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Hydroxyl radical oxidation of phospholipid-coated NaCl particles.

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Journal

Physical chemistry chemical physics : PCCP, 15(24)

ISSN

1463-9084

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Publication Date

2013-06-28

Peer reviewed

Hydroxyl radical oxidation of phospholipid-coated NaCl particles

Cite this: *Phys. Chem. Chem. Phys.*, 2013, **15**, 9833

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Biological organic compounds mixed with NaCl and other inorganic compounds in sea-salt aerosol particles react in air with oxidants such as ozone and hydroxyl (OH) radicals. Laboratory studies of model systems can provide insight into these reactions. We report here studies of the kinetics and mechanism of oxidation of unsaturated 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) on NaCl by gas phase OH in air at room temperature and 1 atm pressure using diffuse reflection infrared Fourier transform spectrometry (DRIFTS) and matrix-assisted laser desorption/ionization-time-of-flight-mass spectrometry (MALDI-TOF-MS) to identify possible structures of surface-bound reaction products. For comparison, some studies were also carried out on the saturated 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) on NaCl. The calculated concentration of hydroxyl radicals, generated by photolysis of isopropyl nitrite, was $(1.6\text{--}6.4) \times 10^8$ radicals cm^{-3} . Surface-bound aldehydes, ketones, organic nitrates and nitrate ions were identified as products of these reactions and structures of potential products were proposed based on mechanistic considerations combined with the MALDI-TOF-MS and DRIFTS spectra. The loss rate of vinyl hydrogen, =C-H , at 3008 cm^{-1} was used to obtain a lower limit for the rate constant (k_1) for addition of OH to the double bond, $k_1 > (3 \pm 1) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (1s), corresponding to a reaction probability of $\gamma^{\text{add}} > (4 \pm 1) \times 10^{-3}$ (1s). Assuming that abstraction from $\text{-CH}_2\text{-}$ groups in POPC is the same as for DPPC, the percentage of the reaction that occurs by addition is $\sim 80\%$. This is similar to the percent addition predicted using structure–reactivity relationships for gas-phase reactions. Decreasing the amount of POPC relative to NaCl resulted in more nitrate ion formation and less relative loss of POPC, and increasing the OH concentration resulted in a more rapid loss of POPC and faster product formation. These studies suggest that under atmospheric conditions with an OH concentration of 5×10^6 radicals cm^{-3} , the lifetime of POPC with respect to OH is < 6 days.

Received 22nd March 2013,

Accepted 2nd May 2013

DOI: 10.1039/c3cp51237a

www.rsc.org/pccp

Introduction

Sea-salt aerosol (SSA) is produced over the ocean by the bursting of bubbles formed by wave action.^{1–5} The composition of SSA particles is variable, but during phytoplankton blooms, biological organic material can make up more than half of the particles by mass.^{6,7} The organics include many different types of compounds, including phospholipids.^{8–16} Some of the SSA particles redeposit into the ocean, while others are entrained upwards and can remain in the atmosphere up to several days.⁵ During this time, SSA particles are exposed to atmospheric oxidants, such as the hydroxyl radical (OH), ozone, chlorine atoms and the nitrate radical (NO_3).¹⁷ These particles can also travel inland, where other pollutants including oxides of nitrogen (NO_x) are present in higher concentrations than over the ocean.

Both the inorganic and the organic components of SSA particles undergo chemical reactions in the atmosphere. The organic components of SSA particles are oxidized by OH and Cl during the day, NO_3 at night and ozone both day and night.¹⁷ Oxides of nitrogen readily react with salts such as NaCl (which is about 0.84 mole fraction of sea salt),^{5,18} producing species such as NO_3^- and NO_2^- in the particles.^{19–21} Both NO_3^- and NO_2^- photolyze to produce $\bullet\text{O}^-$, which in turn reacts with water to form OH.²² Previously, the oxidation of unsaturated 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC) by OH produced *via* the photolysis of NaNO_2 in a mixture with NaCl, *i.e.* oxidation by OH generated at the particle surface which is referred to as oxidation from the “bottom up,” was reported.^{23,24} In this work, studies of the mechanism and kinetics of oxidation of unsaturated 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC), and saturated 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) on NaCl by OH generated in the gas phase are presented. Fig. 1 shows the structures of OPPC, POPC, and DPPC.

