Theoretical Mechanisms and Atmospheric Implications of the Reaction of Methyl Vinyl Ether with the Hydroxyl Radical

Charles Li

Troy High School, Fullerton, California

Dr. Fu-Ming Tao, Professor of Chemistry,

California State University, Fullerton

Section (i) Project Selection

I first started learning the theory behind quantum chemistry during my sophomore year, when a friend first introduced me to Dr. Tao and his lab at the California State University of Fullerton (CSUF). In the summer of 2006, I spent over 40 hours per week in the lab, running calculations and researching more on reactions involving the hydroxyl and chlorine radicals in the atmosphere. After much research, I came across a paper that was published in June 2006 about vinyl ethers that spurred my interest. Although I encountered many roadblocks during my research, I discovered that each failure posed a new question and led to a new approach to my problem. Eventually, it was this buildup of new questions and novel approaches that allowed me to accomplish my research.

My interest in the vinyl ethers was first sparked when I learned about the manufacturing of PVC pipes and the resulting release of vinyl chloride into the atmosphere in my chemistry class. However, as I began researching, I discovered that vinyl chlorides have been investigated extensively and eventually, my research led me to the alkyl vinyl ethers. I found methyl vinyl ether (MVE) to be a far more interesting compound than vinyl chloride.   MVE is not only readily oxidized by radicals, but it has recently been found that the formation of aerosols was detected in the ozonolysis of

MVE. If this is true, then MVE may be the smallest possible molecule capable of forming aerosols, as previous aerosol forming compounds typically consisted of seven carbons or a cyclic six-carbon ring.

Initially, I was attracted to computational chemistry because I was amazed by the immense potential that quantum chemistry has in expanding our chemical knowledge. Through purely empirical means, quantum chemistry can investigate reactions under conditions not achievable in laboratories. In the end, my project ideally combined my interest in quantum chemistry with my curiosity in the chemistry of the life-sustaining troposphere that surrounds us.

Section (ii) Summary of Research

Introduction

Volatile organic compounds, abbreviated VOCs, are released primarily from artificial sources, although there is also a significant amount of biologically released VOCs from trees in the form of isoprene and terpenes [1]. VOCs are further divided into two categories: methane and non-methane organics. Non-methane organics can degrade quickly in the troposphere into harmful products such as formaldehyde. Recently, a study done by *Nature* [2] discovered that there is a large portion of VOCs that has been unaccounted for in the troposphere, especially in the southern hemisphere.

The importance of VOCs in tropospheric chemistry has created much interest in identifying the unaccounted for VOCs [3-5]. Vinyl ethers are non-methane organics used widely in industry as solvents and coatings [6]. They are also being considered for use as motor oil additives [4]. Since solvents and coatings are primarily applied onto items produced indoors, the release of vinyl ethers into buildings can create indoor pollution

that is detrimental to humans. Additionally, vinyl ether emissions can also escape into the troposphere and therefore, they may comprise a portion of the unaccounted for VOCs.

Methyl vinyl ether (MVE) is the simplest of the vinyl ethers. The reaction of MVE with the hydroxyl radical proved to be especially interesting because of the relative abundance of the hydroxyl radical from the photolysis of ozone. The hydroxyl radical plays a major role in the degradation of organics, typically acting in the first steps to their removal [1]. A previous experimental study by Klotz *et al.* [4] determined that three possible reaction pathways exist: (1) addition of the hydroxyl to the central carbon, (2) addition onto the terminal carbon, and (3) abstraction of a hydrogen from the methyl group.

MVE, because it is a non-methane organic, is predicted to have a relatively short atmospheric lifetime. This will affect both indoor and outdoor environments at local and regional levels- levels that humans are exposed to. Additionally, the reactivity of MVE, and VOCs in general, contributes to the formation of smog.

Hypothesis

The importance of MVE in the troposphere poses the following three questions:
(1) What are the theoretical mechanisms of the three degradation pathways?
(2) What is the rate of the overall MVE reaction and what is its temperature dependency? and (3) Which of the three pathways is dominant?

Methods

I investigated the reaction pathways of MVE using the Gaussian 2003 computational program [7]. The stationary points along the reaction pathway were determined using various theories and basis sets. Second order Moller-Plesset

Perturbation theory (MP2) was used for optimization and frequency calculations. Additionally, density functional theory, B3LYP was also used for optimization and frequency calculations. For comparison, a hybrid meta density functional theory developed by Truhlar *et al*. [8] - mpwb1k- was used. Finally, composite Gaussian-3 theory was also used for energy calculations.

