

Effect of Organic Coatings on the Heterogeneous Reactivity of Ozone with Particle-Borne PAHs

Shouming Zhou *, Alex Lee, Robert McWhinney and Jonathan Abbatt

Department of Chemistry, University of Toronto, Toronto, ON M5S 3H6, Canada

* Email: szhou@chem.utoronto.ca



Introduction and Goals

- A dominant fraction of atmospheric aerosol is known to be composed of organic substances. The physical and chemical properties of organic aerosol, e.g. hygroscopicity, density, toxicity and composition, can be affected by atmospheric oxidative 'aging' (1,2). However, the oxidation rate and mechanism remain poorly understood.
- Both field and laboratory studies show evidence that heterogeneous reactions contribute to aerosol aging (2,3). However, it is not clear if the multi-phase reactions in the particle following heterogeneous uptake of reactive species (such as OH, NO₃ and O₃) contribute to the aerosol aging process.
- It is now well recognized that surface-bound PAHs react rapidly under atmospheric oxidant conditions. However, it is not known how the organic coatings that initially bury/dissolve the PAHs affect the reactivity towards the oxidants.
- In the present work, we are expanding upon recent studies of the reactions between O₃ and particle-borne PAHs conducted by both our group and others (4-12). **The goals of this work are to: 1) investigate the kinetics on the heterogeneous/multi-phase reactions of PAHs with ozone using Aerodyne aerosol mass spectrometry (AMS); 2) explore the effect of different coating materials (solid and liquid) on the reactivity of PAHs towards ozone and 3) understand the degree to which this reactivity is suppressed or enhanced by the organic coatings.**

Experimental Setup

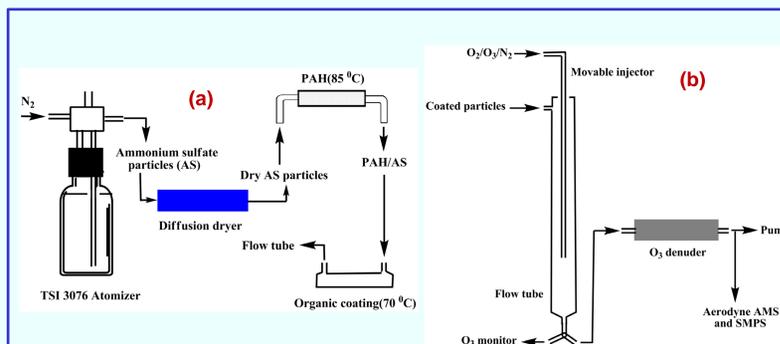


Figure 1. Experimental setup

- (a) Particles generated from atomization of ammonium sulfate, followed by coating with PAH and organics
- (b) Flow tube with movable injector and gas/particle-phase products analysis

- Particles were generated by atomizing 0.005% (w/w) ammonium sulfate (AS) solution;
- AS particles were first coated with benzo[a]pyrene (BaP) by passing AS through a heated glass tube (~85 °C) with inner wall coated with BaP;
- Two organics, i.e. bis(2-ethylhexyl) sebacate (BES, liquid at RT) or eicosane (EC, solid at RT) were chosen to coat BaP/AS. BES was coated by placing the BaP and BES in the same glass tube; while EC was coated by passing BaP/AS particles through another heated glass tube (70 °C) where the EC was placed;
- Particle size distribution and particulate-phase BaP concentration were measured by a scanning mobility particle sizer (SMPS) and Aerodyne aerosol mass spectrometer (AMS), respectively. Particle size distributions of different species were also measured by the P-TOF mode of the AMS.

Results and Discussion

Kinetics on Heterogeneous Reaction of Ozone with Benzo[a]pyrene (BaP)

