

Computational Analysis of Atmospheric Reaction Between Trans-beta-isoprene Epoxydiol (IEPOX) and Sulfates

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I. ABSTRACT

Chemical reactions between trans-beta-isoprene epoxydiols (IEPOX) and inorganic sulfate aerosol particles produce complex secondary organic aerosols (SOA) which contribute to global warming.¹ Under laboratory conditions, the reaction between IEPOX and inorganic sulfate produces the thermodynamically preferred product. This contrasts with atmospheric data which indicates that structure with less hindrance is the primary product. Current mechanistic understanding of the reaction would predict the laboratory behavior but fails to predict the atmospheric data. Computational tools provide a fast and accurate way to replicate the conditions of the atmosphere, which can be difficult in the laboratory. DFT and GSM calculations of the reaction indicated that hydrogen bonding and protonation states might play a role in the anomalous atmospheric behavior. By utilizing the computational methods, I've learned how to use mathematical models to predict precise transition states for the reactions. Also, those methods are important for the calculation of energy diagrams. In conclusion, computational methods allow scientists to make accurate mechanistic predictions for many different reactions.

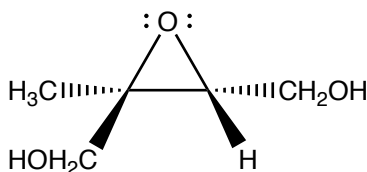
II. INTRODUCTION

Trans-beta-isoprene epoxydiol (IEPOX), an important chemical atmospheric chemistry, was discovered by Wennberg in 2009. IEPOX is a molecule with a five-carbon diene (for structure, see figure 1) produced by plants: they produce IEPOX in order to defend themselves from oxidative or thermal stress.² While IEPOX's importance to the climate is only partially understood, recent studies have shown that it is a significant component of non-methane hydrocarbons (large hydrocarbons) into the atmosphere, which are rarer and have more unusual chemistry than methane. Non-methane hydrocarbons present a ready source of aerosols (similar to smog) in the atmosphere, which can affect the chemistry of the lower atmosphere and the health of living organisms.³ These hydrocarbons can interact with sulfates, which enter the atmosphere through human and natural sources such as by burning fossil fuels or volcanic eruptions. Excessive sulfates in the atmosphere lead to acidic rain and fog which can damage the ecosystem and human structures. Overall, understanding the details of IEPOX reactions has implications for the understanding of climate change, and therefore deserves additional research.

IEPOX reacts with aerosols, but the reaction is mechanistically complex. The low density, and often high energy conditions of the atmosphere allow for non-intuitive mechanisms to be possible. Further, previous studies and experiments have shown that IEPOX can react with sulfate particles under atmospherically relevant aerosol acidities and surface area concentrations. IEPOX is known to react with sulfate particles in different ways under different levels of atmospheric acidity and relative humidity (RH). These reactions are thought to be a dominant pathway in the generation of isoprene secondary organic aerosol.⁴ Aerosol can act as chemical reaction sites for heterogenous chemistry, which is thought to be important in atmospheric

chemical composition.⁵ Understanding how these factors govern atmospheric reactivity provides predictive tools for how atmospheric composition will change with time.

