

## Short communication

Interaction of nitrogen dioxide (NO<sub>2</sub>) with a monolayer of oleic acid at the air–water interface – A simple proxy for atmospheric aerosolMartin D. King<sup>a,\*</sup>, Adrian R. Rennie<sup>b</sup>, Christian Pfrang<sup>c</sup>, Arwel V. Hughes<sup>d</sup>, Katherine C. Thompson<sup>e</sup><sup>a</sup> Department of Earth Science, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK<sup>b</sup> Department of Physics, Uppsala University, 75121 Uppsala, Sweden<sup>c</sup> Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK<sup>d</sup> ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot OX11 3QZ, UK<sup>e</sup> Department of Biological Sciences, Birkbeck University of London, Malet Street, London WC1E 7HX, UK

## ARTICLE INFO

## Article history:

Received 13 October 2009

Received in revised form

18 January 2010

Accepted 22 January 2010

## Keywords:

Oleic acid

Nitrogen dioxide

Aerosol

Monolayer

Nitrate

NO<sub>2</sub>

Film

## ABSTRACT

The reactions between atmospheric oxidants and organic amphiphiles at the air–water interface of an aerosol droplet may affect the size and critical supersaturation required for cloud droplet formation. We demonstrate that no reaction occurs between gaseous nitrogen dioxide (1000 ppm in air) and a monolayer of an insoluble amphiphile, oleic acid (*cis*-9-octadecenoic acid), at the air–water interface which removes material from the air–water interface. We present evidence that the NO<sub>2</sub> isomerises the *cis*-9-octadecenoic (oleic) acid to *trans*-9-octadecenoic (elaidic) acid. The study presented here is important for future and previous studies of (1) the reaction between the nitrate radical, NO<sub>3</sub>, and thin organic films as NO<sub>2</sub> is usually present in high concentrations in these experimental systems and (2) the effect of NO<sub>2</sub> air pollution on the unsaturated fatty acids and lipids found at the air–liquid surface of human lung lining fluid.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

Atmospheric aerosol may act as cloud condensation nuclei (CCN) for cloud formation and are thus important when considering atmospheric radiative transfer and precipitation events (IPCC, 2007). The aerosol particles are often covered in an organic film (Tervahattu et al., 2002a,b; 2005; Gilman et al., 2006; Peterson et al., 2006; Peterson and Tyler, 2003, 2002) including species such as oleic acid (*cis*-9-octadecenoic acid) that accumulates at the air–water interface (Peterson and Tyler, 2003, 2002; Tervahattu et al., 2002a,b; 2005; Russell et al., 2002; Mochida et al., 2002). A detailed review of organic films on atmospheric aerosol has been prepared by Donaldson and Vaida (2006). The presence of an organic film on an atmospheric particle is significant because a surface monolayer of organic material may change the optical properties and the hygroscopic properties of the particle (Andreae and Rosenfeld, 2008). Atmospheric oxidation or removal of this film may thus cause a change in the CCN size and properties with climatic effects.

The reactivity of gas-phase NO<sub>2</sub> with gas-phase organic species containing double bonds has previously been explored by one of us (King et al., 2002). Although the reactions of NO<sub>2</sub> with stable (non-radical) organic compounds in the atmosphere are not generally thought to be significant, in polluted environments, with high mixing ratios of NO<sub>2</sub> and volatile organic compounds, the reaction of NO<sub>2</sub> with carbon–carbon double bonds is important (Harrison et al., 1998; Huie, 1994). There has been much work on the liquid phase reactions between NO<sub>2</sub> and unsaturated fatty acids as this is important for *in vivo* environments (Velsor and Postlethwait, 1997; Postlethwait et al., 1995; Jain et al., 2008; Enami et al., 2009; Balazy and Nigam, 2003; Balazy et al., 2001; Balazy, 2000; Balazy and Chemtob, 2008). The results of these bulk liquid phase studies demonstrate that reaction of NO<sub>2</sub> with the fatty acids leads to isomerisation of the double bond and, at high concentrations of NO<sub>2</sub> and O<sub>2</sub>, nitro compounds are formed and the double bond may be broken. Docherty and Ziemann (2006) review the chemistry that occurs between liquid phase NO<sub>2</sub> and alkenes and conclude that NO<sub>2</sub> adds to the double bond followed by oxygen addition and the formation of hydroxy nitrite, carbonyl nitrite and a nitrooxy nitrite species, (Docherty and Ziemann, 2006), polymerization of the initial reaction products does not seem favorable.