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Fig. 1 Structures of OPPC, POPC and DPPC, shown on the surface of NaCl.

POPC and OPPC are isomers in which the positions of the oleoyl and palmitoyl chains are switched, which is not expected to affect the reactivity of the phospholipids towards OH. DPPC is a saturated phospholipid where only abstraction from the alkyl chains is possible, whereas both OH addition to the C=C and hydrogen abstraction from the alkyl chains will occur with POPC. The current studies are referred to as oxidation from the “top down” because the OH radicals are generated in the gas phase above the phospholipids. The results of these top-down OH oxidation studies are compared to the previous bottom-up OH oxidation studies.^{23,24}

Experimental

Sample preparation

Sodium chloride (99%, Fisher) particles with diameters in the range from 1–10 μm ,²⁴ ideal for diffuse reflection Fourier transform spectrometry (DRIFTS) analysis,^{25,26} were generated by grinding the salt in a Wig-I-bug[®] (Crescent Dental Mfg.) for 5 minutes. After grinding the salt, 0.35 g of NaCl powder was mixed with 0.37 mL of a POPC solution made by dissolving 25 mg of POPC powder (>99%, Avanti Polar Lipids) in a mixture of 9 mL of *n*-hexane ($\geq 99\%$, Aldrich) with 1 mL of ethanol (95%, Omnisolv). This mixture of NaCl and POPC solution was stirred under a stream of ultra-high purity (UHP) N_2 (Oxygen Service Company, 99.9995%) until it was dry, ground briefly with a mortar and pestle to break up clumps, transferred to the DRIFTS sample holder and packed down with manual pressure using a press described elsewhere.²⁷ This amount of POPC would coat 2 μm cubic particles with approximately one monolayer of POPC, assuming a surface concentration of 1.6×10^{14} molecules cm^{-2} obtained from previous studies of surface pressure–area isotherms of OPPC films on water.^{28,29} To examine the effect of varying the amount of POPC in the sample, some experiments were performed with 0.10 mL of POPC solution added to 0.35 g NaCl to give approximately $\frac{1}{4}$ of a monolayer of coverage. Experiments were also performed using 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC, 0.37 mL DPPC solution mixed with 0.35 g NaCl) to elucidate the reactions with

a saturated phospholipid that has the same number of $-\text{CH}_2-$ groups, but no double bond. The DPPC solution was made by dissolving 25 mg of DPPC powder (>99%, Avanti Polar Lipids) in a mixture of 9 mL of *n*-hexane with 1 mL of ethanol.

To test for carboxylic acid products of the reaction, an experiment was conducted in which a sample that had been reacted with OH was exposed to the headspace of an aqueous ammonia solution (Fisher ACS Plus, 28.71%, vapor pressure of NH_3 over the solution at 21 $^\circ\text{C}$ is 557 Torr), and changes in the DRIFTS spectrum were recorded.

OH generation

OH radicals were generated from the photolysis of isopropyl nitrite (IPN, Karl Industries, Ohio) in a mixture of N_2 and air (Ultrapur Air, Scott-Marrin, total hydrocarbons as $\text{CH}_4 < 0.01$ ppm; $\text{CO} < 0.01$ ppm; $\text{NO}_x < 0.001$ ppm; $\text{SO}_2 < 0.001$ ppm), summarized in reactions 1–3:^{30–34}

To introduce IPN vapor into the DRIFTS cell, a flow of dry N_2 was passed over the top of liquid IPN in a bubbler placed in a dry ice-acetone bath at -78 $^\circ\text{C}$ (to produce a lower IPN concentration) or salt (NaCl) water-ice bath at 0 $^\circ\text{C}$ (to produce a higher IPN concentration). The IPN- N_2 mixture was passed through a 10.5 cm glass cell with quartz windows to measure the concentration of IPN in the mixture using a UV-Vis-NIR spectrophotometer (Ocean Optics HR4000CG-UV-NIR) with N_2 as the reference. An absorption cross-section of 1.67×10^{-19} cm^2 molecule $^{-1}$ (base e) at 359 nm was used for calculation of the initial IPN concentration.³⁵ Before entering the DRIFTS cell, the IPN- N_2 mixture was mixed with a measured flow of air in a 1:10 ratio to produce IPN concentrations from $(0.19\text{--}11) \times 10^{16}$ molecules cm^{-3} . This lowers the O_2 concentration from 21% in air to 19% which has negligible effects on the chemistry.