Using the geometries, moments of inertia, and frequencies from the stationary points calculated using Gaussian 2003, classical transition state theory was used to determine the rate constants. Kinetics calculations were performed using the program provided by computational science and engineering online [9]. After rate constants were determined, the lifetime of MVE could be calculated by taking the inverse of the rate constant multiplied by the concentration of hydroxyl in the environment being studied.

Results/Discussion

Using these methods, I was able to answer my first question: What are the theoretical mechanisms of the three degradation pathways? Before the different reaction pathways could be investigated, the stability of MVE first had to be determined. At the B3LYP/6-31+g(d) theory, it was discovered that the near-planar *cis* structure was 2.04 kcal/mol lower, and therefore more stable, in energy than the corresponding linear *trans* structure. Previous studies using microwave spectroscopy also reported a similar energy difference of 1.1 kcal/mol [10]. Thus my study focused on the reactions of MVE's primary *cis* form.

Addition to the central carbon was characterized by an activation energy of approximately -4 kcal/mol. This energy was determined using various theories. Although MP2 energies predict a positive activation energy, spin corrected MP2

calculations, single point CCSD(T) energies, and MPWB1K calculations all confirm the negative activation barrier. Similarly, a negative activation energy around -5 kcal/mol was found for the terminal addition. Respectively, all three activation energies were lower in energy for reaction (2) than for reaction (1). Finally, for the abstraction reaction, a positive activation energy, approximately 1.5 kcal/mol, was predicted by all levels of theory. Unlike the addition reactions, prereactive and product complexes were found. In the prereactive complex, the hydroxyl radical stabilizes itself to the oxygen on the MVE, forming an intermolecular bond of 1.89 angstroms. Once the hydrogen is abstracted, the water will be released after formation of the product complex. All three reaction pathways were found to be exothermic.

Having answered the first question, the second question posed was "What is the rate of the overall MVE reaction and what is its temperature dependency?"

A reaction is positively temperature dependent if it has a positive activation energy and negatively temperature dependent if it has a negative activation energy. In this study, the addition reactions were found to be negatively temperature dependent while the abstraction reaction is positively temperature dependent. What this means is that the abstraction reactions will contribute more to the overall reaction at higher temperatures. The hybrid meta theory MPWB1K produced rate constants closest to experimental values.

My final question was which of the three pathways is dominant. Using rate constants calculated using MPWB1K, at 298 K, the addition reactions onto the central and terminal carbons were found to be far more dominant than the abstraction reactions.

Because the addition reactions are dominant, the reaction is much more likely to form formaldehyde and methyl formate as opposed to methyl anhydride.

Since there is less hydroxyl indoors, there is almost a twofold increase in the lifetime of MVE. On one hand, the prolonged presence of MVE indoors can contribute significantly to indoor pollution. On the other hand, MVE has a relatively fast rate of oxidation outdoors, compared to the lifetime of methane. This short lifetime may contribute to smog formation.

Conclusion

In conclusion, the mechanisms and kinetics of the reaction of methyl vinyl ether with the OH radical have been investigated and the rate constants calculated are found to be in reasonable agreement with previous studies. The hybrid theory MPWB1K/6-31+g(d,p) was found to give results closest to experimental studies. The two addition pathways were found to be highly favored over the abstraction pathway and all three pathways were exothermic. The reaction is found to be negatively temperature dependent overall.

Implications/Further Studies

Since formaldehyde is a dominant product, the emissions of MVE in industry should be monitored. MVE emissions may contribute to the increased concentration of VOCs indoors- typically 2 to 5 times higher than in outdoor environments. Further research involving the reactions of MVE with other atmospherically important molecules such as the nitrate radical, chlorine radical, and ozone will help develop a more complete scheme for the degradation pathways for MVE. Different transitional state theories can also be used to calculate more accurate rate constants. Additionally, the degradation