\* Corresponding author.

E-mail address: [m.king@es.rhul.ac.uk](mailto:m.king@es.rhul.ac.uk) (M.D. King).

There have only been a few studies on the reaction of NO<sub>2</sub> with surface bound unsaturated species. Gross and Bertram (2009) exposed a monolayer of a terminal alkene, undec-10-ene, on a gold coated wafer to an atmosphere of NO<sub>2</sub> and subjected the wafer to XPS analysis. The authors noted no change in the ratio of oxygen to carbon atoms or in the ratio of oxidized carbon to total carbon – suggesting no reaction with NO<sub>2</sub>. Lai et al. (1994), studied the reaction between gas-phase NO<sub>2</sub> and the lipid 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC), which contains the oleoyl moiety as the only unsaturated group, on the surface of glass. Lai and Finlayson-Pitts (1991) found that at very high mixing ratios of NO<sub>2</sub> in air, 15 000 ppm, the NO<sub>2</sub> added to the POPC and reacted to form various nitro and nitrate products. At lower mixing ratios of NO<sub>2</sub> in air, 5000 ppm, the NO<sub>2</sub> catalysed the isomerisation of the double bond in POPC from *cis*- to *trans*-. The reaction between NO<sub>2</sub> and an unsaturated compound at the air–water interface may be expected to follow different reaction kinetics and result in different products from when the organic compound is in the bulk liquid or gas phase, or bound to a solid support. Wadia et al. (2000) have previously shown that the reaction between a double bond and ozone at the air–water interface is kinetically enhanced compared to the corresponding gas-phase system.

We have studied the reaction of NO<sub>2</sub> with an unsaturated organic film at the air–water interface as the formation of polar, soluble, nitrogenated products, that would subsequently be lost from the interfacial region, would be relevant to the hygroscopic properties of atmospheric aerosol.

Knowledge of the reaction of NO<sub>2</sub> with organic compounds is important not just because it may occur in the atmosphere, but because the production of the key night time atmospheric oxidant, the nitrate radical (NO<sub>3</sub>), in the laboratory inevitably involves the presence of high levels of NO<sub>2</sub>, often many orders of magnitude larger than the concentration of NO<sub>3</sub> (Wayne et al., 1991). Thus the reactivity of NO<sub>2</sub> with unsaturated organic compounds must be understood to ensure it is not a source of potential interference of nitrate radical chemistry.

The aim of this work is to investigate the effect of gas-phase NO<sub>2</sub> on a monolayer of oleic acid at the air–water interface using neutron reflection and surface pressure measurements.

## 2. Experimental

The interaction between gaseous nitrogen dioxide and deuterated oleic acid at the air–water interface was studied on a Langmuir trough contained in a 45 L aluminum gas chamber with a float-glass lid. Fused quartz windows were used to allow passage of the neutrons and laser light required for alignment. A more detailed description of the experimental set-up can be found in King et al. (2009). The surface excess (surface coverage) of deuterated organic material at the air–water interface was monitored by neutron reflection as described by Lu et al. (2000) and simultaneously the surface pressure was monitored using a Wilhelmy plate. The neutron reflection measurements were made using the SURF reflectometer at the ISIS pulsed spallation neutron source at Rutherford Appleton Laboratory, Chilton, UK. The incident neutron beam, containing a range of wavelengths, was collimated and inclined so that it fell at a grazing angle of incidence of  $\theta = 1.5^\circ$  to the horizontal of the air–liquid interface. The range of neutron wavelengths,  $\lambda$ , provides data for the reflectivity,  $R$ , as function of momentum transfer,  $Q$ , between about 0.06 and 0.5 Å<sup>-1</sup>. All reflectivity data were normalised for the intensity of the incident beam and the absolute reflectivity obtained by calibration to a pure D<sub>2</sub>O standard.

