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Quantum Chemical and Kinetic Modeling Study of methylvinyl + O₂ Reaction

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Abstract

We present the first detailed theoretical analysis of vinylic radicals 1-methyl-vinyl and 2-methyl-vinyl oxidation reaction and subsequent reactions on the C₃H₅O₂ potential energy surface(PES). The PES was determined at the CCSD(T)-f12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ level theory. Several transition states calculated using multi-reference theory are also be discussed. Temperature- and pressure-dependent rate coefficients for all elementary reactions on the PES are predicted using RRKM/Master Equation methods.

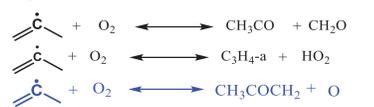
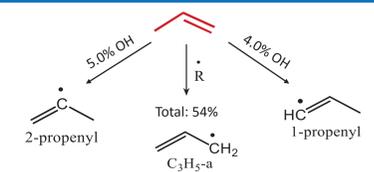
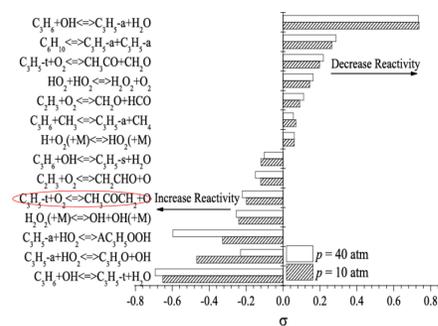
Motivation

Recent numerical analysis has determined that the reactions of the vinylic radicals are critical to predicting the combustion properties of high-temperature propene combustion.

Almost all vinylic radicals react with oxygen.

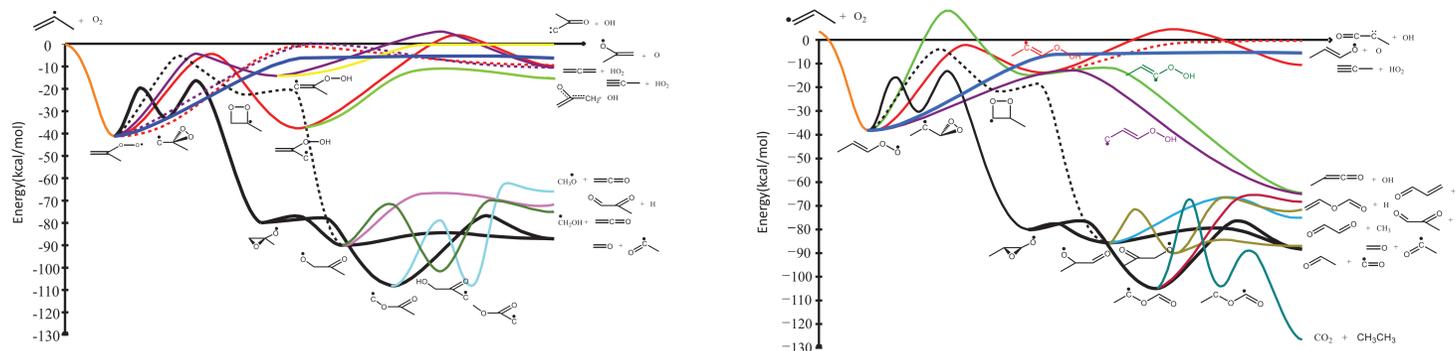
The only estimates of the rate coefficients in the literature are taken by analogy from out-of-date C₂H₃ + O₂ predictions.

It is important to know the crossover temperature between potential chain branching channel and chain propagating channel.



Results

1) Potential energy surfaces for both 1-methyl-vinyl and 2-methyl-vinyl are shown. The pathway to the main propagating channel is shown in black; the pathway to main chain branching channel is shown in blue.



According to the results in Ref.2, we predict that for both PESs, the black channel will dominate at lower temperatures, the blue channel will dominate at higher temperatures.

2) Several transition states require multi-reference theory to quantify the barrier height considering their properties and significance to the overall kinetics.



For each fixed C-O distance, from r = 1.8Å to r = 20Å.

Remaining degrees of freedom were optimized using CASPT2(9,7)/cc-pVTZ. Single point energy calculation applied on CASPT2(11,9) &(13,11), MRCI(9,7).

Although CASPT2 and MRCI individually converged, the two methods differ by roughly 1 kcal/mol in the bottleneck region (2-5Å).

