

Oxidation of HULIS in atmospheric aerosols

M. D. King and O. R. Hunt

Department of Earth Sciences, Royal Holloway
University of London, Egham, Surrey TW20 0EX, UK

Contact | m.king@es.rhul.ac.uk

Introduction

Particulate matter in the atmosphere (aerosol) is a critical component of the Earth's climate system and has a significant impact on climate change^[1]. Aerosol may affect the climate directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei, CCN, and thus inducing cloud formation. Clouds can reduce the incident radiation reaching the Earth's surface, increase solar heating, and suppress rainfall. The concentration and chemical composition of particulate matter forming aerosol may thus alter the water cycle, which in turn affects the quality and availability of fresh water; a global issue.

The effect of aerosol on radiative properties and cloud formation was identified by the intergovernmental panel on climate change, IPCC,^[2] to be the largest uncertainty in assessing the impact of particulate matter on climate^[2]. The effect of inorganic aerosol on cloud formation has been examined and that of organic aerosol has started to be addressed (indirect aerosol effects were reviewed by Lohmann and Feichter^[3]), but yet to be well explored.

HULIS

The term HULIS (HUmic LIke Substances) has been used to describe the organic material found in rain, fog and aerosol that resembles the organic material in river/sea water and soils. HULIS is probably formed in aerosol as opposed to river water and soils where Humic material is formed by biological breakdown of biological material. HULIS may be present in as much as 20-50% of aerosol particles^[4]. The reports of HULIS in cloud, fog and aerosol is reviewed by Graber and Rudich^[4]. Humic and HULIS material can be frustrating to chemically characterise, because HULIS and humic material defies speciation and molecular definition owing to its complexity, size and non-uniformity. However, consensus is now forming on a HULIS model structure consisting of an aromatic core bearing substituted aliphatic chains with -COOH, CH₂OH, -COCH₃ groups^[5]. Indeed one study found HULIS was composed of n-alkanoic acids w-alkenoic acids, benzoic mono- di-, and tri- carboxylic acids, methoxy and acetic and methoxy benzoic acid and few N containing glycerine derivatives^[6]. Kiss *et al.*^[7] attempted to determine the 'size' of a HULIS 'molecule' and suggested 40-520 Da. Sources of HULIS include a small terrestrial, marine, biomass burning and secondary aerosol formation (condensation, reaction and oligomerization). The last route to HULIS is intriguing

A. D. Ward

Central Laser Facility, STFC, Rutherford Appleton
Laboratory, HSIC, Didcot, Oxon OX11 0QX, UK

C. Pfrang

Department of Chemistry, The University of Reading,
PO Box 224, Whiteknights, Reading RG6 6AD, UK

and HULIS has been shown to be formed by reaction of OH radical with 3,5-dihydroxybenzoic acid on the time scale of hours to days^[6] by oligomerization. Oxidation or the presence of HULIS in cloud, fog and aerosol may have a droplet activation (cloud forming) effect as studied by Dinar *et al.*^[8] Droplets containing HULIS were found to activate at lower diameters and thus make cloud formation more facile. Dinar *et al.*^[8] also found that HULIS extracted from daytime filter samples has a lower critical supersaturation diameter than nighttime samples. This strongly suggests the reaction with daytime atmospheric oxidants to be important in oxidising HULIS and to increase the hygroscopic properties of cloud droplets. Thus the reactions between HULIS and atmospheric oxidants such as ozone need to be studied to determine if they (1) lower the critical supersaturation required for cloud formation and (2) form oligomers. The rate for these reactions must be quantified to determine if they are atmospherically important.

Experimental

Aerosols were generated by ultrasonically nebulising a solution of HULIS type molecule in either water or organic solvent (dodecane) each aerosol trapped typically has a concentration of ~0.2-1M. The aerosols were mixed with a humidified stream of nitrogen (RH ~95%) and oxygen and blown into a small aluminum chamber on the focus stage of an optical microscope. A droplet (3-15 μ m diameter) was trapped in the focus of an argon-ion laser ($\lambda=514.5$ nm, ~7 mW at the point of focus). The remaining particles were flushed from the cell. The scattered laser radiation was collected and analyzed on a spectrometer via a notch filter. Spectra were recorded over 5-10 second timescales continuously. The particle in the laser trap was illuminated with an optically filtered microscope light onto a CCD via the microscope optics to provide an optical image of the particle. A still image was recorded every 10-30 seconds in order to size the droplet.