### 2.1. Neutron reflection

A full account of the use of neutron reflection to study organic molecules at the air–water interface can be found in the review by Lu et al. (2000) and only a brief description is provided here. The reflectivity of an interface depends on the effective refractive index,  $n$ , for neutrons of the material at the interface. The value of  $n$  for any compound can be calculated from known values of the coherent scattering lengths (Sears, 1992) of different nuclei using:

$$n = 1 - \frac{\lambda^2 \sum_i b_i}{2\pi V}, \quad (1)$$

where  $\sum_i b_i$  is the sum of scattering lengths for elements in volume  $V$  and  $\lambda$  is the wavelength of the neutrons. As the scattering lengths of hydrogen ( $b = -3.74$  fm) and deuterium ( $b = 6.68$  fm) are of opposite sign it is possible to mix 8% (by volume) of D<sub>2</sub>O with H<sub>2</sub>O to produce an aqueous solution with the same refractive index for neutrons as air,  $\sim 1$ . When a monolayer of an organic species is placed at the air–water interface of such a mixture the reflection occurs from the interfacial region only and the reflected signal can be interpreted simply in terms of the amount of material at the interface. Thus neutron reflection is an excellent method to study organic films at the air–water interface.

For the experiments described here the data were modelled as a single uniform layer between two semi-infinite media of zero scattering length density. The layer is characterised by its thickness,  $\delta$ , and the scattering length density,  $\rho$ , which is  $b$  per unit volume. A least-squares fitting procedure was used to compare modelled data calculated according to Abeles optical matrix method (Abelès, 1950) with each experimental data set measured in a time sequence. In a layer of thickness,  $\delta$ , and scattering length density,  $\rho$ , the surface excess (surface coverage),  $\Gamma$ , of C<sub>17</sub>D<sub>33</sub>COOH with a total scattering length  $b_m$  is then given by:

$$\Gamma = \frac{\rho\delta}{b_m} \quad (2)$$

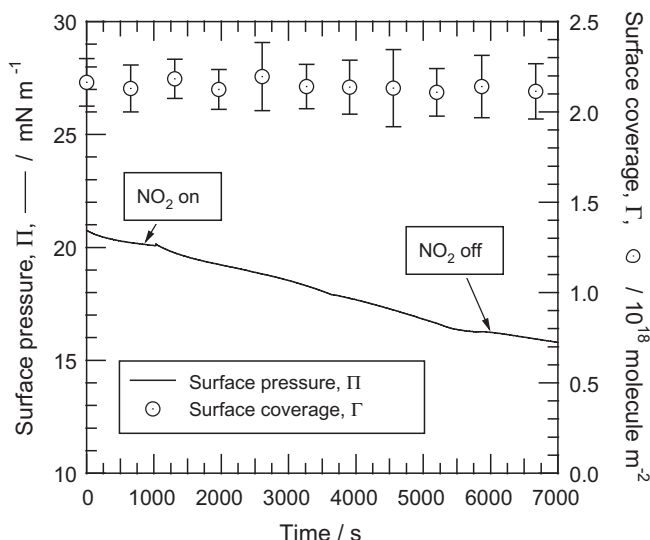
The fitted parameters can thus be used to directly obtain the surface coverage of deuterium atoms as a function of time.

### 2.2. Generation of nitrogen dioxide atmosphere

Nitrogen dioxide in air was blown into the gas chamber at 1.2 L min<sup>-1</sup> for time durations of 60–30000 s. All tubing was PTFE and all connections were made of PTFE or stainless steel. The concentration of the gas flowing into the chamber was 1000 ppm in synthetic air at atmospheric pressure. The gas (Microgas) was supplied as a calibration gas for atmospheric chemiluminescence NO<sub>x</sub> instruments and was used within 15 days of delivery.

### 2.3. Monitoring surface active species

A monolayer of deuterated oleic acid (C<sub>17</sub>D<sub>33</sub>COOH), synthesized at the Oxford Isotope Facility, University of Oxford) was placed at the air–water interface of null reflecting water. The oleic acid film was spread on the surface as a 1 mg mL<sup>-1</sup> solution of oleic acid in chloroform using a micro-litre syringe. The film was compressed to an initial surface pressure,  $\Pi$ , of 10–25 mN m<sup>-1</sup>. The film was then exposed to the dilute flow of nitrogen dioxide in air whilst the surface coverage of deuterated material and surface pressure were recorded. During a typical measurement the surface pressure was recorded at rates greater than 1 Hz and the neutron reflectivity recorded continuously in intervals of  $\sim 900$  s. Each kinetic run took about 7000–30 000 s.

