Real-time monitoring of the ozonolysis of unsaturated organic monolayers

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The reaction of ozone with unsaturated organic molecules at the air–water interface of a pendant drop was followed by axisymmetric drop shape analysis (ADSA).

Organic monolayers have been widely used as simple models to represent and resemble complex real systems. For instance, the study of the oxidation of unsaturated organic monolayers is the scope of several studies aimed at understanding how organic aerosols are processed in the atmosphere.[1]

Atmospheric aerosols comprise 10% organic content by mass as determined by aerosol field measurements.[2] The most suitable model to account for this composition is that of an inverted micelle which is described as a monolayer of organic molecules covering the air–liquid interface of the aqueous aerosol core.[3] Proof of the presence of this organic coating has also been reported by laboratory analysis of collected particles.[4] In addition, recent field measurements have described how physical properties of the aerosol depend on this organic content by calling attention to the surface activity of collected atmospheric organic aerosols.[5]

This type of particle is likely to be processed by atmospheric oxidants such as ozone molecules or hydroxyl radicals.[3] This process would bring, as a consequence to climate, a higher absorption and scattering of solar light by the chemically processed monolayer of these particles, an increase of the radicals and oxidants budget of the atmosphere and a probable water adsorption and consequent growth of the particle.[3,6,7] The latter can lead to the aerosol acting as a nucleus for cloud condensation.

At the laboratory level, the characteristics and properties of atmospheric aerosols are difficult to simulate due to their complexity.[1] Numerous aerosol proxies are described in the literature which are chosen according to the purpose of the research and the instrumentation available. These proxies include frozen and non-frozen bulk liquids, self-assembled monolayers, monolayers on Langmuir troughs, and laboratory generated aerosols.[1] Recent studies have also used droplets as feasible proxies to investigate aerosol properties.[8] More specifically, King *et al.*[9] studied the oxidation by ozone of a mixed oleic acid–seawater droplet by following droplet size changes and the concentration of reactants and products by Raman spectroscopy. Other techniques, which are directly related to the selected proxy, have been applied as well to monitor the reaction of aerosols with atmospheric oxidants. Mass spectrometry and infrared spectroscopy are among the most frequently utilized techniques[1] for the analysis of the kinetics and mechanism of the reaction, as well as for the detection of reaction products.

The mechanism of the ozonolysis of alkenes has been described in the literature.[10] The formation of an unstable primary ozonide is followed by its decomposition to a Criegee intermediate together with either an acid or an aldehyde. A secondary ozonide is likely to form if the reaction takes place in an inert liquid phase. For example, the ozonolysis of oleic acid will produce as the most probable products a diacid and either nonanal or nonanoic acid, both with shorter chain lengths than the starting compound. Consequently, for a monolayer of oleic acid the overall effect would be a decrease in the surface activity regardless of the products of the ozonolysis. This reduction would also be proportional to the extent of the reaction.

For that reason, the ozonolysis of oleic acid was monitored by measuring the changes in surface pressure occurring as a result of monolayer processing. The reaction was carried out on a monolayer of oleic acid spread at the air–water interface of a pendant drop. The drop was placed in a reaction chamber into which a mixture of ozone in air was flowed (Fig. 1).

A PAT-1 surface tensiometer (Sinterface Technologies) was used to accomplish our objectives. This instrument acquires images of a pendant drop to obtain the coordinates of the drop profile which is fitted to theoretical Laplacian curves of known surface tension values.[11] This method, called axisymmetric drop shape analysis (ADSA), has been used before for the determination of drop surface area, drop volume, contact angles and surface tension, as well as for surface pressure–area isotherm measurements.[12] For the processing of an oleic acid monolayer by ozone, the instrument provides the possibility of real-time measurements of the surface tension while the drop surface area is simultaneously and precisely controlled. The surface tension values obtained for a drop of ultrapure water (Barnstead, 18.2 MΩ cm, pH 5.5–6.0) were used as reference.

A solution of oleic acid (Sigma-Aldrich) in chloroform (Fisher) of concentration 0.1 mM was first prepared. Known volumes of this solution were spread on the aqueous drop surface depositing a fatty acid monolayer. This was achieved by touching the drop surface with the tip of the syringe while delivering the spreading solution (Fig. 1, top). Once the chloroform had evaporated, isotherms of surface pressure versus molecular area were obtained by changing the drop volume and hence surface area.[12] The behaviour of the oleic acid monolayer was essentially identical to that observed using a traditional Langmuir film balance (data not shown). Small differences in the molecular areas obtained from the two techniques are a result of spreading effects, however reproducibility was attained.

