Kinetic Double-layer Modelling of Aerosol Surface and Bulk Chemistry

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Abstract: This paper focuses on the kinetic double-layer model (K2-SUB). It has been established that models clearly resolve the mass transfer and chemical reactions at the surface and inside most aerosol particles. The K2-SUB is applied to the atmospheric heterogeneous chemical model system: the interaction of ozone and oleic acid. It can be used to model volatile and non-volatile substances at the gas-particle interface and inside the particle, time and concentration distribution, as well as surface concentration and gas absorption coefficient. Modelling the reaction of oleic acid particles- a proxy system for kitchen exhaust gas- with the atmospheric oxidant ozone (O_3) provides evidence that when the particle size of oleic acid gradually increases, the decay time of oleic acid in ozone is longer. K2-SUB is less sensitive to the surface reaction rate coefficient and the bulk reaction rate coefficient but is sensitive to the bulk diffusion coefficient of ozone and initial surface accommodation coefficient of ozone.

Keyword: Kinetic Double-Layer Model; Oleic Acid; Aerosol

1. Introduction

Oleic acid is an important component of atmospheric organic aerosols, a key model species that can predict the physical and chemical properties of aerosols (Reynolds et al, 2006). The reaction products of the ozonolysis of oleic acid are 1-nonanal, pelargonic acid, 9-oxonanoic acid and azelaic acid, resulting in a product with a shorter chain length than the starting molecule. Compared with oleic acid, these products become more soluble in water. Therefore, it can be inferred that when a single layer of oleic acid is exposed to ozone, the result will be a decrease in surface activity at the water-air interface. (González-Labrada, Schmidt and DeWolf, 2007). Oleic acid has always been a single-layer component of particular concern. Its main sources are anthropogenic organic emissions mainly produced by meat cooking (Shrivastava et al., 2007) and biological marine aerosols (Fu et al., 2013).

The atmospheric lifetime of volatile organic compounds largely depends on the reaction rate coefficient with NO_3, OH, and O_3 (McGillen, 2011). This paper focuses on the research models for simulating the reaction between ozone and pure oleic acid droplets in the laboratory. Aerosol surface material transport and the bulk chemical reaction results in the continuous conversion and change of atmospheric aerosol composition (Pöschl, 2005). The aerosol produced during the cooking process has a particular impact on urban aerosol. For example, acid particles emitted from kitchen cooking undergo a series of oxidation reactions with ozone. This study uses the model of the oxidation reaction of pure oleic acid particles with ozone to analyse the effects of aerosol surface material transport and bulk chemical reaction rate on the reaction process. By studying the decomposition products of oleic acid and ozone, Zahardis et al. (2008) found that a surface barrier is formed during the ozonolysis of oleic acid. This is a finding that is consistent with the actual observation data, because under very high concentrations of ozone, the oleic acid particles will not disappear completely, and the oleic acid will remain in the mixed particles (Zahardis, Geddes, & Petrucci, 2008).

For the study of the model, the kinetic two-layer model (K2-SUB) artificial resistor model is usually used to study and describe the chemical processes of homogeneous and heterogeneous reactions in the atmosphere and to simulate the real atmospheric reactions (King et al., 2009). Because the simple two-layer model needs to meet many objective conditions, it

presents the disadvantages and limitations mentioned above. Thus, to improve this deficiency, Pöschl, Rudich and Ammann (2007) designed a new kinetics model which is suitable for proton transfer and chemical reactions. The model, PRA framework (Pöschl, Rudich and Ammann, 2007), uses this model to create a universally applicable parameter and rate equation that solves the complexity of the original model.

Pfrang, Shiraiwa and Pöschl (2010) proposed that the K2-SUB double-layer model uses the formula of traditional resistors, which requires artificial simplifying assumptions, such as uniform mixing and steady-state. The overall diffusion is limited by the K2-SUB double-layer model. When compared with the multi-layer model in the literature, the two-layer models may overestimate the degradation rate and gas absorption rate of oleic acid, which bring some difficulties to the interpretation of the concentration distribution in oleic acid particles.