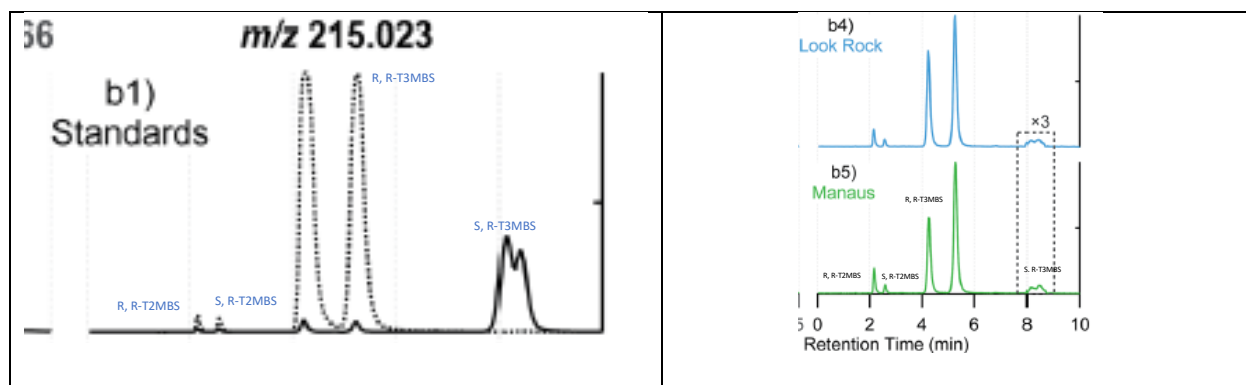
Figure 1: IEPOX structure.



Specifically, the reaction between IEPOX and sulfates can proceed by two pathways, specifically S_N1 and S_N2 reactions. An S_N1 reaction involves the formation of a carbocation as an intermediate, and the overall reaction has two steps. On the other hand, a S_N2 reaction happens in one step without intermediates. There are two possible products formed for each reaction pathway. These two products are non-superimposable (or “mirror”) images of each other, known as enantiomers. For the S_N1 pathway, the products are (2R,3R)-1,3,4-trihydroxy-2-methylbutan-2-yl hydrogen sulfate (R, R-T2MBS) and (2S,3R)-1,3,4-trihydroxy-2-methylbutan-2-yl hydrogen sulfate (S, R-T2MBS), shown in figure 3. For the S_N2 pathway, the products are (2R,3R)-1,3,4-trihydroxy-3-methylbutan-2-yl hydrogen sulfate (R, R-T3MBS) and (2S,3R)-1,3,4-trihydroxy-3-methylbutan-2-yl hydrogen sulfate (S, R-T3MBS), shown in figure 4. In the atmosphere, as the pH changes from low to high values (more acidic to more basic), the IEPOX reaction with sulfate changes its mechanism. At low pH the S_N1 pathway is preferred (selective to the more substituted carbon), and the preferred enantiomer in atmosphere is S, R-T2MBS. At high pH the S_N2 pathway is preferred (selective to the less substituted carbon), and the preferred enantiomer in the atmosphere is R, R-T3MBS.

However, under laboratory conditions IEPOX shows different product yields when reacting with sulfate, and the enantioselectivity is unexpected. When IEPOX is under low pH condition, the reaction favors the more substituted carbon, but the amount of S, R-T2MBS formed during the S_N1 reaction is larger than that of R, R-T2MBS, which is an unexpected and intriguing result.

Figure 2: The results from both the labs (left) and the atmosphere (right).⁶



The difficulty of replicating the conditions of the upper atmosphere in laboratory prevents determining the mechanism by experiment. QM simulations are in vacuo, which can be like atmospheric conditions though often reactions can occur inside aerosols like water droplets., so they are similar to the low density of atmosphere. Furthermore, QM simulations provide accurate energies for bond forming and breaking, a common occurrence in chemical reactions. Also, deeper mechanistic understanding is possible by zooming on the reaction energy diagram so that we can determine which reaction is energetically more favorable.

These computational tools will provide specific mechanistic insight into the atmospheric reaction between IEPOX and sulfates. Exploring IEPOX reactions by analyzing the transition states will

determine what makes the reactions forward differently in atmosphere and in labs. Further, these transition states can be examined for specific steric and electronic parameters that explain why certain reactions are preferred in the atmosphere but not in the laboratory.

Figure 3: IEPOX S_N1 reaction mechanism. The products are R, R-T2MBS and S, R-T2MBS as shown.