A typical experiment would monitor the size and Raman signal of the droplet for a few minutes and then the oxygen flow would be subjected to a Hg pen-ray lamp to produce a sub picomolar concentration of O₃ in the chamber. The reaction was monitored until there was no discernable HULIS remaining in the Raman spectra. Experiments were also undertaken without ozone present. Raman spectra were used to detect possible products; containing the peroxide (-O-O-) and carbonyl (RC=O) groups.

Analysis

The reaction between a gas-phase oxidant i.e. ozone and an organic compound dissolved in a droplet is measured by the uptake coefficient, γ , which is the ratio of reactive collisions to un-reactive collisions for ozone with the droplet. The uptake coefficient depends on the rate of mass transfer of ozone to the droplet, Γ_g , the accommodation of the ozone at the air-droplet interface, α , the competing process of diffusion of ozone and reaction in solution in the droplet Γ_{sol} and Γ_{rxn} . The uptake coefficient can be calculated from

$$\frac{1}{\gamma_{net}} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{rxn} + \Gamma_{sol}}$$

Depending on the relative values of these processes the uptake equation can be solved to calculate the uptake coefficient.

Results

We report here our ongoing analysis of this work by focusing on the oxidation of squalene (a tri-terpene, $C_{30}H_{50}$ ubiquitous in the biosphere) by ozone. Figure 1 demonstrates the exponential decay of squalene in the particle mirrored by rises in products containing peroxide and carbonyl moieties. These moieties suggest the stabilized Criegee intermediate^[9] is reacting with the dodecane and products of the reaction. The peroxide moiety may suggest oligomer formation^[12]. Peroxide and oligomer formation will prevent carboxylic acid formation and the particle will not become activated, i.e. will not uptake gas-phase water and will not grow in size.

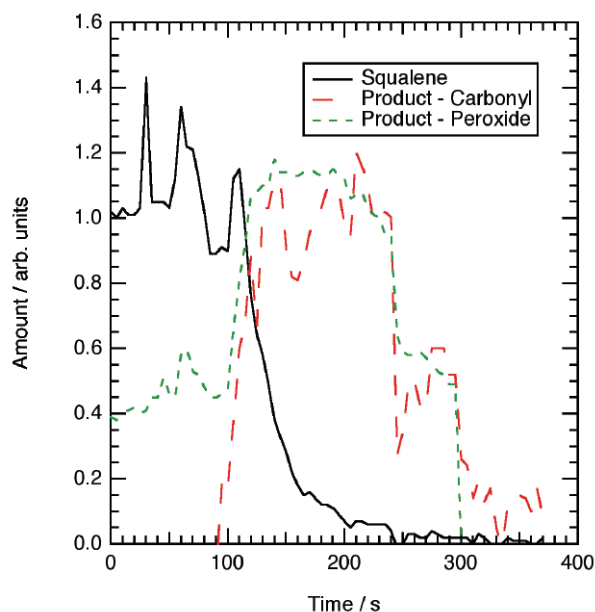


Figure 1. Amount of squalene and product peaks present in a particle of squalene and dodecane that is oxidized by gas-phase ozone. The ozone is added at a 100 s and the squalene decays to be replaced by products containing carbonyl and peroxide bonds.

The kinetics of the ozonolysis may also be analyzed to interpret mechanism^[10,11]. The diffuso-reactive length (the characteristic distance an ozone molecule will diffuse into the droplet before reacting) is ~80 nm, suggesting reaction of ozone at or near the surface of the particle. Figure 2 demonstrates a linear relationship exists between the logarithm of the concentration of squalene and the reaction time suggesting reaction at the surface of the particle. A linear relationship between the square root of the squalene concentration and time would have suggested reaction near the surface of the particle.