In this study, the experimental data (provided by Adam Milsom, doctoral student), was obtained from Raman spectroscopy. The data shows how oleic acid decays over time when exposed to the ozone. In this case, the ozone concentration is 52 ppm, which is much higher than the ozone concentration in the atmosphere (around 100ppb). What the above observation implies is that ozone reacts with C=C, and it is this double bond that gives the signal which is at ~ 1650 cm^{-1} in the Raman spectrum. All of the decays start at 1 because Adam's measurements are normalized to the initial amount of oleic acid. The ozone decomposition experiment was conducted with three different sizes of oleic acid particles. The experimental data is then normalised oleic acid concentration. The oleic acid concentration at each moment is divided by the initial oleic acid concentration (when t=0) to get the experimental data in this article (provided by Adam Milsom).

With regards to the reaction between oleic acid particles and ozone, this study mainly focused on the kinetic double-layer, which simulate the process of ozone oxidation of oleic acid. Changing the diameter of the model, for the exploration of the parameter factors that affect the model changes and can accurately reflect the oleic acid ozone reaction process. Currently this description may not be extended to the reaction process of aerosols and oxides in the atmosphere. Because of the limitations in this study, there is only experimental data (provided by Adam Milsom) of 52ppm ozone concentration. This article can only limit one type of ozone concentration increase. The problem is that the ozone concentration is high. Therefore, experiments with lower ozone concentration may be required in future work.

2. Methodology

The K2-SUB model is used to simulate the oxidation process of oleic acid particles with different particle sizes by ozone. This is achieved by changing specific parameters, studying the surface substance transfer and bulk chemical reaction in the oleic acid and ozone reaction. The concentration of the gas phase ozone was set to 52 ppm. The description of all the involved physicochemical processes is made possible by a general set of equations provided by the K2-SUB. The K2-SUB permits for the free variation of all pertinent parameters, particularly reaction rate and mass transfer coefficients.

As can be seen in Figure 1, layers and compartments form the volume and surface of the kinetic double model of aerosol. These layers and compartments include the gas phase, near-surface gas phase, quasi-static surface layer, near-surface bulk, and bulk. As is also illustrated in Figure 1, there are distances and model compartments from the core of the particles. In the same figure, the model species, transport fluxes are represented by the black arrows. The red arrows denote the chemical reactions. Particle radius is represented by rp while the effective molecular diameters and molecular layer thicknesses for volatile species X and non-volatile species Y are represented by δX and δY respectively. In the gas phase, the average X free path is represented by λx.
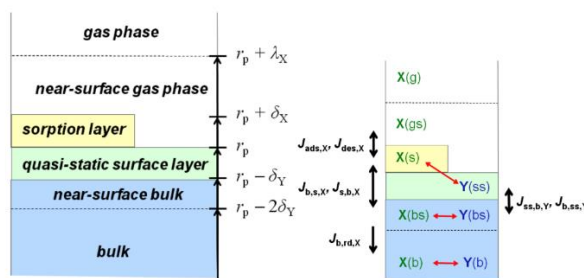

Figure 1　Kinetic double-layer surface model (K2-SUB) (Pfrang, Shiraiwa and Pöschl, 2010)

The K2-SUB model has a system of equations that mechanically describe time and a concentration-dependent absorption

of trace gas and particulate components in one or more systems of chemical and physicochemical processes. A scenario of a chemical reaction that changes with time is simulated, including the effects of reversible reaction adsorption, surface bulk transport, and chemical ageing on trace gases and solids.