processes of larger vinyl ethers should also be investigated in order to find possible trends and to better understand the atmospheric impacts of VOCs.
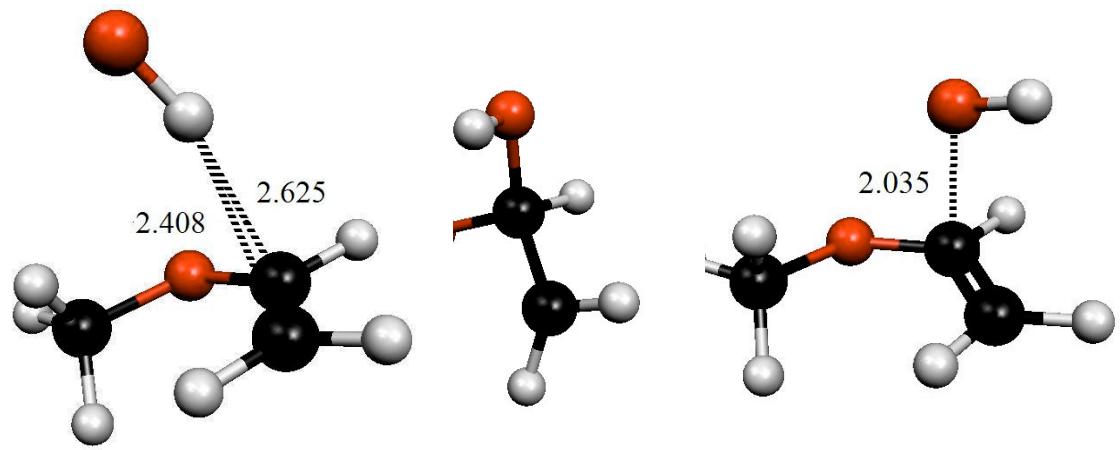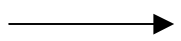
Citations

[1] Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, 2000.

[2] Singh, H.; Chen, Y.; Staudt, A.; Jacob, D.; Blake, D.; Heikes, B.; Snow, J. *Nature* **2001**, *410*, 1078.

[3] Zhou, S.; Barnes, I.; Zhu, T.; Bejan, I.; Benter, T. *J. Phys. Chem. A* **2006**, *110*, 7386.

[4] Klotz, B.; Barnes, I.; Imamura, T. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1725.

[5] Riemer, D.; Pos, W.; Milne, P.; Farmer, C.; Zika, R.; Apel, E.; Olszyna, K.; Kliendienst, T.; Lonneman, W.; Bertman, S.; Shepson, P.; Starn, T. *J. Geophys. Res.* **1998**, *103*, 28111.

[6] Thiault, G.; Thévenet, R.; Mellouki, A.; Le Bras G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 613.

[7] Gaussian 03, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[8] Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A.* **2004**, *108*, 6908.

[9] S. Zhang, T. W. Truong, VKLab version 1.0, University of Utah, 2001.

[10] Cahill, P.; Gold, L. P.; Owen, N. L. *J. Chem Phys.* **1968**, *48*, 1620

FIGURE 1: Two possible conformers of MVE[a].
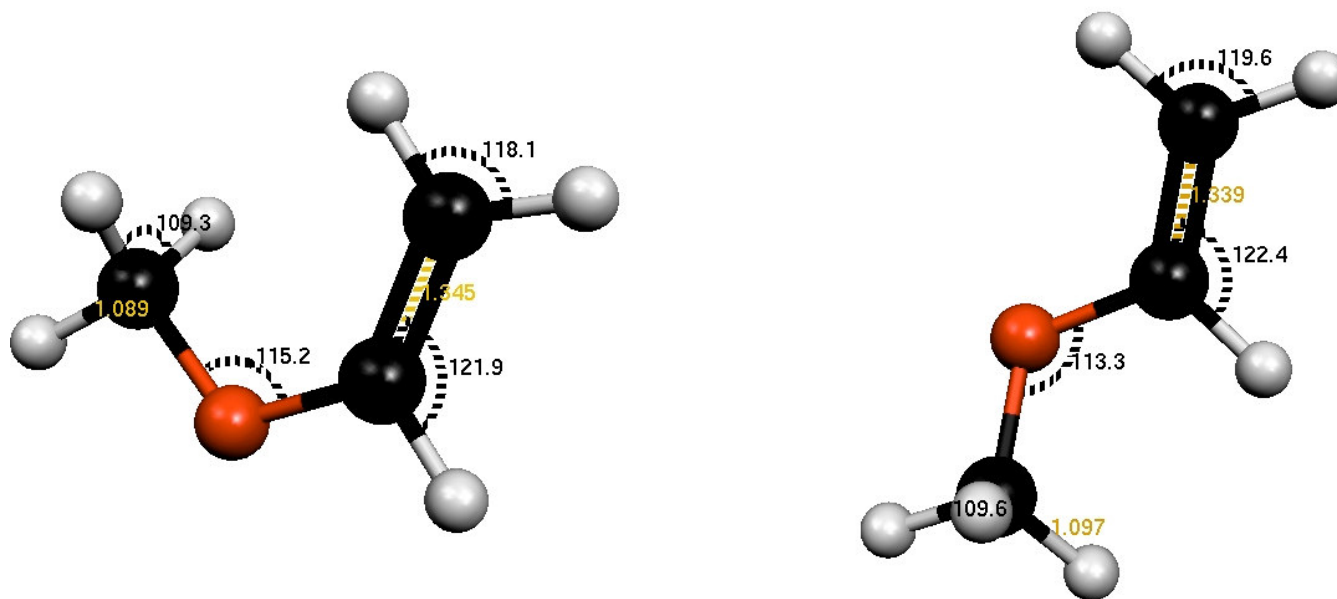
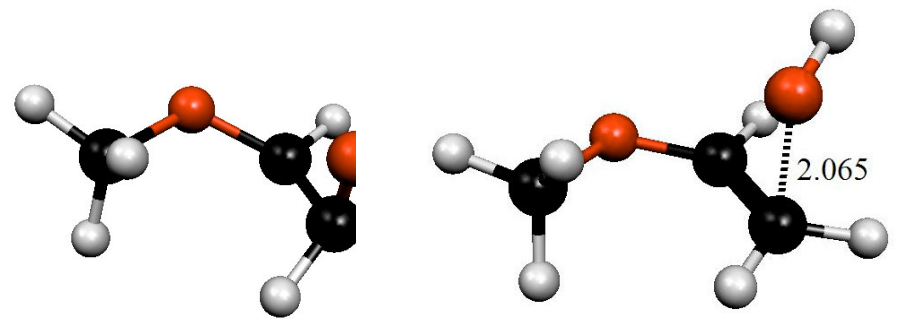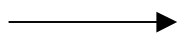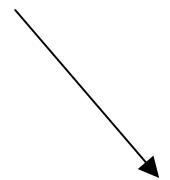[a] Bond distances (in gold) given in angstroms.