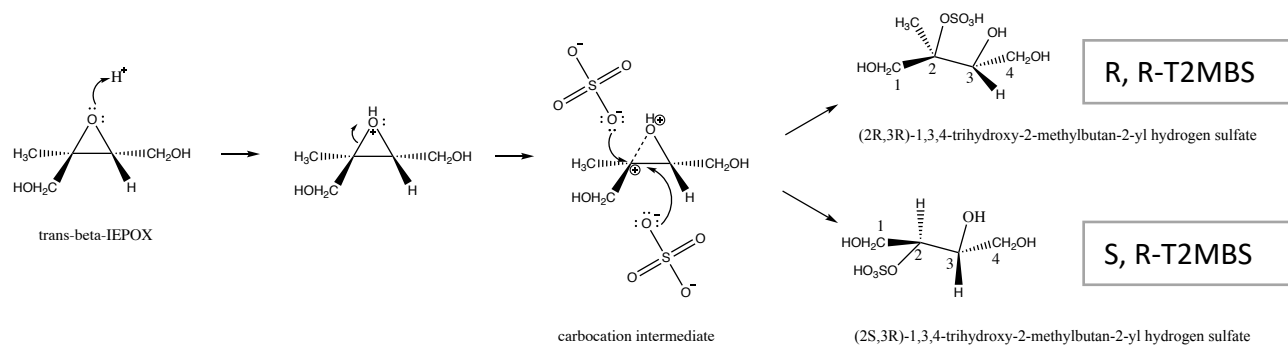
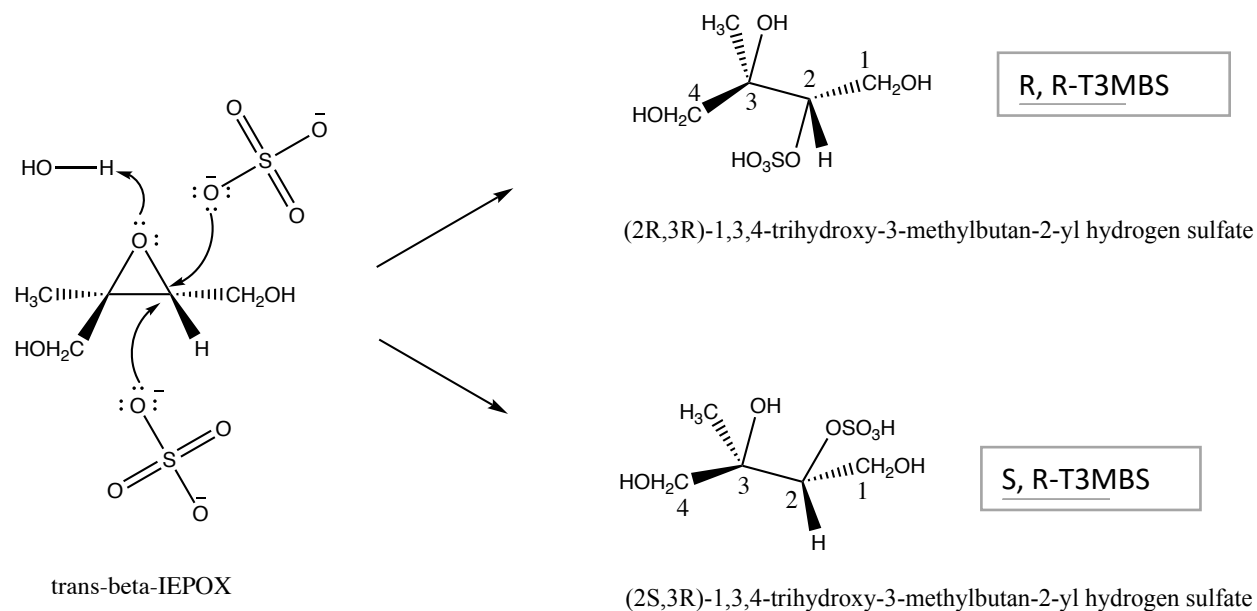


Figure 4: IEPOX S_N2 reaction mechanism. The products are R, R-T3MBS and S, R-T3MBS as shown.