3. Data Modelling Result

3.1 Data Collection

In this study, the experimental data (provided by Adam Milsom) shows how oleic acid decays over time when exposed to the ozone. Through learning the basic knowledge of Matlab, in this paper, I will try to change different model parameters, observe the model and experimental data fit. The parameter is the size of oleic acid particle size.
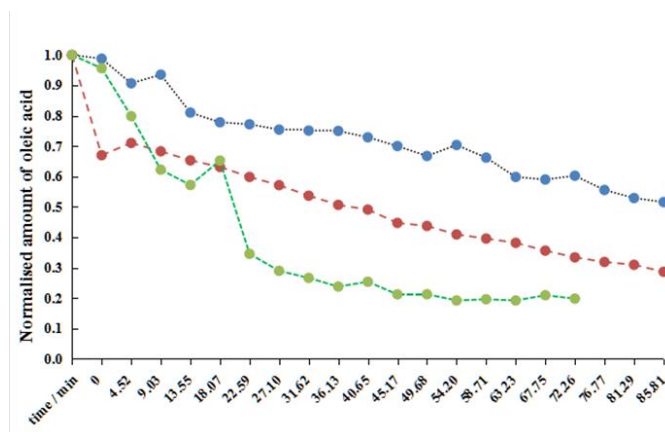

Figure 2   Decay process of 62.5μm、108μm and 200μm oleic acid with time in the laboratory. The experimental data is the normalized oleic acid concentration. The oleic acid concentration at each moment is divided by the initial oleic acid concentration (when t=0) to get the experimental data.

From Figure 1, it can be seen in the green line that the oleic acid particles with 62.5μm   show a significant downward trend with time. At about 14 minutes, the number of oleic acid particles increase significantly, and then immediately fall. And it can be noted that the oleic acid particles in the orange line, with a particle diameter of 108μm   also shows a significant downward trend with time. In the first five minutes, the number of particles shows a rapid decline. The inflexion point was earlier than that of the 62.5μm oleic acid particles, which was about 14 minutes. For the next 80 minutes, the decay of oleic acid particles is negatively linear with time. The blue line represents the oleic acid particles with a particle diameter of 200μm which have a downward trend with time. The overall downward trend is relatively gentle. In three occasions, inflexion points appear 14 minutes, 59 minutes, and 81 minutes respectively, and the oleic acid particles fluctuate widely at the beginning. The collected data shows the oxidation reaction of oleic acid particles with three different particle sizes in ozone.

The kinetic double-layer model simulates the experiment of oleic acid decomposing ozone. The relationship between the normalised oleic acid molecule output by the model and time is linear. Consistent with the results obtained in other literature (Pfrang et al., 2009), larger particles require longer reaction times. This may be due to the change in the surface volume ratio. For oleic acid with smaller particles, the surface area ratio is more important to the surface reaction rate.

3.2 Basic Kinetic Modelling：Oleic Acid is Oxidized by Ozone

To test and prove the applicability of the K2-SUB model, the reaction process of oleic acid particles is assumed to be oxidised by ozone. When the model data is compared with the experimental data provided by Adam, it can be seen how well the simulated reaction process of the model fits the real process. The average concentration [X]g and surface concentration [X]gs of ozone in the gas phase were set to 52ppm (at 296K and 1013hPa).

The K2-SUB is a two-layer model and describes the surface, volume and a molecular number of oleic acid particles in the studied particles in detail. This study multiplies the oleic acid volume concentration by the particle volume to obtain the absolute molecular number of oleic acid.

3.3 The Effect of Oleic Acid Particle Size on the Kinetic Double-Layer Mode

The kinetic double-layer model simulates the experiment of oleic acid decomposing ozone. The relationship between the normalised oleic acid molecule output by the model and time is linear. Consistent with the results obtained in other literature (Pfrang et al., 2009), larger particles require longer reaction times. This may be due to the change in the surface volume ratio. For oleic acid with smaller particles, the surface area ratio is more important to the surface reaction rate.