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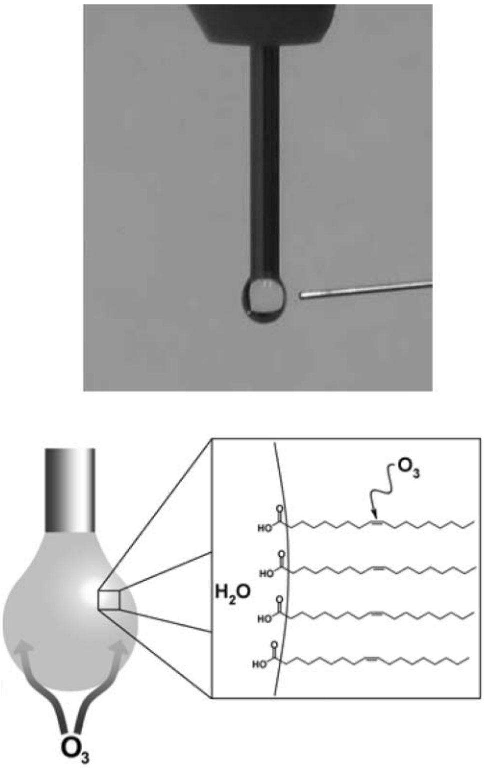

Fig. 1 Top: photograph showing approach of syringe to pendant drop. Bottom: schematic representation of the experimental setup in which a monolayer spread on a pendant drop is left to react with a mixture of ozone in air.

Fig. 2 shows the progress of the ozonolysis reaction. At first, 0.6 μL of the above mentioned oleic acid solution were spread on the drop surface. After spreading, the drop was left for 2 min outside and 3 min inside the reaction chamber before starting the experiment in order to permit drop equilibration and evaporation of the chloroform. At this point, air with no ozone was allowed to flow into the chamber. The drop surface area was initially set to 0.4 cm^2 for 1 min before the drop was gradually compressed at a rate of 6×10^{-4} cm^2 s^{-1} (0.13 $Å^2$ $molecule^{-1}$ s^{-1}). Compression was stopped at 0.2 cm^2 (around 0.01 cm^3 in volume) and the drop held at this surface area; this corresponds to a surface pressure of about 20 mN m^{-1}. When the surface pressure reached a stable value, ozone was allowed to flow into the reaction chamber (approximate volume of 28 cm^3) at a rate of 100 cm^3 min^{-1} and a concentration of about 8 ppm in air. The ozone was generated using a UV lamp and the concentration was measured directly before entering the chamber using an ozone monitor (2B Technologies). The plot of ozone concentration versus time is presented in Fig. 2 as a dotted-dashed line.

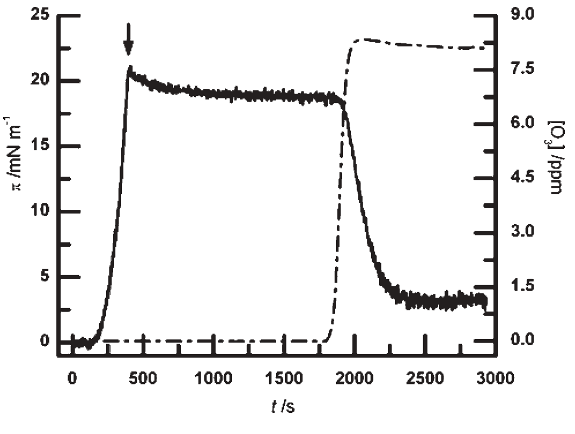

Fig. 2 Reaction of a monolayer of oleic acid on an aqueous drop (surface area 0.4 cm^2) with a mixture of 8 ppm O_3 in air flowed at 100 cm^3 min^{-1}: surface pressure π (—), ozone concentration (–·–). The arrow indicates the time at which compression was stopped, at a drop surface area of 0.2 cm^2. The monolayer was deposited using 0.6 μL of 0.1 mM oleic acid in $CHCl_3$ spreading solution.

An appreciable decrease in surface pressure was observed as soon as the mixture of ozone in air was allowed into the chamber. After less than 8 min, the surface pressure became constant at values close to zero which suggests that the reaction was complete. In addition, the final surface tension at the interface is close to that of water, which indicates that oleic acid completely reacted and that product molecules at the air–water interface have almost no surface active properties at the corresponding molecular area. In other words, the amount of product molecules present at the interface after reaction does not considerably decrease the surface tension of water at this particular drop surface area. As a control experiment, a monolayer of stearic acid (fully saturated) was exposed to identical experimental conditions and no changes in surface pressure were observed.