IPN photolysis under static conditions

To calculate the photolysis rate constant for IPN in the DRIFTS cell, a known concentration of gaseous IPN in the range from $(3.6\text{--}5.3) \times 10^{16}$ molecules cm^{-3} was photolyzed over a sample of NaCl in the DRIFTS cell under static conditions. The IPN- N_2 -air mixture flowed through the DRIFTS cell for 10 minutes before the inlet and outlet valves were closed to trap 1 atm of the mixture in the chamber. The sample was irradiated through a quartz window with a high-pressure xenon arc lamp (Spectra Physics, Oriel 300 W, model 6258 OF) to photolyze the IPN. The light passed through a 10 cm cell filled with water to eliminate infrared radiation and minimize heating of the cell and sample compartment. A 1 mm thick Pyrex[®] glass slide cover was used to filter out light below 290 nm; the transmission was 50% at 309 nm and 3% at 290 nm. The gas phase IPN signal above the NaCl powder was monitored using FTIR at 782 cm^{-1} to measure the loss of IPN. The initial IPN loss was determined

from the slope of a plot of $\ln(A_{\text{IPN}})_t/(A_{\text{IPN}})_0$ vs. time as $t \rightarrow 0$, where $(A_{\text{IPN}})_t$ and $(A_{\text{IPN}})_0$ are the absorbances of IPN at time t and 0, respectively. This initial loss of IPN is due solely to photolysis. Thus the slope of the plot gives the first order photolysis rate constant k_p , which was determined to be $k_p = (1.1 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ (1s).

Estimates of OH concentrations

The OH concentrations were calculated from a kinetics model consisting of 115 reactions involving 60 species. The differential equations were solved numerically using Acuchem.³⁶ Rate constants for the reactions were taken from the JPL Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 17,³⁷ when available. Additional reactions and rate constants were added from the IUPAC database,³⁸ from Raff and Finlayson-Pitts,³⁵ and from Curran.³⁹ The gas phase chemistry and rate constants are known, except for the IPN photolysis rate constant k_p which was measured as described above, and the rate constant for wall loss of OH, which represents the largest uncertainty in calculating OH concentrations. The first order rate constant for wall loss of OH (k_w) at temperature T is related to the uptake probability (γ) by $k_w = (A/V)\gamma(RT/2\pi M)^{1/2}$, where A and V are the cell area and volume ($A = 74 \text{ cm}^2$, $V = 29 \text{ cm}^3$), R is the gas constant and M is molar mass of OH. An uptake coefficient of $\gamma = 1$ gives $k_w = 3.9 \times 10^4 \text{ s}^{-1}$. However part of the cell was coated with halocarbon wax for which an uptake coefficient of 6×10^{-4} has been reported,⁴⁰ corresponding to $k_w = 23 \text{ s}^{-1}$. A value of $k_w = 7.5 \times 10^3 \text{ s}^{-1}$ gave the best agreement between the model-predicted and experimentally-observed loss of IPN under the static conditions described above. The calculated OH concentration was in the range of $(1.6\text{--}6.4) \times 10^8 \text{ radicals cm}^{-3}$ for these experiments using this value of k_w . The uncertainty in the OH concentration due to uncertainties in the wall loss can be assessed by comparing calculated OH concentrations as k_w is varied. For example, for an IPN concentration of $3.0 \times 10^{15} \text{ molecules cm}^{-3}$, OH is calculated to be $2.3 \times 10^8 \text{ radicals cm}^{-3}$ using $k_w = 7.5 \times 10^3 \text{ s}^{-1}$. Varying k_w over the full range from 3.9×10^4 to 23 s^{-1} changed the predicted OH concentration to 0.6×10^8 and $6.6 \times 10^8 \text{ radicals cm}^{-3}$, respectively. The Acuchem model predicts $1.8 \times 10^{10} \text{ O}_3 \text{ cm}^{-3}$ at 2 s, and reaction with ozone is calculated to account for less than 1% of the total reaction.