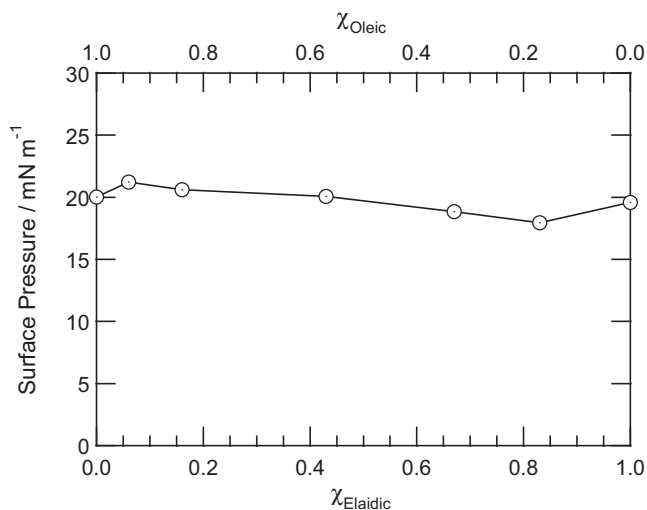


**Fig. 1.** Surface pressure,  $\Pi$ , and surface coverage,  $\Gamma$ , of oleic acid film at air–water interface exposed to 1000 ppm  $\text{NO}_2$  in air at  $1.2 \text{ L min}^{-1}$ . There is no observable change in the surface coverage of deuterated material at the air–water interface.

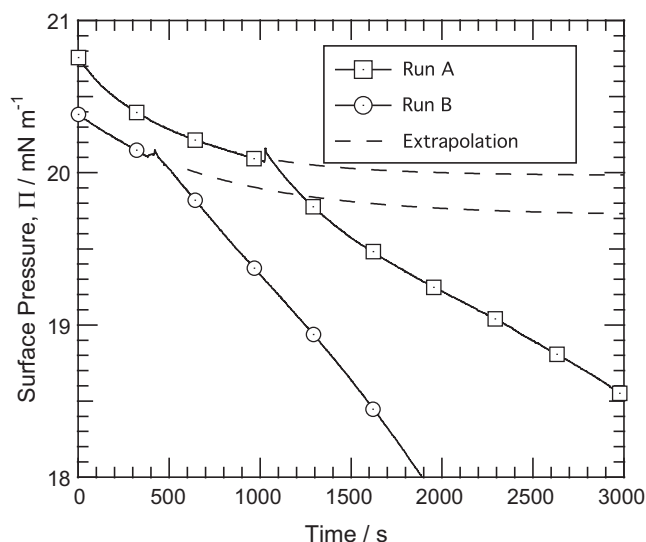
### 3. Results and discussion

Five separate experiments (kinetic runs) were performed and in each case no reaction between  $\text{NO}_2$  and oleic acid was observed. The surface coverage data, an example is shown in Fig. 1, demonstrates that there is no loss of deuterated material from the interface, in contrast to the reaction of ozone with deuterated oleic acid at the air–water interface which leads to a pronounced decrease in the surface coverage of deuterated material (King et al., 2009). Thus there is no evidence that  $\text{NO}_2$  reacts with oleic acid at the air–water interface and no evidence for cleavage of the carbon–carbon double bond.

Two subtle changes are shown in Fig. 1. The first change is the gradual change in surface pressure with time. The surface pressure of the deuterated oleic acid decays with time in the absence of  $\text{NO}_2$  owing to a very small loss of material to the trough barriers (Hardy et al., 2006) (too low to be detected by neutron reflection measurements over the timescale of the experiment). After the



**Fig. 2.** Surface pressure,  $\Pi$  of oleic and elaidic acid at the air–water interface versus mole fractions of elaidic and oleic acids. Data re-plotted from (Feher et al., 1977).



