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Unusual Oxidation of Organics at Interfaces from the Bottom Up and Atmospheric Implications

Federico Karagulian, Christopher W. Dilbeck, and Barbara J. Finlayson-Pitts*

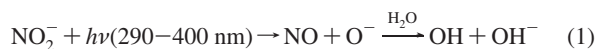
Department of Chemistry, University of California Irvine, Irvine, California 92697-2025

Received June 3, 2008; E-mail: bjfinlay@uci.edu

Oxidation of organic compounds in the lower atmosphere drives a variety of atmospherically relevant processes, from the formation of ozone to secondary organic aerosol (SOA).¹ While a great deal is known about gas phase oxidations, e.g., by OH radicals, very little is known about such processes for organics adsorbed on surfaces, which are ubiquitous in the troposphere. In the absence of other information, it is generally assumed that oxidation of these surface-bound organics occurs from the “top down” via the uptake and further reaction of the oxidant gases.²

We report here a new mechanism of oxidation of organics on surfaces under atmospherically relevant conditions. It involves the photochemical formation of OH from an underlying substrate—a mixture of NaNO₂ and NaCl. Wave action generates airborne sea salt particles,³ and as they are transported, reactions with various oxides of nitrogen replace the chloride ion with nitrate, which photolyzes in part to form nitrite.⁴ Nitrite is also found in small amounts in seawater itself,⁵ and additional nitrite is generated in the particles through the heterogeneous hydrolysis of NO₂ and the uptake of nitrous acid.⁶ The adsorbed organic studied here is the phospholipid 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC). This is used as a model for phospholipids and fatty acids found in seawater due to the decomposition of marine organisms⁷ which form a coating on airborne sea salt particles.⁸

Nitrite ions absorb light in the atmospherically important region above 290 nm, generating NO and O[•] which reacts with water to form hydroxide and the highly reactive OH radical:⁴



An important question is whether the OH thus generated is available to oxidize adsorbed organics “from the bottom up”.

Diffuse reflection infrared Fourier transform spectrometry (DRIFTS)⁹ was used to follow the change in the OPPC-coated NaNO₂/NaCl in real time during photolysis with a high pressure Xe lamp (Spectra Physics, Oriel 300 W, model 6258 OF). A 1 mm Pyrex glass filter (<10% transmission at $\lambda < 290$ nm) and a water filter to remove the infrared radiation and minimize heating were placed between the UV lamp and the quartz window on the DRIFTS cell. A mixture of NaNO₂ and NaCl (0.35 mol% NaNO₂) was prepared by mixing the two salts after grinding individually in a Wig-L-Bug. This mixture was coated with OPPC (Sigma Aldrich, 97%) as described elsewhere¹⁰ to give the equivalent of a monolayer coverage for an average particle size of 2 μm . The experimental conditions were chosen to resemble the lower atmosphere: 1 atm in air at a temperature of 297 ± 4 K and a relative humidity (RH) of $\sim 52\%$. Air (Scott-Marrin, Ultrahigh purity) that had been humidified by mixing dry air with water-saturated air was pumped through the sample, keeping the total pressure at 750 Torr. After photolysis and infrared analysis, the organic products were further identified using matrix-assisted laser