III. MATERIALS AND METHODS

QChem, ORCA and Growing String Method (GSM) are used to computationally study the reactions of this work. These simulations used density functional theory (DFT) with the B3LYP functional to perform quantum mechanical modeling. DFT uses functionals to compute the electronic structure of a molecule rather than solving the Schrödinger Equation. It can well approximate the electron ground-state energy for determining both the geometries of molecules and the relative stability of the reactants and products.⁷

QChem is a comprehensive *ab initio* quantum chemistry package for accurate predictions of molecular structures and reactivities.⁸ *Ab initio* calculation packages rely on solving the fundamental equations of quantum mechanics, rather than an empirical basis, to predict molecular properties. As such, QChem was used to generate optimized reactant, product, and transition state molecular geometries and vibrational modes. Using the Gibbs free energy equation, energies and enthalpic information from QChem can be used to predict accessible reaction pathways.

ORCA is another *ab initio* quantum chemistry program package that contains a different set of computational tools.⁹ ORCA was used for its ability to calculate solvation effects using the SMD model.¹⁰ Combining the solvation energy in the Gibbs equation give the solvated Gibbs free energy. This was used to compare *in vitro* laboratory (solvated) conditions to *in situ* atmospheric (gas phase) ones.

Within this work one of the key issues is discovering the exact mechanism of sulfidation of IEPOX. To better elucidate these mechanisms, the Growing string method (GSM) was used to facilitate exact transition state discovery. GSM is highly useful to optimize reaction pathways and can locate the exact TS without using traditional, less reliable TS-finding methods.¹¹ GSM can discover non-intuitive mechanisms by systematically exploring the potential energy surface of the reaction. In this research, the hybrid strategy of GSM initiated the string calculation at a low level of theory, and then refined by a high level of theory (B3LYP/6-31G*).¹² For the GSM predicted TS states, QChem was used to conduct a final optimization of the structure and determination of the TS energy.

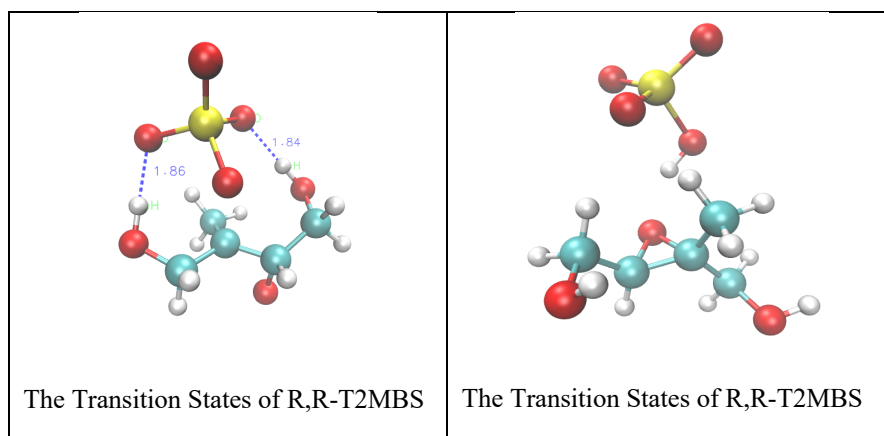
Stationary points are points with zero gradient on the PES and represent the energy saddle-point corresponded to transition states. The stationary points on potential energy surface (PES) relate to the free energy. In order to accurately determine reaction energy barriers, the Gibbs Free Energy of species was calculated both for solvated (aqueous) and non-solvated (gas phase) systems. We calculate the Gibbs free Energy according to the reaction pathways through the equation: $G = H - T S$. In the equation, G stands for Gibbs free energy, H stands for the enthalpy of the reaction, T stands for the temperature in unit [K] and S stands for the entropy of the reaction. Measuring stationary points provides the lowest potential energy on the PES, so that we can estimate the free energy based on free energy corrections.