**Fig. 3.** An expanded version of the surface pressure versus time data of Fig. 1 (labeled run A) and an additional repeat experiment (labeled run B) at a similar starting surface pressure. The markers occur for every 300th data point. The  $\text{NO}_2$  was introduced into the chamber at approximately 400 s (run B) and 1100 s (run A).

flow of  $\text{NO}_2$  is initiated there is an enhanced decrease of surface pressure with time. The reaction of the  $\text{NO}_2$  with the null reflecting water sub-phase causes the pH of the sub-phase to decrease from neutral to a pH of  $\sim 3.4$ . It is unlikely that the decrease in surface pressure is brought about by the decrease in sub-phase pH as oleic acid is less soluble in acid solutions than neutral solutions. Isomerization of the double bond from oleic acid (*cis*-9-octadecanoic acid) to elaidic acid (*trans*-9-octadecanoic acid) would explain the enhanced decrease in surface pressure observed in the presence of  $\text{NO}_2$ . Pressure-area isotherm of elaidic and oleic acids, Linden and Rosenholm (1995), Cullen et al. (1971), are similar but elaidic acid has a surface pressure 3–10  $\text{mN m}^{-1}$  lower than oleic acid for the same surface coverage. Feher et al. (1977) recorded  $\Pi$ –area isotherms of six binary mixture of oleic and elaidic acid at the air–water interface. Re-plotting the data of Feher et al. (1977) as  $\Pi$  versus the mole fraction of elaidic acid for an initial surface pressure of 20  $\text{mN m}^{-1}$  (Fig. 2) displays a similar  $\Pi$  behavior as shown in Fig. 1, including the initial positive inflection when the  $\text{NO}_2$  is first exposed to the film. Further evidence for isomerisation comes from the study of Lai and Finlayson-Pitts (1991), who noted isomerisation of the double bond in the oleic acid moiety of the POPC lipid in the presence of  $\sim 5000$  ppm  $\text{NO}_2$ . Fig. 3, re-plots the surface pressure data (run A) in Fig. 1 along with other data (run B) from an identical experiment on an expanded abscissa and ordinate scale. The points of addition of  $\text{NO}_2$  can clearly be seen on this figure as an enhanced decrease in surface pressure. The decay of surface pressure in the presence of  $\text{NO}_2$  is non-exponential function whilst the decay of surface pressure in the initial absence of  $\text{NO}_2$  is exponential with time and can be extrapolated to longer exposure times (dashed lines) to demonstrate the increased decay of surface pressure in the presence of  $\text{NO}_2$ . The noise in the surface pressure measurements is too small to be observed on the scale of this plot.

### 4. Conclusions

The work reported here demonstrates that the reaction between oleic acid at the air–water interface and  $\text{NO}_2$ , at mixing ratios usually found in the atmosphere, is not important for the removal of oleic acid from the atmosphere or in altering the hygroscopic

properties of an equivalent aqueous particle coated with a monolayer of oleic acid. The double bond may be isomerised to the *trans*-form, and this will give a small change in the surface tension of the droplet, but there will be no noticeable effect on the critical supersaturation of the droplet and thus the slight change in surface tension is of minimal atmospheric relevance. It should be noted that these comments pertain to oxidation of unsaturated surface active compounds at the air–water interface and are relevant to aqueous particles coated with an organic film. An aerosol particle with an organic core may effectively dissolve and accumulate a relatively high concentration of NO<sub>2</sub> (with respect to the gas phase) and thus, in the presence of dissolved oxygen, an irreversible reaction between NO<sub>2</sub> and unsaturated species can occur in particles of this type leading to the formation of nitro products as suggested by the work relevant to *in vivo* studies Jain et al. (2008), Balazy and Chemtob (2008).

Although the isomerisation of oleic acid to elaidic acid does not change the hygroscopic properties of atmospheric aerosol significantly it would be prudent to remember that the reaction kinetics of the two isomers are likely to differ slightly. Although the primary species emitted into the atmosphere may be the *cis*-isomer (oleic acid), reaction with atmospheric NO<sub>2</sub> in highly polluted regions may lead to conversion to the *trans*- form. When studying the reactions of unsaturated species in these environments the use of a substrate with a *trans*- double bond might therefore be more appropriate.

Experimentalists studying the reaction between NO<sub>3</sub> radicals and unsaturated acid molecules at the air–water interface should be aware that the presence of NO<sub>2</sub> in their system may lead to complications if present in very high levels only (Lai and Finlayson-Pitts, 1991). At high NO<sub>2</sub> mixing ratios the literature suggests that reaction with NO<sub>2</sub> can lead to cleavage of the double bond or the formation of various nitro products, (Docherty and Ziemann, 2006). At the relatively low mixing ratios of NO<sub>2</sub> used in this work ( $\leq 1000$  ppm) the formation of irreversible addition products was not found although the double bond may be isomerised under these conditions.