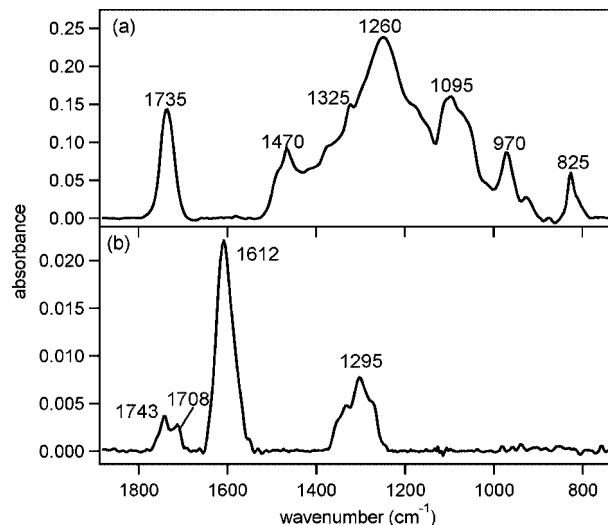


Figure 1. (a) DRIFTS spectrum (baseline corrected) of an unreacted OPPC/NaNO₂/NaCl mixture at $\sim 52\%$ RH. The y axis is $\log_{10}(S_1/S_2)$ where S_1 is the single beam spectrum of NaCl alone and S_2 is that of OPPC/NaNO₂/NaCl. (b) Difference spectrum of photolyzed OPPC/NaNO₂/NaCl. The y axis is $\log_{10}(S_2/S_3)$ where S_3 is the single beam spectrum of OPPC/NaNO₂/NaCl after 90 min irradiation. There were no significant peaks formed if NaNO₂ was not present.

desorption ionization mass spectrometry (MALDI) with 2,5-dihydroxybenzoic acid (DHB, Fluka, 99.5%) as the matrix.

Figure 1a shows the infrared spectrum of a typical unreacted OPPC/NaNO₂/NaCl mixture at 52% RH. The following assignments¹¹ are made: 1735 cm⁻¹ is due to the ester carbonyl stretch of the OPPC, 1470 cm⁻¹ is from the -CH₃ bend, and 1325 and 825 cm⁻¹ bands are stretching and bending vibrations in the NO₂⁻.¹¹ The broad peak at ~ 1260 cm⁻¹ is due primarily to NO₂⁻, with a small contribution from a band at 1255 cm⁻¹ from -PO₂⁻ in the OPPC headgroup. The 1095 and 970 cm⁻¹ peaks are assigned to the -PO₂⁻ and N-(CH₃)₃ groups in OPPC (Scheme 1).

Figure 1b shows the difference spectrum after photolysis for 90 min; i.e., these are the net changes that occur during irradiation. New peaks appear in the 1700–1750 cm⁻¹ region and at 1612 and ~ 1295 cm⁻¹. The latter two peaks are assigned to organic nitrate(s). The broad peak in the 1200–1400 cm⁻¹ region represents a combination of loss of nitrite and the formation of organic nitrates. The 1708 cm⁻¹ peak is assigned to an aldehyde C=O. That at 1743 cm⁻¹ is also due to C=O but in a multifunctional product, with possibly some contribution from incomplete compensation for the parent spectrum.

Figure 2a shows the MALDI mass spectrum before, and Figure 2b, after 90 min irradiation. The unreacted sample shows two ions at $m/z = 761$ and 783 reflecting addition of H⁺ or Na⁺ to OPPC (MW = 760). After photolysis, additional peaks at $m/z = 651$, 673, 728, and 862 are seen. The latter corresponds to the sodium