The importance of surface reaction kinetics in reactive gas uptake by aerosols has been highlighted in a recent review.[8] Previous spectroscopic studies have focused on the quantitative determination of reaction products as a function of time.[9,13,14] As the techniques utilized are not surface specific but rather bulk phase measurements, they enable the overall reaction to be followed, regardless of where the products reside (surface or liquid phase). Our pendant drop method provides a different perspective of the same system with complementary information, namely a continuous monitoring of the surface activity of the reactant–product mixture. The surface activities of individual components could additionally be determined by coupling of the pendant drop to a surface specific, reflectance spectroscopic technique such as PM-IRRAS or UV absorption or fluorescence. The application of glancing angle fluorescence measurements on a planar interface to monitor the reaction of an adsorbed layer of anthracene with ozone has previously been demonstrated.[15] We present here a much simpler experimental set-up which is applicable to a wide range of organic monolayer constituents including those that lack a chromophore and are not easily monitored spectroscopically, *e.g.* phospholipids or fatty acids. Furthermore, the surface pressure–area isotherms and interfacial rheology can be measured prior to, during and after exposure to ozone to evaluate the influence of the chemical reaction on these surface properties. Surface pressure–area isotherms can also be evaluated using a traditional Langmuir film balance set-up,[13,15] however these systems often have large headspace volumes and can require considerable time to reach constant ozone concentration.[13] This is a significant drawback for real-time monitoring of the surface ozonolysis reactions which exhibit relatively fast interfacial kinetics.[13,16–18]

The results obtained also permit a kinetic study of the reaction by relating the decrement of surface pressure to changes in surface concentration. This variable can be determined using the isotherms recorded previously, as has been described before.[19] Determination of kinetic parameters is then possible not only under the experimental conditions shown above but also with variation of drop surface area, gas flow rate, ozone concentration in air, and monolayer surface concentration. While an oleic acid monolayer has been used here as a proof of principle, this proxy can easily be modified to better reflect a real aerosol system. For instance, the ozonolysis of an organic monolayer of mixed composition at the air–water interface of an aerosol with any selected inorganic aqueous core is a practical and feasible experiment. In addition, the application of this system can be extended beyond ozonolysis to include processing of aerosols by competing atmospheric oxidants.[3] Thus, this system provides a means not only of measuring surface activity of aerosol constituents but also permits real-time monitoring of atmospheric processing reactions under a wide range of experimental conditions.

Notes and references

1 Y. Rudich, *Chem. Rev.*, 2003, **103**, 5097.
2 A. M. Middlebrook, D. M. Murphy and D. S. Thomson, *J. Geophys. Res.*, 1998, **103**, 16475.
3 G. B. Ellison, A. F. Tuck and V. Vaida, *J. Geophys. Res.*, 1999, **104**, 11633.
4 H. Tervahattu, K. Hartonen, V.-M. Kerminen, K. Kupiainen, P. Aarnio, T. Koskentalo, A. F. Tuck and V. Vaida, *J. Geophys. Res.*, 2002, **107**, D7.
5 S. Decesari, M. C. Facchini, S. Fuzzi, G. B. McFiggans, H. Coe and K. N. Bower, *Atmos. Environ.*, 2005, **39**, 211.
6 J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry & Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York, 1998.
7 C. N. Cruz and S. N. Pandis, *J. Geophys. Res.*, 1998, **103**, 13111.
8 P. Davidovits, C. E. Kolb, L. R. Williams, J. T. Jayne and D. R. Worsnop, *Chem. Rev.*, 2006, **106**, 1323–1354.
9 M. D. King, K. C. Thompson and A. D. Ward, *J. Am. Chem. Soc.*, 2004, **126**, 16710.
10 R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 745.
11 M. Hoorfar and A. W. Neumann, *J. Adhes.*, 2004, **80**, 727.
12 D. Y. Kwok, D. Vollhardt, R. Miller and A. W. Neumann, *Colloids Surf., A*, 1994, **88**, 51.
13 Y. Wadia, D. J. Tobias, R. Stafford and B. J. Finlayson-Pitts, *Langmuir*, 2000, **16**, 9321.
14 D. A. Knopf, L. M. Anthony and A. K. Bertram, *J. Phys. Chem. A*, 2005, **109**, 5579.
15 B. T. Mmereki and D. J. Donaldson, *J. Phys. Chem. A*, 2003, **107**, 11038.
16 J. A. de Gouw and E. R. Lovejoy, *Geophys. Res. Lett.*, 1998, **25**, 931.
17 T. Moise and Y. Rudich, *J. Phys. Chem. A*, 2002, **106**, 6469.
18 G. D. Smith, E. Woods, III, C. L. DeForest, T. Baer and R. E. Miller, *J. Phys. Chem. A*, 2002, **106**, 8085.
19 F. K. Hansen and R. Myrvold, *J. Colloid Interface Sci.*, 1995, **176**, 408.