- Figure 1 gives the size distributions of ammonium sulfate and coating organics measured by P-TOF mode of the AMS.
- It is clear from Figure 1 that the AS particles are coated with BaP, BES and EC. The same distributions of BaP and EC with AS (Figure 1 (c)) may be due to a re-distribution of BaP after passing through the second heating tube. Measurement suggests a sub-monolayer coating of BaP on AS particles and a 5-10 nm coating of BES/EC under assumption that the AS particles are uniformly coated.
- An example of sulfate and BaP concentrations along the flow tube during O₃ exposure are shown in Figure 2 (a) and the corresponding kinetic plot is given in Figure 2 (b), suggesting a first-order loss of BaP by gas-phase ozone. The pseudo-first-order rate coefficient is derived from the slope of the plot. The BaP (m/z252 signal) concentration is normalized with SO₄ in the kinetic measurements.
- Figure 3 plots the pseudo-first-order rate coefficients as a function of gas-phase ozone concentrations. The plots indicate the Langmuir-Hinshelwood reaction mechanism for all three type of experiments. The data are, therefore, fit with the Langmuir-Hinshelwood mechanism and the fitting parameters provide adsorption equilibrium constants (K_{O₃}) and maximum pseudo-first-order rate coefficients (k¹_{max}).

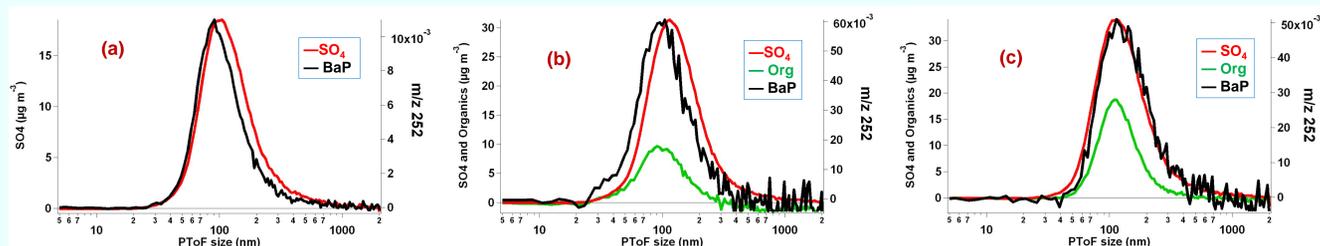


Figure 2. Size distributions of ammonium sulfate (SO₄) and coated organics measured by P-TOF mode of the AMS. (a) AS+BaP; (b) AS+BaP+BES and (c) AS+BaP+EC

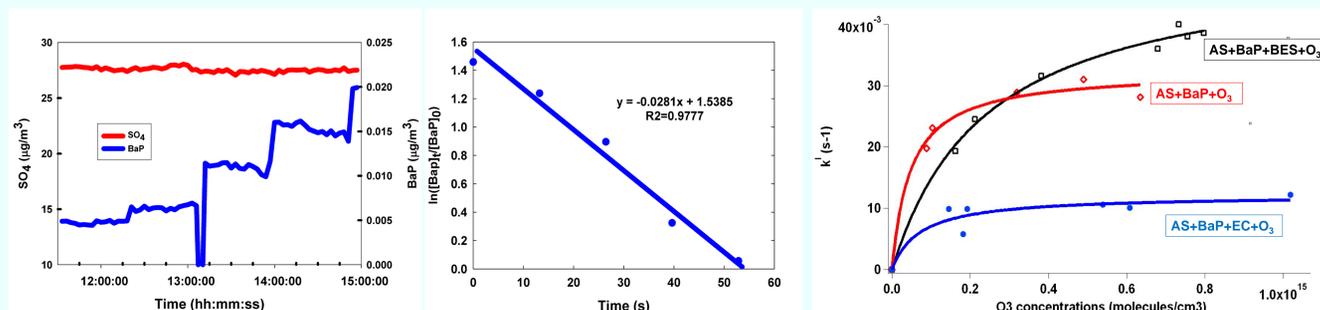


Figure 2. (a) Examples of the sulfate and BaP concentrations during the ozonolysis reaction; (b) Corresponding kinetic plot. The pseudo-first-order rate constant is derived from the slope of the plot.

Figure 3. Pseudo-first-order rate coefficients as a function of gas-phase ozone concentration. The data are fit with Langmuir-Hinshelwood mechanism.