DRIFTS

Reactions of OH with POPC–NaCl and DPPC–NaCl were performed at 293–295 K and 1 atm pressure. Changes in the POPC–NaCl or DPPC–NaCl mixtures were monitored using DRIFTS. Spectra were recorded while the IPN–N₂ mixture flowed over the salt in the dark to provide a reference prior to the generation of OH. No evidence of reaction was observed upon addition of IPN to the sample. Irradiation of the sample was then initiated and spectra were measured every 4 minutes, beginning 2 minutes after the shutter to the lamp was opened. A total of 512 scans at 2 cm^{-1} resolution were averaged for each spectrum. A control experiment was conducted in which no IPN was present but POPC–NaCl was irradiated with the Xe arc lamp while N₂–air was pumped through the sample. Only small changes in the spectrum were observed during irradiation, mostly due to water desorption from the sample.

MALDI-TOF-MS

Samples were analyzed with matrix-assisted laser desorption/ionization-time-of-flight-mass spectrometry (MALDI-TOF-MS) after reaction in the DRIFTS cell. Samples were prepared for MALDI-TOF-MS analysis by dissolving 20 mg of the reacted POPC–NaCl or DPPC–NaCl mixture in 160 μL of a 1:1 mixture of acetonitrile (OmniSolv, HPLC grade) and water (Fisher, HPLC grade), mixing on a vortex mixer and micro-centrifuging for 30 seconds. Drops (0.5 μL) of these solutions were placed on a stainless steel 384 well plate to which were added 0.5 μL drops of a saturated 2,5-dihydroxybenzoic acid solution in 1:2 acetonitrile:water. An AB Sciex 5800 TOF/TOF spectrometer was used to collect spectra from 1000–5000 accumulated shots in positive reflectron mode at 400 Hz.

Results and discussion

Given the size and complexity of the phospholipid, there are many potential reaction sites for OH, and hence many potential products. Schemes 1–3 show selected reaction pathways and products for reaction of POPC–NaCl with OH. For simplicity, we focus here on some typical potential reaction pathways that lead to reaction products that are consistent with the MALDI-TOF-MS and DRIFTS spectra discussed below. We emphasize that these schemes are intended to be illustrative, not comprehensive or unique, in their treatment of the chemistry, and that products

Scheme 1 Mechanism of OH addition to the double bond of POPC.

Scheme 2 Mechanism of formation of selected products from addition of OH to the double bond of POPC.

Scheme 3 Mechanism of formation of selected products from hydrogen abstraction from the alkyl chain of POPC.

other than those shown here may contribute to the observed peaks in the mass and infrared spectra. In Schemes 1–3, the oleoyl chain of POPC is shown and “PL” represents the rest of

the POPC molecule. Either addition of OH to the double bond (Schemes 1 and 2) or abstraction from the alkyl chain (Scheme 3) leads to formation of an alkyl radical which in the

presence of O_2 and NO generates an alkoxy radical (RO) or an organic nitrate.¹⁷ In the gas phase, alkoxy radicals can react with O_2 , decompose or isomerize, leading to products such as A through G in Schemes 2 and 3.

Fig. 2 shows the MALDI-TOF mass spectra of POPC-NaCl (a) before and (b) after reaction with OH. Since MALDI is a soft ionization technique, fragmentation of ions is not significant. Before reaction (Fig. 2a), two major peaks are observed that are assigned to the proton and sodium adducts of the parent molecule POPC (m/z 761 and 783, respectively). Because POPC contains 42 carbon atoms, several peaks due to ^{13}C isotopes also have significant intensity for these two adducts. After reaction (Fig. 2b), a number of additional peaks due to products are observed. The exact masses of the proton and sodium adducts of POPC were used as internal standards to obtain more accurate mass measurements of the peaks in the mass spectra. A second set of masses at m/z 650 and 672 was also used as an internal standard in that region, based on the assumption that they are attributable to the proton and sodium adducts of the phospholipid aldehyde B (Scheme 2) observed previously in the ozone oxidation of POPC^{28,41} and its isomer OPPC.^{42,43} Table 1 lists the measured m/z of the proton adduct peaks, the formulae and exact masses of the closest matches to the measured m/z that are chemically and mechanistically

reasonable, the relative error in ppm, and the assigned structures as shown in the schemes. For some of the peaks, potential additional formulae and structures are listed which may contribute to the peaks.