Scheme 1. Reaction Mechanism

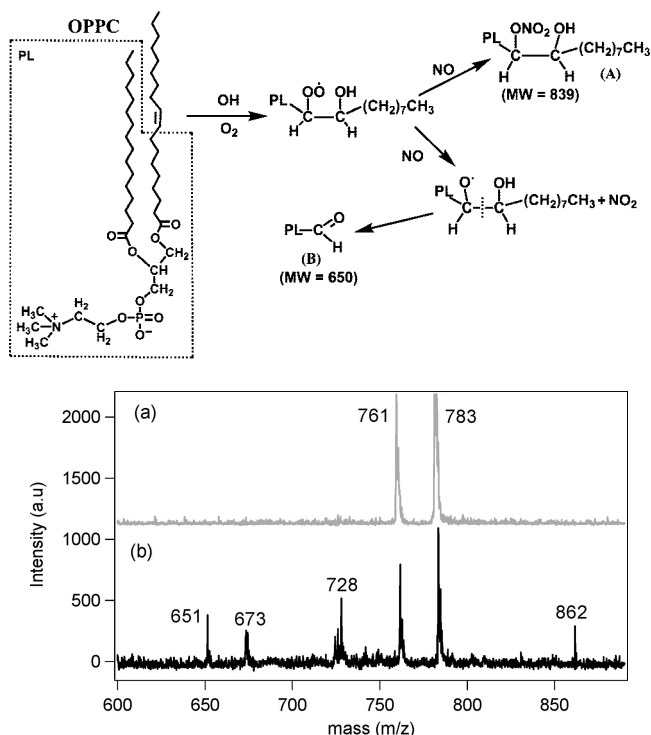


Figure 2. MALDI-TOF mass spectra of OPPC/NaNO₂/NaCl (a) before photolysis and (b) after 90 min of UV photolysis.

adduct of the product formed by addition of $-\text{OH}$ to one side of the double bond and $-\text{ONO}_2$ to the other, product **A** in Scheme 1. The peaks at 651 and 673 amu correspond to $[\text{M} + 1]$ and $[\text{M} + \text{Na}]$ for the aldehyde formed by scission of the double bond and termination of the larger fragment with a $-\text{CHO}$ group, product **B** in Scheme 1.

Scheme 1 shows a feasible reaction mechanism. The OH radical is generated in reaction (1). From the measured products, it is clear that OH can reach the adsorbed organic and add across the double bond to generate an alkyl radical, which in the presence of O₂ reacts to generate an alkylperoxy radical. Nitric oxide formed in the photolysis converts the RO₂ radical in part to organic nitrate. This gives product **A** in Scheme 1, which corresponds to the 862 amu MALDI peak and the infrared peaks at 1612 and 1295 cm⁻¹. Another pathway¹ in the RO₂ + NO reaction generates NO₂ and an alkoxy radical for which there are a number of possible fates. One is decomposition to generate the phospholipid aldehyde, product **B** in Scheme 1. We assign the MALDI peaks at 651 and 673 amu and the C=O bands at 1743 and 1708 cm⁻¹ to the phospholipid aldehyde. The product responsible for the peak at $m/z = 728$ is not clear; it may be due to an organic nitrate formed by initial attack of OH on a saturated $-\text{C}-\text{H}$ bond followed by secondary reactions.

The number of organic nitrate molecules formed was obtained by comparison of the infrared asymmetric NO₂ stretch at 1612 cm⁻¹ to the comparable vibration at 1647 cm⁻¹ in a known mixture of isosorbide mononitrate. For a typical experiment, $\Delta\text{RONO}_2/\Delta\text{NO}_2^- \approx 18\%$. This is a lower limit because in addition to photolysis (1), NO₂⁻ may also be removed by reaction with OH to form gas phase NO₂.⁴

In short, irradiation of OPPC-coated NaNO₂/NaCl clearly results in oxidation of the phospholipid, in the absence of gas phase oxidants. To the best of our knowledge, this is the first illustration of oxidation of an organic on a solid “from the bottom up”. While the experiments reported here were carried out using solid substrates, similar chemistry should occur for organic-coated aqueous particles¹² where surface passivation will not be as significant as in the present experiments. Similar chemistry will occur for nitrate ions, which also generate O⁻ and hence OH during photolysis.⁴ Indeed, oxidation of gaseous α -pinene at the surface of deliquesced NaNO₃ films during irradiation has been reported recently.¹³

This photochemistry may be important for oxidation of organics on airborne particles as well as on boundary layer surfaces such as buildings and vegetation. Nitrate as well as organic compounds are ubiquitous on such surfaces.¹⁴ This chemistry should also be considered in polar snowpacks where photolysis of nitrate ions generates gaseous nitrogen oxides and leads to organic oxidation with products such as HCHO.¹⁵ Oxidation from the “bottom up” as reported here may contribute to this chemistry.

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