

A New Mechanism for Ozonolysis of Unsaturated Organics on Solids: Phosphocholines on NaCl as a Model for Sea Salt Particles

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Distinguished EMSL user Barbara Finlayson-Pitts (University of California, Irvine) collaborated with EMSL researcher Scott Lea to determine the effect of ozone and ultraviolet light exposure on phospholipid coated salt crystals using Fourier transform infrared spectrometry, matrix-assisted laser desorption/ionization mass spectrometry, and Auger electron spectroscopy. They found a new mechanism for the ozonolysis of unsaturated organics on aerosols that may increase the understanding of chemistry, photochemistry, and toxicity of these aerosols in dry, polluted environments.

Sea salt particles are a major contributor to the global aerosol burden. They are formed by wave action, which carries along organic material with the sea salt. A major source of this organic layer is the decomposition of marine organisms, which have biomembranes that are a mixture of lipids, hydrophobic proteins, and carbohydrates. Phospholipids and fatty acids are common products of biomembrane disintegration. Previous work has indicated that fatty acid lipids in sea salt particles can be enhanced by factors of $(5-9) \times 10^4$ compared to ocean surface water. An organic coating on sea salt particles is expected to modify the chemical and physical properties of the particles.

We report on the oxidation of an unsaturated phospholipid, 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC), adsorbed on NaCl (Figure 1) as a model for lipids on sea salt. The primary ozonide formed in the reaction has a sufficiently long lifetime that it can react with other species such as O₃ or H₂O. The reaction of OPPC/NaCl with ozone was studied in a flow apparatus equipped with a Fourier transform infrared spectrometer (DRIFTS). O₃ and relative humidity were controlled and measured in these experiments. In some experiments, the reacted mixture was photolyzed using a high pressure xenon arc lamp to probe for photochemically active products.

Figure 2 shows spectra for OPPC/NaCl during reaction with ozone. A new, strong absorption band is formed at $\sim 1110 \text{ cm}^{-1}$ that is characteristic of the peroxide C-O bond of the secondary ozonide ring (SOZ) known to be formed in ozone-alkene reactions. Bands at $\sim 1751 \text{ cm}^{-1}$ and $\sim 1708 \text{ cm}^{-1}$ are assigned to carboxylic acids and aldehydes, respectively. It is noteworthy that these bands are

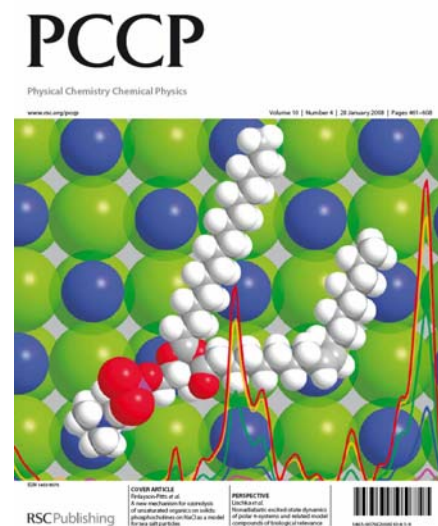


Figure 1. Model of OPPC adsorbed onto NaCl with corresponding DRIFTS spectra upon exposure to ozone superimposed.

Research Highlights

much smaller in intensity than the SOZ 1110 cm^{-1} band, despite the fact that their absorption coefficients are larger. This establishes that the SOZ is the major product.

Figure 3 shows the spectra obtained when the reaction was carried out at 2, 10 and 25% RH. There is a dramatic decrease in the SOZ band at 1110 cm^{-1} with increasing RH. Changes in SOZ were monitored at an RH of 10% and at O_3 concentrations of 7.0×10^{13} and 1.7×10^{12} molecule cm^{-3} . The relative decrease in SOZ on adding water vapor is more dramatic at the lower ozone concentration, suggesting that the Criegee intermediate (CI) which forms the SOZ can also react with water vapor in competition with SOZ formation. However, even at 10% RH, the water vapor concentration is large so that this reaction competes with other fates of the CI. It should be noted that in separate experiments, addition of water after the reaction had ceased did not change the SOZ peak, showing that it is not the SOZ itself that reacts with water vapor. After photolysis, the elemental composition measured using Auger spectroscopy is similar to that of unreacted OPPC/NaCl. This suggests that during photolysis, volatile products containing oxygen are generated.