Two groups of peaks in Fig. 2b assigned to aldehydes differing by $-CH_2-$ units (products B, A, and C in Scheme 2 and Fig. 2) are observed at m/z 650, 636, and 622 for the $[-CHO + H]^+$ species and 672, 658, and 644, for the $[-CHO + Na]^+$ species. Peaks at m/z 652 and 674 are assigned to the proton and sodium adducts, respectively, of product D (Scheme 2), while peaks at m/z 666 and 688 are assigned to the proton and sodium adducts, respectively, of product E. Peaks at m/z 775 and 797 are assigned to the proton and sodium adducts, respectively, of product F (Scheme 3), formed from abstraction of an allylic hydrogen, or the multifunctional dinitrate product shown in Table 1. Finally, peaks at m/z 777 and 799 are assigned to the proton and sodium adducts, respectively, of product G (Scheme 3), formed from abstraction processes along the oleoyl chain.

Changes in the DRIFTS spectra of POPC-NaCl before and after reaction with OH are also consistent with the mechanisms outlined in Schemes 1–3. Fig. 3a shows a DRIFTS spectrum of POPC-NaCl before reaction. Peaks due to the hydrocarbon groups occur at 3008 cm^{-1} ($\nu_{\text{str}}, =C-H$), 2960 cm^{-1} ($\nu_{\text{asym str}}, -CH_3$), 2920 cm^{-1} ($\nu_{\text{asym str}}, -CH_2-$), and 2850 cm^{-1} ($\nu_{\text{sym str}}, -CH_2-$), as

Fig. 2 MALDI-TOF mass spectra of POPC-NaCl (a) before and (b) after reaction with $1.7 \times 10^8\text{ OH cm}^{-3}$ for 500 minutes.

Table 1 Accurate mass measurements from MALDI-TOF-MS and potential formulae and structures

Measured m/z of proton adduct	Formula of proton adduct	Exact mass	Error (ppm)	Potential structures
POPC				
622.4120	$C_{31}H_{61}NO_9P$	622.4079	7	C (see Scheme 2 or 3)
636.4222	$C_{32}H_{63}NO_9P$	636.4235	2	A (see Scheme 2)
650.4417	$C_{33}H_{65}NO_9P$	650.4392	4	B (see Scheme 2)
652.4225	$C_{32}H_{63}NO_{10}P$	652.4297	6	D (see Scheme 2)
666.4391	$C_{32}H_{61}NO_{11}P$	666.3977	62	E (see Scheme 2)
760.5879	$C_{42}H_{83}NO_8P$	760.5856	3	POPC
774.5663	$C_{42}H_{81}NO_9P$	774.5644	3	F (see Scheme 3)
	$C_{32}H_{61}N_3O_{16}P$	774.3790	242	
776.5770	$C_{41}H_{79}NO_{10}P$	776.5436	43	G (see Scheme 3)
	$C_{40}H_{75}NO_{11}P$	776.5072	90	
DPPE				
697.3594	$C_{31}H_{58}N_2O_{13}P$	697.3671	11	L (see Scheme 4)
	$C_{32}H_{62}N_2O_{12}P$	697.4035	63	
713.3446	$C_{31}H_{58}N_2O_{14}P$	713.3620	24	M (see Scheme 4)
	$C_{32}H_{62}N_2O_{13}P$	713.3984	75	
734.5699	$C_{40}H_{81}NO_8P$	734.5670	4	DPPE
758.4349	$C_{33}H_{65}N_3O_{14}P$	758.4199	20	K (see Scheme 4)
	$C_{32}H_{61}N_3O_{15}P$	758.3835	68	
772.4612	$C_{34}H_{67}N_3O_{14}P$	772.4355	33	J (see Scheme 4)
	$C_{33}H_{63}N_3O_{15}P$	772.3991	80	