## Acknowledgements

The work was supported by the STFC under grant RB610190 and in-part by NERC (NE/F007116/1), ARR wishes to thank the Swedish research council for a travel grant. CP wishes to thank the Lev-erhulme Trust (F/07537/W).

## References

- Abélès, F., 1950. La théorie générale des couches minces. *Le Journal de Physique et le Radium* 11, 307–310.
- Andreae, M.O., Rosenfeld, D., 2008. Aerosol-cloud-precipitation interactions. part 1. the nature and sources of cloud-active aerosols. *Earth-Science Reviews* 89 (1–2), 13–41.
- Balazy, M., 2000. Trans-arachidonic acids: new mediators of inflammation. *Journal of Physiology and Pharmacology* 51 (4), 597–607.
- Balazy, M., Chemtob, S., 2008. Trans-arachidonic acids: new mediators of nitro-oxidative stress. *Pharmacology & Therapeutics* 119 (3), 275–290.
- Balazy, M., Iesaki, T., Park, J., Jiang, H., Kaminski, P., Wolin, M., 2001. Vicinal nitro-hydroxyecosatrienoic acids: vasodilator lipids formed by reaction of nitrogen dioxide with arachidonic acid. *The Journal of Pharmacology and Experimental Therapeutics* 299 (2), 611–619.
- Balazy, M., Nigam, S., 2003. Aging, lipid modifications and phospholipases – new concepts. *Ageing Research Reviews* 2 (2), 191–209.
- Cullen, J., Phillips, M.C., Shipley, G., 1971. The effects of temperature on the composition and physical properties of the lipids of *Pseudomonas fluorescens*. *Biochemical Journal* 125 (3), 733–742.
- Docherty, K., Ziemann, P., 2006. Reaction of oleic acid particles with NO<sub>3</sub> radicals: products, mechanism, and implications for radical-initiated organic aerosol oxidation. *Journal of Physical Chemistry A* 110 (10), 3567–3577.
- Donaldson, D., Vaida, V., 2006. The influence of organic films at the air–aqueous boundary on atmospheric processes. *Chemical Reviews* 106 (4), 1445–1461.
- Enami, S., Hoffmann, M.R., Colussi, A.J., 2009. Absorption of inhaled NO<sub>2</sub>. *Journal of Physical Chemistry B* 113 (23), 7977–7981.
- Feher, A., Collins, F., Healy, T., 1977. Mixed monolayers of simple saturated and unsaturated fatty-acids. *Australian Journal of Chemistry* 30 (3), 511–519.
- Gilman, J.B., Tervahattu, H., Vaida, V., 2006. Interfacial properties of mixed films of long-chain organics at the air–water interface. *Atmospheric Environment* 40 (34), 6606–6614.
- Gross, S., Bertram, A.K., 2009. Products and kinetics of the reactions of an alkane monolayer and a terminal alkene monolayer with NO<sub>3</sub> radicals. *Journal of Geophysical Research-Atmospheres* 114, D02307.
- Hardy, N.J., Richardson, T.H., Grunfeld, F., 2006. Minimising monolayer collapse on langmuir troughs. *Colloid Surface A* 284, 202–206.
- Harrison, R., Shi, J., Grenfell, J., 1998. Novel nighttime free radical chemistry in severe nitrogen dioxide pollution episodes. *Atmospheric Environment* 32 (16), 2769–2774.
- Huie, R., 1994. The reaction kinetics of NO<sub>2</sub>. *Toxicology* 89 (3), 193–216.
- IPCC, 2007. Climate change 2007: the physical science basis. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Contribution of Working Group I to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.
- Jain, K., Siddam, A., Marathi, A., Roy, U., Falck, J.R., Balazy, M., 2008. The mechanism of oleic acid nitration by NO<sub>2</sub>. *Free Radical Biology & Medicine* 45 (3), 269–283.
- King, M., Canosa-Mas, C., Wayne, R., 2002. A structure activity relationship (SAR) for predicting rate constants for the reaction of nitrogen dioxide (NO<sub>2</sub>) with alkenes. *Physical Chemistry Chemical Physics* 4 (2), 295–303.