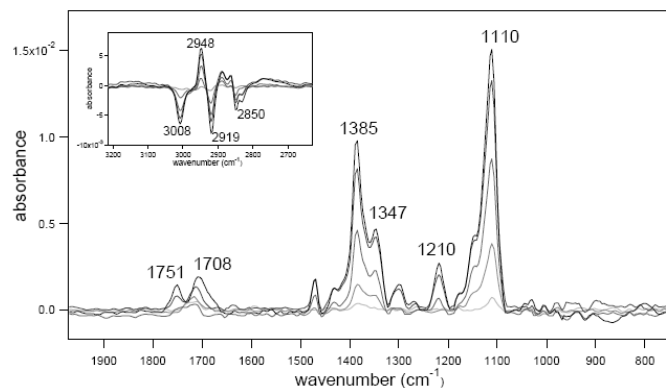


Figure 2. DRIFTS spectra of OPPC/NaCl upon exposure to $5 \times 10^{13}\text{ O}_3\text{ cm}^{-3}$ at RH $\sim 0\%$ at increasing ozone exposure times (light gray to black, respectively) of 1, 3, 10, 32 and 56 min.

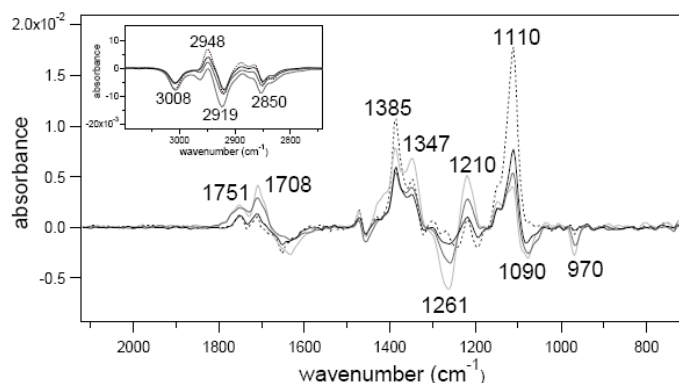


Figure 3. DRIFTS spectra of OPPC/NaCl upon exposure to $5 \times 10^{13}\text{ O}_3\text{ cm}^{-3}$ in the presence of water vapor at relative humidities of 2%, 10%, and 25% RH (black to light gray, respectively). The dashed line is the DRIFTS spectrum for a sample reacted with ozone at RH $\sim 0\%$.

Research Highlights

These experiments show that the ozone-alkene chemistry on solids is quite different from that in the gas phase or in solution. In particular, the primary ozonide formed on addition of O_3 to the double bond is sufficiently stable, with a lifetime of ~ 100 ms that it can undergo further reactions with O_3 and with water vapor. The ozone reaction with OPPC is sufficiently fast that a lifetime of only 15 minutes is expected in the atmosphere at 100 ppb O_3 . Even at typical concentrations of O_3 in remote regions, the OPPC lifetime will still only be on the order of an hour. It is clear from the data that the reaction with H_2O will under most circumstances be the major removal path for the POZ in the atmosphere.

There may be situations where formation of the SOZ represents a significant part of the reaction. For example, consider polluted, dry areas such as Mexico City with O_3 peaks of ~ 400 ppb. Under dry conditions with RH of $\sim 20\%$, the lifetime of the POZ is about 90 ms for reaction with O_3 and 5 ms for reaction with H_2O . While hydrolysis still dominates the removal of POZ, some SOZ would be formed. The health effects of SOZ are not known. However, given that it is an oxidant and that the organic side chains will increase its solubility in lipids and cell membranes, it has the potential to negatively impact health. This work was featured on the cover of *Physical Chemistry Chemical Physics* in January 2008.

Citation:

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