well as at 1470 cm^{-1} (ν_{scissor} , $-\text{CH}_2-$, $\nu_{\text{asym bend}}$, $-\text{N}(\text{CH}_3)_3^+$).⁴⁴ There are also peaks due to the ester groups at 1735 cm^{-1} (ν_{str} , $\text{C}=\text{O}$) and 1180 cm^{-1} ($\nu_{\text{asym str}}$, $\text{C}(\text{O})-\text{O}-\text{C}$), the PO_2^- group at 1255 ($\nu_{\text{asym str}}$) and 1095 cm^{-1} ($\nu_{\text{sym str}}$), and the $-\text{N}(\text{CH}_3)_3^+$ group at 970 cm^{-1} ($\nu_{\text{asym str}}$, CN).^{44–46}

Fig. 3b shows changes in the infrared spectra as a function of time during the oxidation by OH. Although specific compounds cannot be identified from infrared spectra, the functional group information provided by DRIFTS complements the MALDI-TOF mass spectral data. The spectra have been normalized for the initial amount of phospholipid in each sample by dividing by the initial absorbance of the $-\text{CH}_2-$ groups at 2850 cm^{-1} . Loss of double bonds, as evident from a decrease in intensity of the $=\text{C}-\text{H}$ (vinyl hydrogen) stretch at 3008 cm^{-1} , $-\text{CH}_3$ groups at 2960 cm^{-1} , and $-\text{CH}_2-$ groups at 2920 and 2850 cm^{-1} is observed (a decrease in intensity of the $=\text{C}-\text{H}$ stretch is referred to as loss of double bonds from this point on, as it results from addition of OH to the double bond). There are also some decreases in the headgroup absorptions at 1255 and 1095 cm^{-1} , which were attributed previously²⁴ to OH attack at the $-\text{CH}_2-$ and $-\text{CH}_3$ groups in the polar zwitterionic end of the molecule.

New peaks at 1755 and 1710 cm^{-1} that grow in during the reaction are assigned to ketones and aldehydes, respectively.⁴⁴ Although carboxylic acids could also contribute in this region, the following experiment indicates they are not major products.

Fig. 3 DRIFTS spectra of POPC-NaCl (a) before reaction and (b) during reaction with $2.3 \times 10^8\text{ OH cm}^{-3}$. In (a), absorbance is calculated as $\log_{10}(S_0/S_1)$ where S_0 is the single beam spectrum of NaCl and S_1 is the single beam spectrum of POPC/NaCl. In (b), absorbance is calculated as $\log_{10}(S_1/S_n)$ where S_1 is the same as in (a) and S_n is the single beam spectrum of POPC-NaCl reacted for n minutes. Spectra in (b) were normalized for the initial amount of phospholipid by dividing by the initial value of A_{2850} in (a). The spectrum at 200 minutes reflects 19% loss at 2850 cm^{-1} .

A sample of POPC-NaCl after reaction with $1.9 \times 10^8\text{ OH cm}^{-3}$ for 330 min was exposed to gaseous ammonia from the headspace over an aqueous solution of the base. In previous studies,^{43,47} the reaction of carboxylic acids with NH_3 converted $-\text{COOH}$ to carboxylate ($-\text{COO}^-$) whose carbonyl absorption band shifts significantly, to $\sim 1580\text{ cm}^{-1}$. In the case of the OH reacted sample, there was no significant carboxylate formation upon exposure to NH_3 , indicating that carboxylic acids are not major products of oxidation by gas phase OH.

Peaks at 1630 and 860 cm^{-1} are assigned to organic nitrates. An additional peak due to organic nitrates would be expected at 1280 cm^{-1} , but is obscured by the peak at 1350 cm^{-1} assigned to nitrate ions. The MALDI-TOF-MS data (Fig. 2) do not clearly show evidence of organic nitrates. The molecule shown in Table 1 whose proton adduct has the formula $C_{32}H_{61}N_3O_{16}P$ is a mechanistically reasonable dinitrate that could be formed and has a mass close to that of product F. However, the exact mass of this dinitrate is a poorer fit to the measured m/z . This suggests that some of the species formed from chain scission that are no longer attached to the phospholipid headgroup contain nitrate groups. If their proton and sodium adducts are below the mass range ($m/z \geq 500$) probed by MALDI-TOF-MS, they would not have been observed in the mass spectra but would be evident in the DRIFTS spectra.

