance and under-predicts the O-O bond distance.

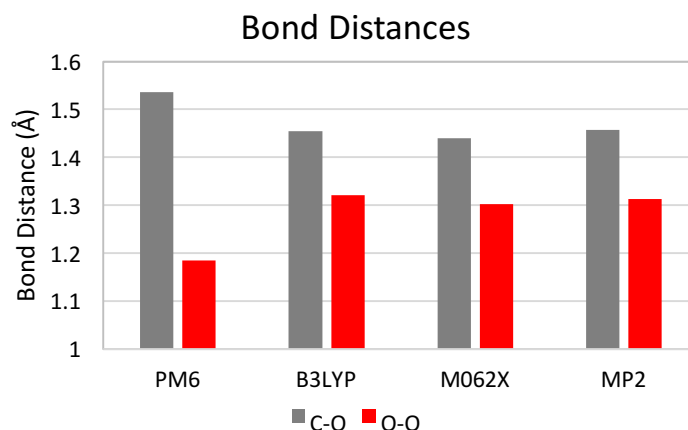


Figure 1: C-O and O-O bond distances calculated at the PM6, B3LYP, M062X, and MP2 levels of theory. The latter 3 used the 6-31G(d) basis set. All calculations used a multiplicity of 2.

In conclusion, PBMetaD+SPRINT simulations were performed in CP2K using the PM6 Hamiltonian. One reaction was observed in which O<sub>2</sub> added to the isobutenyl radical. This product was shown to be unstable in PM6. Moving forward, a higher level of theory should be considered when simulating the reaction mechanism between an isobutenyl radical and O<sub>2</sub> due to the low apparent energy barrier. Because of this low energy barrier, decomposition to reactants is more favorable than evolving through the remainder of the reaction network.

#### References:

- (1) Chen, C.-J.; Bozzelli, J. W. Thermochemical Properties, Pathway, and Kinetic Analysis on the Reactions of Allylic Isobutenyl Radical with O<sub>2</sub>: An Elementary Reaction Mechanism for Isobutene Oxidation. *J. Phys. Chem. A* **2000**, *104* (43), 9715–9732.
- (2) Pfaendtner, J.; Bonomi, M. Efficient Sampling of High-Dimensional Free-Energy Landscapes with Parallel Bias Metadynamics. *J. Chem. Theory Comput.* **2015**, *11* (11), 5062–5067.
- (3) Zheng, S.; Pfaendtner, J. A CPMD + Metadynamics Study of High Temperature Methanol Oxidation Reactions Using Generic Collective Variables. *J. Phys. Chem. C* **2014**, 140421120937004.