Table 1. Comparison of experimental maximum pseudo-first-order rate coefficients (k¹_{max}) and adsorption equilibrium constants (K_{O₃}) obtained from this work with those of previous studies

Substrate	k ¹ _{max} (s ⁻¹)	K _{O₃} (10 ⁻¹⁵ cm ³)	Ref.
Soot aerosols	0.015 ± 0.001	280 ± 20	(7)
Phenylsiloxane oil aerosols	0.010 ± 0.003 ^{a)}	100 ± 40	(8)
Aqueous NaCl droplets		40 ± 30	(9)
Self-assembled monolayers		25	(10)
Azelaic acid aerosols	0.048 ± 0.008	1.2 ± 0.4	(4)
Octanol thin films	0.0055 ± 0.0002	0.36	(11)
Water		0.466	(12)
Ammonium sulfate (AS)	0.032 ± 0.002	21.0 ± 5.0	This work
AS+BES	0.051 ± 0.002	4.1 ± 0.5	This work
AS+EC	0.012 ± 0.002	13.9 ± 9.8	This work

a) Measurement of anthracene with O₃

Effect of Coatings on Reactivity of PAH towards Ozone

- The present work is the first use of AMS to study kinetics of sub-monolayer PAH reaction with ozone.
- The maximum pseudo-first-order rate coefficients (k¹_{max}) obtained in this work are similar to previous studies (Table 1), except for that reported by Kahan et al. (11), whose k¹_{max} is 2-10 times lower than others. The reason for such a discrepancy is not known.
- Ozone adsorption equilibrium constants (K_{O₃}) are varying by orders of magnitude depending on the surface available for ozone to adsorb (Table 1). Much higher K_{O₃} values for aromatic surfaces (7,8) suggest that O₃-aromatic binding may be significant.
- The relatively low k¹_{max} for AS+EC compared to that for AS and AS+BES of this work indicates a small suppression of BaP reactivity towards ozone, which might be due to the BaP burial with EC coating. However, we are not able to provide direct evidence of the burial so far. Further studies are, therefore, needed.

Acknowledgement

Financial support of this work by NSERC (Canada) is gratefully acknowledged. Thanks to Jay Slowik and Rachel Chang for their assistance in AMS setting-up and operation.

Literature

- Rudich, Y.; Donahue, N.M.; Mentel, T.F. *Annu. Rev. Phys. Chem.* **2007**, *58*, 321.
- Jimenez, J.L.; Canagaratna, M.R.; Donahue, N.M. et al. *Science*, **2009**, 1525.
- George, I. J.; Abbatt, J.P.D. *Nature Chem.*, **2010**, *2*, 713.
- Kwamena, N.A.; Thornton, J.A.; Abbatt, J.P.D. *J. Phys. Chem. A* **2004**, *108*, 11626.
- Alebic-Juretic, A.; Cvitas, T.; Klasinc, L. *Environ. Sci. Technol.* **1990**, *24*, 62.
- Wu, C.-H.; Salmeen, I.; Niki, H. *Environ. Sci. Technol.* **1984**, *18*, 603.
- Pöschl, U.; Letzel, T.; Schauer, C.; Niessner, R. *J. Phys. Chem. A* **2001**, *105*, 4029.
- Kwamena, N.A.; Staikowa, M.G.; Donaldson, D.J.; George, I.J.; Abbatt, J.P.D. *J. Phys. Chem. A* **2007**, *111*, 11050.
- McNeil, V.F.; Wolfe, G.M.; Thornton, J.A. *J. Phys. Chem. A* **2007**, *111*, 1073.
- Dubowski, Y.; Veciel, J.; Tobias, D.J.; Gomez, A.; Lin, A.; Nizkorodov, S.A.; McIntire, T.M.; Finlayson-Pitts, B.J. *J. Phys. Chem. A* **2004**, *108*, 10473.
- Kahan, T.F.; Kwamena, N.A.; Donaldson, D.J. *Atmos. Environ.* **2006**, *40*, 3448.
- Mmerekhi, B.T.; Donaldson, D.J. *J. Phys. Chem. A* **2003**, *107*, 11038.

Future Work:

- In order to compare kinetic results from different approach experiments on the reaction of O₃ with AS+BaP coated with aromatic material, e.g. phenylsiloxane oil (PSO), will be performed using the same set-up as this work.
- Comparison of the results from this work with those from a different coating process, i.e. coating homogeneously nucleated BES or EC with BaP, may provide more indirect evidence for the PAH burial, hence provide more information on the effect of coating materials on the reactivity of PAH towards O₃.