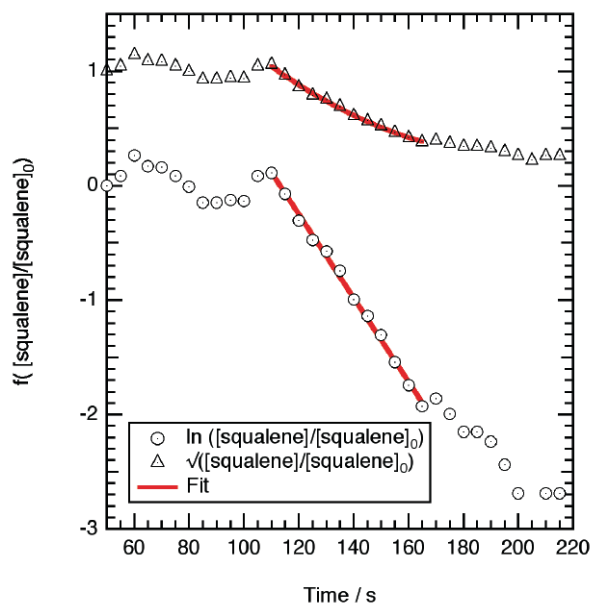


Figure 2. Kinetic analysis of the temporal profile of the squalene data demonstrates a surface reaction.

Further analysis may demonstrate a Langmuir-Hinshelwood dependence. The value of the slope of the line in figure 2 can be used to estimate an uptake coefficient of ozone on the particle of 0.003, reasonable large for an organic reaction and will be of atmospheric importance^[12].

Conclusions

- Oligomer formation in atmospheric droplets may be occurring producing higher molecular weight species that may be interpreted as HULIS in atmospheric measurements.
- The reaction between squalene and ozone occurs at the surface of the particle and not within it.
- Stabilized Criegee intermediates are forming peroxide species and not re-arranging to form carboxylic acid species. The reaction of ozone on these particles is not likely to form a cloud droplet through hygroscopic growth.

Acknowledgements

We are very grateful to the CLF, Rutherford Appleton Laboratory, UK for grant CM4E1/07. This work was in part supported by NERC CASE award NER/S/U/2006/14253.

References

1. R. J. Charlson, J. H. Seinfeld, *et al.*, *Science* **292** (5524): 2025-2026 (2001); V. Ramanathan, P. J. Crutzen, *et al.*, *Science* **294** (5549) (2001): 2119-2124; F. M. Breon, D. Tanre, *et al.*, *Science* **295** (5556) (2002): 834-838; M. Ammann, U. Pöschl and Y. Rudich, *Phys. Chem. Chem. Phys.*, **5**, 351 (2003); U. Pöschl, *Angew. Chem. Int. Ed.*, **44**, 7520 (2005); S. Fuzzi, *et al.*, *Atmos. Chem. Phys.*, **6**, 2017 (2006).
2. IPCC 2007 climate change reports CUP.
3. U. Lohmann and J. Feichter, *Atmos. Chem. Phys.*, **5**, 715 (2005).
4. E.R. Graber and Y. Rudich, *Atmos. Chem. Phys.* **6**, 729-753 (2006).
5. S. Decesari, M. C. Facchini, S. Fuzzi and E. Tagliavini, *J. Geophys. Res., D*, **105**, 1481-1489 (2000).
6. Gelencser *et al.*, *J. Atmos. Chem.* **37**, 173-183 (2000); Gelencser *et al.*, *J. Atmos. Chem.* **45**, 25-33 (2003).
7. G. Kiss, *et al.*, *Atmos. Environ.* **37**, 3783 (2003).
8. E. Dinar, *et al.*, *Atmos. Chem. Phys. Discuss.* **6**, 1073-1120 (2006).
9. Criegee. *Angew Chem Int Edit.* **14**, (11) 745-752 (1975).
10. M. D. King, K.C. Thompson and A.D. Ward, *J. Am. Chem. Soc.* **126**, 51 16711 (2004).
11. G. D. Smith, E. Woods, C. L. DeForest, T. Baer and R. E. Miller, *J. Phys. Chem. A*, **106**, 8085-8095 (2002).
12. M. D. King, K. C. Thompson, A. D. Ward, C. Pfrang and B. R. Hughes, *Faraday Discussions* **137**, 173-192 (2008).