points for the Addition Reactions (Reactions 1 and 2)[a].

2.625

2.408

2.035

Product

Transition State

ex

Transition State

2.065

Transition State

Product

ven in angstroms.

FIGURE 3: Stationary Points for the Abstraction Pathway (Reaction 3)[a]

1.894   3.433

Prereactive Complex

1.329

1.209

Transition State

2.822

1.988

Product Complex
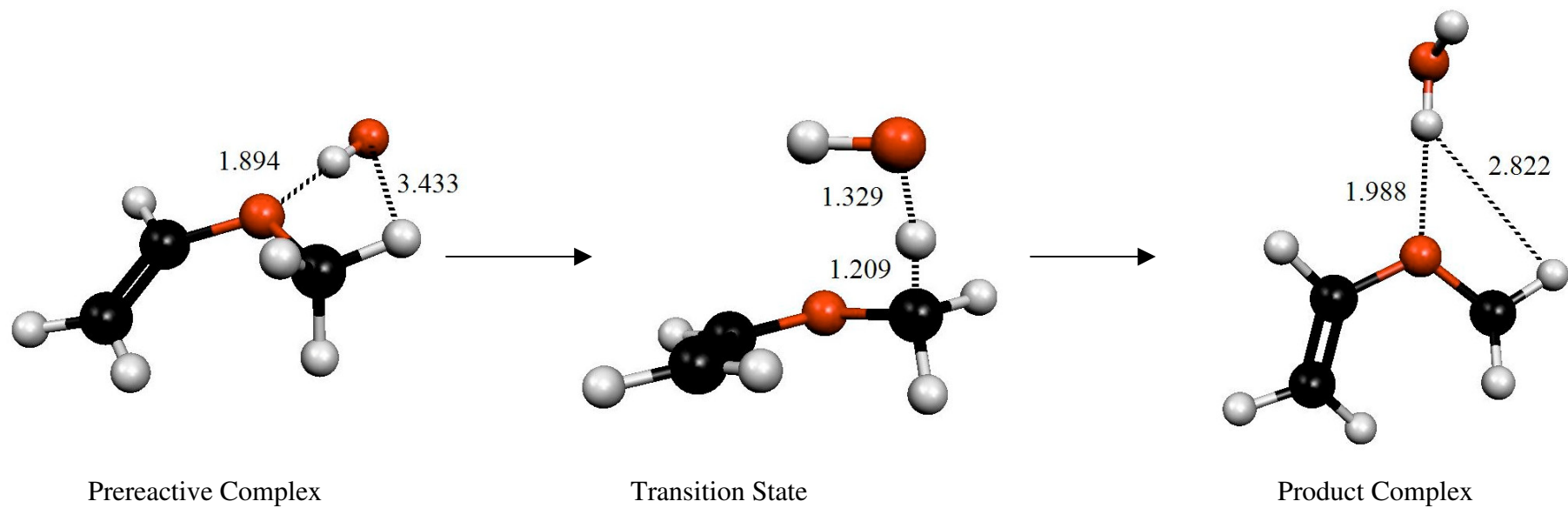
[a] All distances given in angstroms.