IV. RESULTS

Table 1: Summary of Interesting Transition States.

	H Bond Length (Å)	Bond Angle (°)
R, R-T2MBS (stringfile 3)	1.84	128.8
	1.86	
R, R-T2MBS (stringfile 13)	N/A	118.3
R, R-T2MBS (stringfile 17)	1.57	116.1
R, R-T2MBS (stringfile 27)	1.75	118.1
S, R-T2MBS (stringfile 6)	1.68	124.3
	1.74	
R, R-T3MBS (stringfile 11)	N/A	118.4
S, R-T3MBS (stringfile 14)	N/A	123.7
S, R-T3MBS (stringfile 24)	1.86	132.5

Figure 5: The Transition States of IEPOX Reacts with Sulfate.



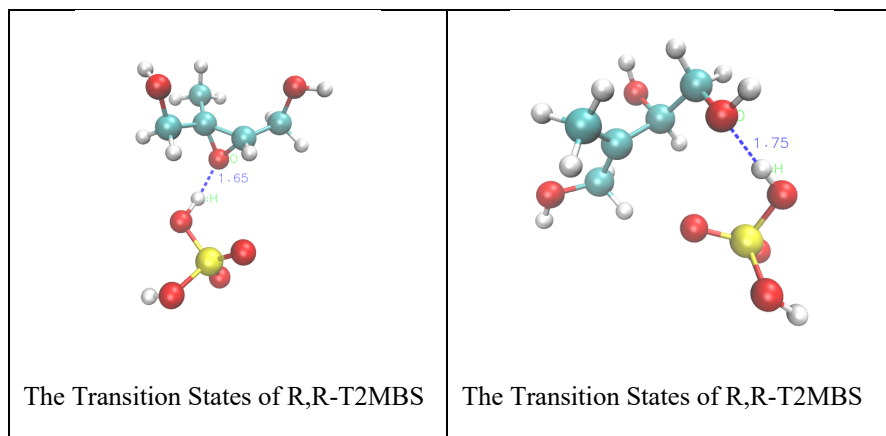


Figure 6: The Transition States of IEPOX Reacts with Sulfate.

