Effect of Nucleation Precursors on the Atmospheric Oxidation of Organic Compounds

J. Elm[1], M. Bilde[2], K. V. Mikkelsen[1]

[1]Department of Chemistry, University of Copenhagen, Copenhagen, Universitetsparken 5, 2100, Denmark
[2]Department of Chemistry, Aarhus University, Aarhus, Langelandsgade 140, 8000, Denmark
Keywords: Nucleation, QM, Kinetics, SOA.
Presenting author email: elm@chem.ku.dk

The goal of this work is to determine the effect of common aerosol precursors H_2O, NH_3 and H_2SO_4 on the OH initiated oxidation mechanism of volatile organic molecules in the atmosphere. We use methanol as a model compound due to its relatively high atmospheric abundance and long residence time. We have investigated the interaction between methanol and each of the molecules H_2O, NH_3 and H_2SO_4 to assess cluster stabilities. This has been done by calculating statistical Gibb's free energies of formation. Subsequently the effect of the aerosol precursors on the reaction rate and mechanism of hydrogen abstraction reactions by the OH radical have been calculated.

Theory

To evaluate the rate constant of the i'th hydrogen abstraction conventional transition state theory is applied:

$$k_i = \sigma_i \kappa_i(T) \frac{k_B T}{h} \frac{Q_{TS,i}}{Q_R Q_{OH}} \exp\left[-\frac{\Delta E_i^{\ddagger}}{k_B T}\right]$$

The tunnelling correction κ_i is evaluated using an asymmetrical Eckart barrier. σ_i is the symmetry factor which denotes the reaction path degeneracy. From the individual rate constants the total rate constant (k_{total}) and branching ratio (Γ_i) can be calculated.

Methodology

To systematically scan the configurational space each nucleation step was performed by adding 1000 randomly oriented nucleate molecules (H_2O, NH_3 and H_2SO_4) randomly distributed around the target methanol molecule/complex. The 1000 generated structures were geometry optimized using the semi-empirical PM6 method to yield initial guesses. The identified conformations were then optimized with M06-2X/6-311++(3df,3pd) to yield the final structures. All local minima within 3 kcal/mol of the identified "global" minima were then thermally averaged to calculate the statistical Gibb's free energy of formation. For calculating the rate constants and branching ratios BH&HLYP/aug-cc-pVTZ geometries and frequencies were used. The single point energy was corrected with a high level explicitly correlated Coupled Cluster Singles Doubles with perturbative triples CCSD(T)-F12a calculation using the VDZ-F12 basis set.
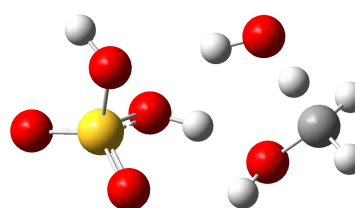

Figure 1: Transition state structure of C-H hydrogen abstraction by the OH radical from methanol in the $(CH_3OH)(H_2SO_4)$ complex.

Conclusions

The interaction between methanol and H_2O/NH_3 is found to be thermodynamically unfavourable suggesting that neither water nor ammonia catalyse the gas phase reaction of methanol with the OH radical.. We find that methanol is able to form stable complexes with H_2SO_4 which is more favourable than the corresponding hydrate. The incorporation of methanol into a pre-nucleation cluster does not hinder the subsequent addition of nucleation precursors. Due to stabilization of the transition state complex trough hydrogen bonding the complex formation is found to be able to both catalyse and change the reaction mechanism of the hydrogen abstraction reactions of methanol by the OH radical depending on collision mechanism. This intriguing result indicates that complex formation with sulfuric acid is able to alter the reaction mechanism of a simple organic compound by acting as a stabilizing scaffold and it thereby indicates an alternative new pathway for oxidation products of various organic compounds.