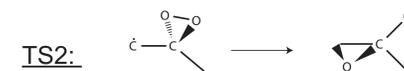
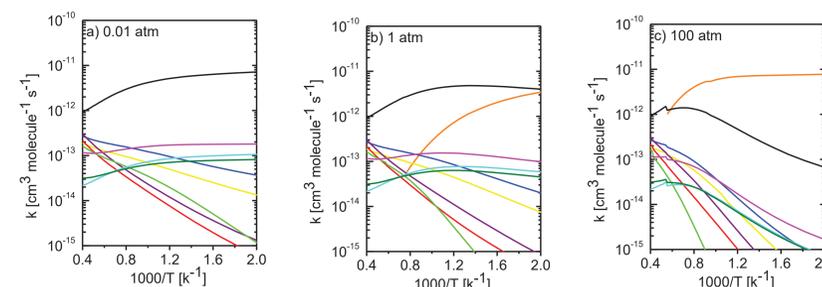
A new method was developed, based upon the doublet/quartet splitting.

$$\Delta E_{\text{Total, doublet}} = \Delta E_{\text{CC, total, quartet}} - (\Delta E_{\text{multi-reference, quartet}} - \Delta E_{\text{multi-reference, doublet}})$$

The new potentials are shown as the circle marker lines. As the figure shows, the differences between CASPT2 and MRCI potentials now decrease to within 0.5 kcal/mol in the bottleneck region.

3) Product formation

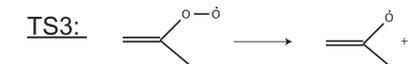
Arrhenius plots for the individual product channels at three different pressures for the addition of C₃H₅+O₂.



Based on Ref.2, although this isomerization proceeds through a tight transition state, the CCSD(T)/cc-pVTZ result showed that a multi-reference method is needed to acquire higher accuracy result.

Geometry optimized using CASPT2(9,8)/cc-pVTZ. Active space: C-centered radical; O-O sigma, sigma*; 2 C-O sigma, sigma*; O lone pair. CASPT2(9,8) calculations were used to compute the reactant and product to get relative barrier height.

Barrier height: $\Delta E_{\text{TS}} - \text{reactant} = 16.86 \text{ kcal/mol}$
 $\Delta E_{\text{TS}} - \text{product} = 62.49 \text{ kcal/mol}$

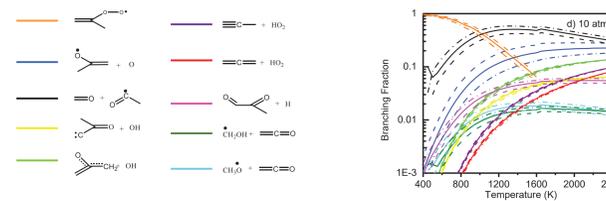


This decomposition is complicated:

Low-lying excited state. Electronic degeneracies in O and resonances and near degeneracies in CH₂C₂OO-CH₂. Ground-state was optimized at CASPT2(7,6) level of theory. The excited-state was calculated by adding the difference between ground state and excited state.

4) Sensitivity analysis

Vary the the barrier height of the two key transition states by ± 1 kcal/mol.



The chain branching channel always remains secondary. The sensitivity analysis does not change the qualitative behavior.

Computational Methods

Electronic structure method:

1) The O-O torsion mode were scanned as a test case for benchmark. 5 DFT methods, 7 basis-sets for each method were employed. CCSD(T)/cc-pVTZ level calculations performed to stationary point were set as standard criteria.

2) Single-point energy calculation//B2PLYPD3/cc-pVTZ benchmark for vinyl + O₂ system.

CCSD(T)-f12a/cc-pVTZ-f12//B2PLYPD3/cc-pVTZ was applied for C₃H₅O₂ PES.

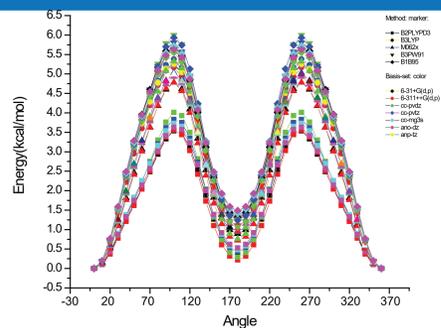
Microcanonical Rate Constants

For reaction C₃H₅ + O₂, Variable Reaction Coordinate Transition State Theory (VRC-TST) was used.

For CH₃C₂OO-CH₂ -> CH₃CO-CH₂ + O, variational transition state theory was used to optimize the location of the dynamic bottleneck.

RRKM/ME

A newly developed RRKM/ME code, PAPER was used to calculate the temperature and pressure dependent phenomenological rate coefficients.



References

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- Goldsmith, C. F., Harding, L. B., Georgievskii, Y., Miller, J. A., Klippenstein, S. J. (2015). Temperature and pressure-dependent rate coefficients for the reaction of vinyl radical with molecular oxygen. *The Journal of Physical Chemistry A* 119.28 (2015): 7766-7779.

Future work

- The similarities between C₂H₃ + O₂ and the methyl-substituted reactions for C₃H₅ + O₂ will be discussed.
- The new rate constants will be included in propene oxidation kinetic models to test the effects on propene combustion.

Acknowledgement:



BROWN Engineering School