- King, M.D., Rennie, A.R., Thompson, K.C., Fisher, F.N., Dong, C.C., Thomas, R.K., Pfrang, C., Hughes, A.V., 2009. Oxidation of oleic acid at the air–water interface and its potential effects on cloud critical supersaturations. *Physical Chemistry Chemical Physics* 11 (35), 7699–7707.
- Lai, C., Finlayson-Pitts, B., 1991. Reactions of dinitrogen pentoxide and nitrogen-dioxide with 1-palmitoyl-2-oleoyl-sn-glycerol-3-phosphocholine. *Lipids* 26 (4), 306–314.
- Lai, C., Yang, S., Finlayson-Pitts, B., 1994. Interactions of monolayers of unsaturated phosphocholines with ozone at the air–water-interface. *Langmuir* 10 (12), 4637–4644.
- Linden, M., Rosenholm, J., 1995. Influence of multivalent metal ions on the monolayer and multilayer properties of some unsaturated fatty acids. *Langmuir* 11 (11), 4499–4504.
- Lu, J., Thomas, R., Penfold, J., 2000. Surfactant layers at the air/water interface: structure and composition. *Advances in Colloid and Interface Science* 84 (1–3), 143–304.
- Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., Suzuki, K., 2002. Fatty acids in the marine atmosphere: factors governing their concentrations and evaluation of organic films on sea-salt particles. *Journal of Geophysical Research-Atmospheres* 107 (D17), 4325.
- Peterson, R., Tyler, B., 2002. Analysis of organic and inorganic species on the surface of atmospheric aerosol using time-of-flight secondary ion mass spectrometry (TOF-SIMS). *Atmospheric Environment* 36 (39–40), 6041–6049.
- Peterson, R., Tyler, B., 2003. Surface composition of atmospheric aerosol: individual particle characterization by TOF-SIMS. *Applied Surface Science* 203, 751–756.
- Peterson, R.E., Nair, A., Dambach, S., Arlinghaus, H.F., Tyler, B.J., 2006. Characterization of individual atmospheric aerosol particles with SIMS and laser-SNMS. *Applied Surface Science* 252 (19), 7006–7009.
- Postlethwait, E., Langford, S., Jacobson, L., Bidani, A., 1995. NO<sub>2</sub> reactive absorption substrates in rat pulmonary surface lining fluids. *Free Radical Biology & Medicine* 19 (5), 553–563.
- Russell, L., Maria, S., Myneni, S., 2002. Mapping organic coatings on atmospheric particles. *Geophysical Research Letters* 29 (16), 1779.
- Sears, V., May 1992. Neutron scattering lengths and cross sections. *Neutron News* 3 (3), 26–37.
- Tervahattu, H., Hartonen, K., Kerminen, V., Kupiainen, K., Aarnio, P., Koskentalo, T., Tuck, A., Vaida, V., 2002a. New evidence of an organic layer on marine aerosols. *Journal of Geophysical Research-Atmospheres* 107 (D7–8), 4053.
- Tervahattu, H., Juhanoja, J., Kupiainen, K., 2002b. Identification of an organic coating on marine aerosol particles by TOF-SIMS. *Journal of Geophysical Research-Atmospheres* 107 (D16), 4319.
- Tervahattu, H., Juhanoja, J., Vaida, V., Tuck, A., Niemi, J., Kupiainen, K., Kulmala, M., Vehkamäki, H., 2005. Fatty acids on continental sulfate aerosol particles. *Journal of Geophysical Research-Atmospheres* 110 (D6), D06207.
- Velsor, L., Postlethwait, E., 1997. NO<sub>2</sub>-induced generation of extracellular reactive oxygen is mediated by epithelial lining layer antioxidants. *American Journal Physiology -Lung C* 273 (6), L1265–L1275.
- Wadia, Y., Tobias, D., Stafford, R., Finlayson-Pitts, B., 2000. Real-time monitoring of the kinetics and gas-phase products of the reaction of ozone with an unsaturated phospholipid at the air–water interface. *Langmuir* 16 (24), 9321–9330.
- Wayne, R., Barnes, I., Biggs, P., Burrows, J., Canomas, C., Hjorth, J., LeBras, G., Moortgat, G., Perner, D., Poulet, G., Restelli, G., Sidebottom, H., 1991. The nitrate radical – physics, chemistry, and the atmosphere. *Atmospheric Environment* 25 (1), 1–203.