The formation of NO_3^- is caused by reaction of the NaCl substrate^{19,20,48} with NO_2 and HNO_3 that are formed in secondary chemistry following IPN photolysis. In principle, products such

as organic nitrates and NO_3^- could be destroyed by photolysis simultaneously while they are being formed. However, at the end of one experiment, IPN was purged from the system and photolysis was continued for two additional hours; there was less than 10% change in any of the peaks.

For comparison, the oxidation of the saturated DPPC was also studied. Scheme 4 shows some typical potential reaction pathways that are consistent with the mass spectral and infrared data. One of the palmitoyl chains is shown, and "PPC" represents the rest of the DPPC molecule. Products J, K, L, and M may all be nitrates for which peaks corresponding to their proton or sodium adducts are seen in Fig. 4b, in addition to those of the unreacted phospholipid (Fig. 4a). The exact masses of the proton and sodium adducts of DPPC were used as internal standards to obtain more accurate mass measurements of the peaks in the mass spectra. Table 1 lists the measured m/z of the proton adduct peaks, the formulae and exact masses of the closest matches to the measured m/z that are chemically and mechanistically reasonable, the relative error in ppm, and the assigned structure shown in Scheme 4. Additional formulae and structures of products that are mechanistically reasonable are listed which may also contribute to the peaks. Non-nitrate products are likely to be formed as well, but if they are smaller than the m/z 500 probed by MALDI-TOF-MS, they would not be detected.

Fig. 5 shows DRIFTS spectra of DPPC-NaCl (a) before and (b) during reaction with OH. The spectrum of DPPC-NaCl is similar to that of POPC-NaCl except the 3008 cm^{-1} peak is absent and that due to $-\text{N}(\text{CH}_3)_3^+$ ($\nu_{\text{asym str}}, -\text{CH}_3$) at 3030 cm^{-1} becomes more evident. During reaction of DPPC-NaCl with OH, loss of $-\text{CH}_3$ groups at 2960 cm^{-1} , $-\text{CH}_2-$ groups at 2920 and 2850 cm^{-1} , and headgroup absorptions at 3030 , 1255 , and 1095 cm^{-1} is observed. Similar product peaks to those for POPC are observed at 1755 (ketones), 1710 (aldehydes), 1630 (organic nitrates), 1350 (NO_3^-), and 860 cm^{-1} (organic nitrates). The relative heights of the peaks due to ketones (1755 cm^{-1}) and aldehydes (1710 cm^{-1}) compared to that for POPC indicate the formation of more ketones in the DPPC oxidation relative to aldehydes. This is consistent with typical oxidation mechanisms for the two phospholipids, where oxidation of POPC leads to more aldehyde formation (Schemes 2 and 3) and oxidation of DPPC leads to more ketone formation (Scheme 4).

The results of the present studies can be compared to previous work on OH oxidation of OPPC from the bottom up, in which OH was generated at the salt surface by photolysis of NaNO_2 -NaCl mixtures.^{23,24} We only consider NaNO_2 experiments carried out in the presence of water, where the $\cdot\text{O}^-$ generated on photolysis is converted to OH radicals. Bottom-up oxidation was slower than top-down oxidation. This is seen in the loss of the $=\text{C}-\text{H}$ and $-\text{CH}_2-$ groups after a given reaction

Scheme 4 Mechanism of formation of selected products from reaction of OH with DPPC.

Fig. 4 MALDI-TOF mass spectra of DPPC-NaCl (a) before and (b) after reaction with $2.0 \times 10^8 \text{ OH cm}^{-3}$ for 330 minutes.

time, where the changes in absorption at 3008 and 2850 cm^{-1} are three to four times smaller^{23,24} for the NaNO_2 photolysis studies compared to the present case. Assuming that OH generated either at the surface or in the gas phase reacts with these functional groups, there must be less OH available from NaNO_2 photolysis^{23,24} compared to photolysis of gas phase precursors. Thus, not only is the location of OH generation relative to the phospholipid fatty acid chains different in the present studies, but the opportunity for secondary reactions is much greater. This is consistent with the much larger range of products that are shown in Schemes 2 and 3.