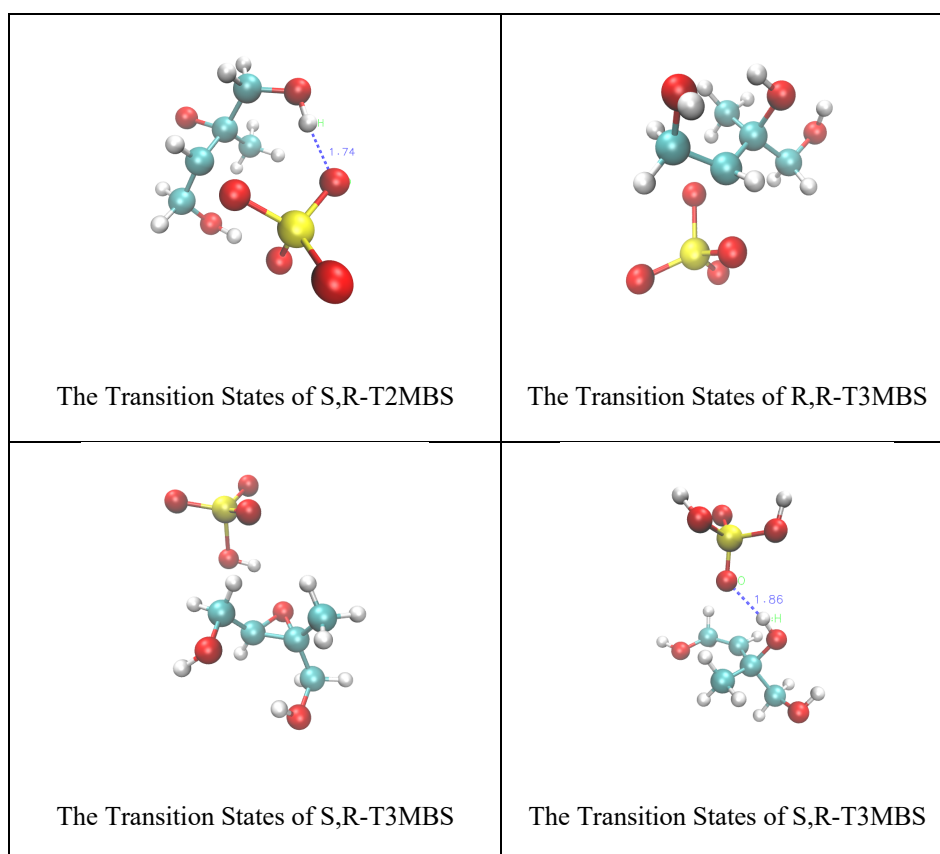


Figure 7: The Energy Diagram of the Transition States.

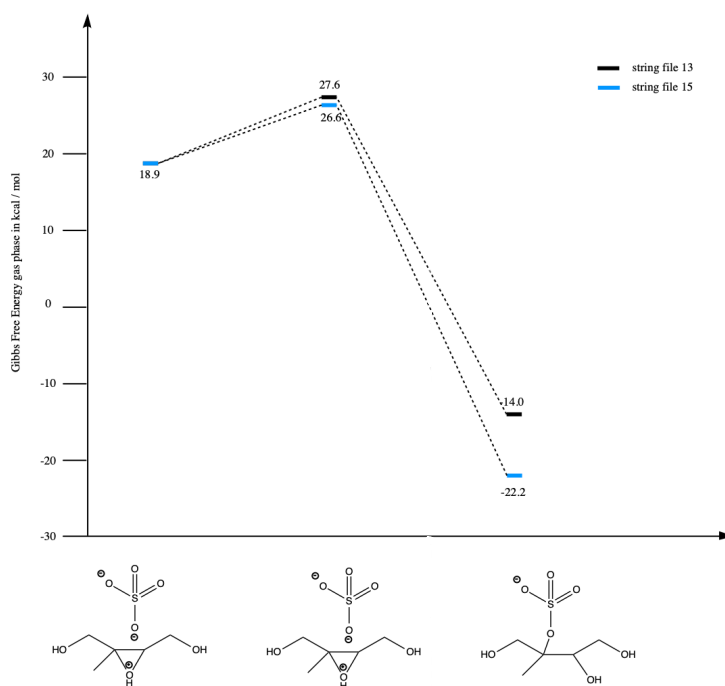
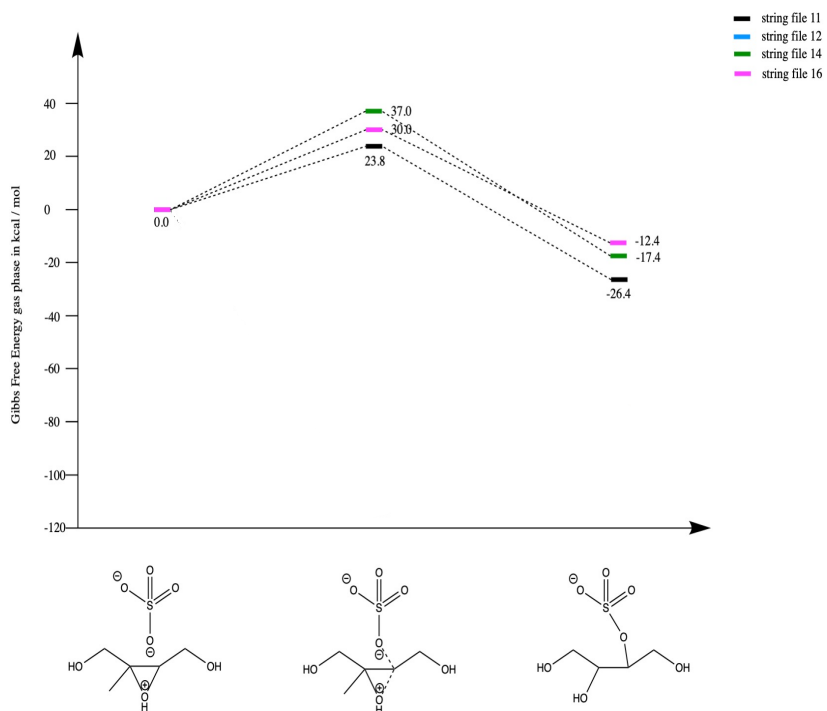