3.4 Atmosphere Implications

As mentioned above, the fitting of K2-SUB model to experimental data can explain and describe the reaction process of oleic acid and ozone in the laboratory. In a laboratory environment, the experimental data is usually obtained by the reaction at a higher ozone concentration; the ozone concentration in this article is 52ppm. At higher ozone levels, K2-SUB provide a good description of the three particle sizes of oleic acid, respectively, to observe the change of oleic acid decay on a short-term experimental time scale. They also provide model parameters for later extrapolation to thin atmosphere conditions. In the case of a high concentration of ozone in the laboratory ([Xg]=52ppm, studies have shown that K2-SUB simulates the ozone reaction of oleic acid. The transformation of oleic acid under the three particle sizes is all in about 1 hour. The results show that the particle transformation and chemical reaction on the surface of oleic acid depend on the particle size, the change of the bulk diffusion coefficient and the change of the initial surface accommodation coefficient.

Although oleic acid has a short lifespan in the laboratory, oleic acid particles have also been detected in ageing atmospheric aerosols (Morris et al., 2002), which may be due to the chemical reaction, self-reaction, or decomposition of oleic acid with other substances reduces the concentration of ozone in the bulk of oleic acid, resulting in an incomplete reaction. In future research work, it is necessary to discuss the impact of the reaction of oleic acid and ozone on the real atmosphere under conditions that simulate the real atmosphere.

References

[1]   Andreae, M.O. and Rosenfeld, D., 2008. Aerosol–cloud–precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. Earth-Science Reviews, 89(1-2), pp.13-41.

[2]   Fu, P.Q., Kawamura, K., Chen, J., Charrière, B. and Sempere, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation.

[3]   González-Labrada, E., Schmidt, R. and DeWolf, C.E., 2007. Kinetic analysis of the ozone processing of an unsaturated organic monolayer as a model of an aerosol surface. Physical Chemistry Chemical Physics, 9(43), pp.5814-5821.

[4]   McGillen, M.R., Archibald, A.T., Carey, T., Leather, K.E., Shallcross, D.E., Wenger, J.C. and Percival, C.J., 2011. Structure–activity relationship (SAR) for the prediction of gas-phase ozonolysis rate coefficients: an extension towards heteroatomic unsaturated species. Physical Chemistry Chemical Physics, 13(7), pp.2842-2849.

[5]   Morris, J.W., Davidovits, P., Jayne, J.T., Jimenez, J.L., Shi, Q., Kolb, C.E., Worsnop, D.R., Barney, W.S. and Cass, G., 2002. Kinetics of submicron oleic acid aerosols with ozone: A novel aerosol mass spectrometric technique. Geophysical Research Letters, 29(9), pp.71-1.

[6]   Moise, T. and Rudich, Y., 2002. Reactive uptake of ozone by aerosol-associated unsaturated fatty acids: Kinetics, mechanism, and products. The Journal of Physical Chemistry A, 106(27), pp.6469-6476.

[7]   Pfrang, C., Shiraiwa, M. and Pöschl, U., 2010. Coupling aerosol surface and bulk chemistry with a kinetic double layer model (K2-SUB): oxidation of oleic acid by ozone. Atmospheric Chemistry and Physics, 10(10), pp.4537-4557.

[8]   Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angewandte Chemie International Edition, 44(46), pp.7520-7540.

[9]   Pöschl, U., Rudich, Y. and Ammann, M., 2007. Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions? Part 1: General equations, parameters, and terminology.

[10]   Reynolds, J.C., Last, D.J., McGillen, M., Nijs, A., Horn, A.B., Percival, C., Carpenter, L.J. and Lewis, A.C., 2006. Structural analysis of oligomeric molecules formed from the reaction products of oleic acid ozonolysis. Environmental science & technology, 40(21), pp.6674-6681.

[11]   Shrivastava, M.K., Subramanian, R., Rogge, W.F. and Robinson, A.L., 2007. Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models. Atmospheric Environment, 41(40), pp.9353-9369.

[12]   Zahardis, J., Geddes, S. and Petrucci, G.A., 2008. The ozonolysis of primary aliphatic amines in fine particles.