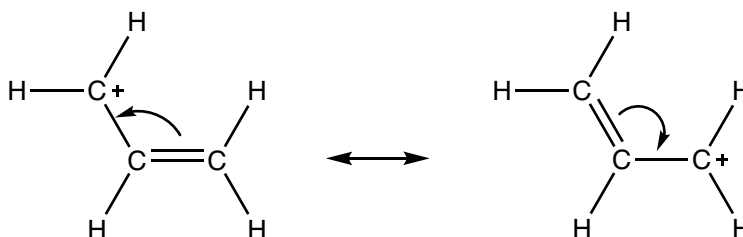
Figure 8: The Energy Diagram of the Transition States.



V. DISCUSSION

Transition states are important to reaction analysis as they can help to explain the formation of final products. The summary table listed above contains some interesting transition state structures. Figure 5 represents the transition states for product R, R-T2MBS, figure 6 represents the transition states for product S, R-T2MBS, R, R-T3MBS and S, R-T3MBS. From Table 1, most of the angle of the carbon bonds in transition states are close to 120° , generally sp^2 carbon forms trigonal planar structures. sp^2 carbons contain more delocalized electrons, enhancing the stability of the transition state (Figure 9).

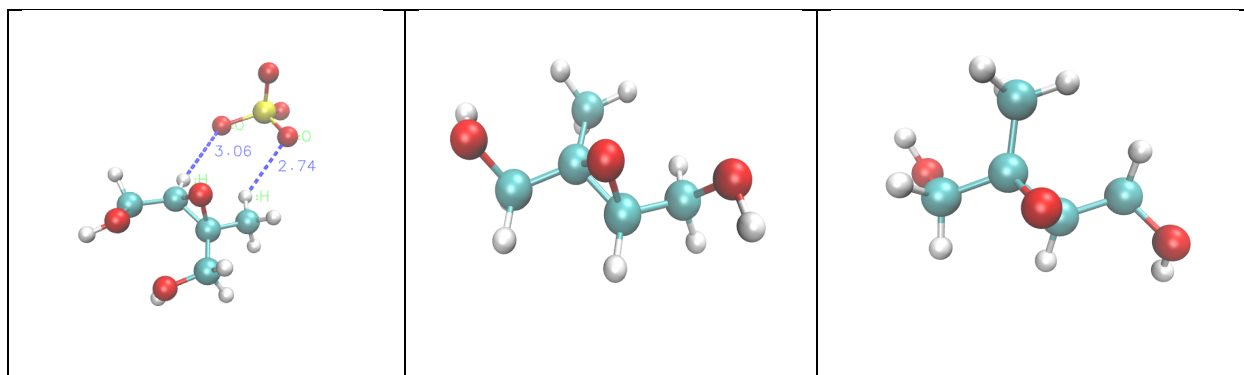
Figure 9: Resonance structure of sp^2 carbon to show that it contains more delocalized electrons and stabilizes the structure.



Transition states have a range of activation barriers: the highest activation energy (E_a) is 37.0 kcal/mol and the lowest E_a is 23.8kcal/mol (Figure 8). Another possible stabilizing feature of IEPOX is the ability to form hydrogen bonds with other molecules. For those transition states that do not contain hydrogen bonds, the transition state energy is relatively high (Figure 7 and 8). This would indicate that hydrogen bonds play a role in transition state stability. The orientation of IEPOX hydroxide groups limits specific avenues in which hydrogen bonds can form (Figure 10): only the first structure can form both the sulfate reaction and hydrogen bonds, and it has a

clear steric pocket guiding towards the hydrogen side of the less substituted carbon. For the other two structures, either only one of the hydrogen bonds is available during the reaction or neither are, and they do not contain a clear steric pocket. This might provide some indication as to why unexpected directional preference is observed.

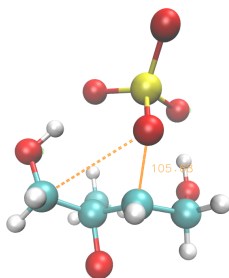
Figure 10: Images showing that only certain orientations are accessible for hydrogen bonds.



Most of the transition states of product R, R-T2MBS and S, R-T2MBS contain a H bond, and some of them contain two. Furthermore, most of the angles of carbon bonds are around 120° . Looking at the transition states of product R, R-T2MBS (Figure 5), even though they have sp^2 carbons which stabilize the transition states, the energy diagram (Figure 7 and 8) shows that the transition energy is relatively high. This would indicate that the electronic interaction is dominated by the stability of the transition states of product R, R-T2MBS (Figure 5). Looking at the transition state of product S, R-T2MBS (Figure 6), the hydrogen bonds stabilize the transition state structure. However, it requires a larger carbon bond angle (124.3°) so that it can prevent steric hinderance. This would indicate that the loss of sp^2 hybridization is contributor to the destabilizing of the transition state (Figure 11). Since there are more transition states for R, R-

T2MBS product, the yield of R, R-T2MBS is larger than that of S, R-T2MBS. Given these details, it would seem that sp^2 hybridization is a must for TS stability, and that further stability from hydrogen bonding is only possible when the loss of sp^2 doesn't occur.

Figure 11: The improper torsion to show the loss of sp^2 hybridization for the transition state of product S, R-T2MBS.



For the transition state of product R, R-T3MBS (Figure 6), it does not contain hydrogen bonds, but it involves sp^2 carbon with an angle of 118.4° . For the transition states of product S, R-T3MBS (Figure 6), they contain both hydrogen bonds and sp^2 carbons. Therefore, the transition states of product S, R-T3MBS are less stable than those of R, R-T3MBS. Besides, the transition state structure of product R, R-T3MBS contains more steric repulsion which further destabilize the structure. As a result, the formation of product S, R-T3MBS is more favored with higher yield.

Overall, both hydrogen bond formation and sp^2 carbon stabilize the transition states, and the protonated sulfate is prone to a high energy barrier (but energetically favorable) proton transfer to the deprotonated IEPOX in some geometries. Additionally, the trigonal planar geometry is

more favorable with 3 carbons (more substituted carbon) than with 2 carbons and a hydrogen (less substituted carbon).

VI. ACKNOWLEDGEMENTS

First, I would like to sincerely thank Dr. Paul Zimmerman for giving me mentorship, support, and this precious opportunity to conduct research in his laboratory about physical organic chemistry for the last two years. It is his suggestions that draw my attention and make things much clearer. Without his help, the thesis would not been the current form.

I am also especially grateful for Timothy Raz Jugovic, a graduate student in Dr. Zimmerman's lab, for answering a large amount of my questions, working closely with me, helping me to grow on a personal and professional level. It has truly been a privilege to study with them, and I have no doubt that the I've gained plenty of skills and learned some new knowledge that will prove to be valuable in all my future endeavors.

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