The MALDI-TOF mass spectra contained fewer peaks in the bottom-up case, consistent with two major products: the hydroxynitrate formed by addition of $-\text{OH}$ to one side of the $\text{C}=\text{C}$ and $-\text{ONO}_2$ to the other (Scheme 1), and the phospholipid aldehyde formed by scission of the double bond (B in Scheme 2). The infrared spectra showed relatively weak absorptions in the carbonyl region. An additional product from abstraction of an allylic hydrogen was also tentatively identified in bottom-up oxidation.²⁴ In the present top-down studies, abstraction of an allylic hydrogen could lead to products C and F, as shown in Scheme 3. Also, in the present top-down studies, many more products were observed by MALDI-TOF-MS, indicating relatively more scission of the alkyl chains in top-down oxidation *versus*

bottom-up oxidation. This is also supported by the decrease in $-\text{CH}_2-$ groups compared to the decrease in double bonds, $\Delta A_{-\text{CH}_2-}/\Delta A_{\text{C}=\text{C}}$, which is about two times larger for these experiments than in bottom-up oxidation. Furthermore, reasonable mechanisms for products that are consistent with the m/z of peaks in Fig. 2 and the masses of the molecules in Schemes 2 and 3 involve significant amounts of secondary chemistry. The infrared peaks in the carbonyl region were also relatively more intense compared to the bottom-up case. The hydroxynitrate observed at m/z 862 in bottom-up oxidation is not observed in top-down oxidation, probably because the OH concentration is higher and more secondary chemistry occurs. Scheme 2 shows a mechanism by which hydroxynitrates (dashed box in Scheme 1) formed in these top-down reactions could subsequently undergo additional reactions, yielding product A.

Effect of varying POPC coverage

Experiments were performed in which the amount of POPC relative to NaCl was decreased by about a factor of four. Fig. 6 compares the spectra for reaction of the equivalent of one monolayer (top) and $\sim \frac{1}{4}$ monolayer (bottom) of POPC on NaCl after reaction with OH for 200 minutes. The spectra have been normalized for the initial amount of POPC by dividing by the initial absorbance of $-\text{CH}_2-$ at 2850 cm^{-1} . Based on the loss of

Fig. 5 DRIFTS spectra of DPPC-NaCl (a) before reaction and (b) during reaction with 2.2×10^8 OH cm $^{-3}$. In (a), absorbance is calculated as $\log_{10}(S_0/S_1)$ where S_0 is the single beam spectrum of NaCl and S_1 is the single beam spectrum of DPPC-NaCl. In (b), absorbance is calculated as $\log_{10}(S_1/S_n)$ where S_1 is the same as in (a) and S_n is the single beam spectrum of DPPC-NaCl reacted for n minutes. Spectra in (b) were normalized for the initial amount of phospholipid by dividing by the initial value of A_{2850} in (a). The spectrum after 200 minutes of reaction reflects 7% loss at 2850 cm $^{-1}$.

=C-H and -CH $_2$ - groups, the fraction of total POPC that reacts is smaller for the lower coverage. A possible explanation is that at the lower coverage, POPC self-aggregates to a greater degree, making molecules in the interior of the aggregates less available for reaction (see below). Significantly more NO $_3^-$ is formed with the lower phospholipid coverage, consistent with less coverage of the substrate that leaves NaCl more available for reaction with HNO $_3$ and NO $_2$.

Fig. 6 DRIFTS spectra of POPC-NaCl containing one monolayer and $\frac{1}{4}$ monolayer of POPC after reaction with 2.3×10^8 OH cm $^{-3}$ and 1.6×10^8 OH cm $^{-3}$, respectively, for 200 minutes. Spectra were normalized for the initial amount of phospholipid by dividing by the initial value of A_{2850} for each spectrum. Absorbance is calculated as $\log_{10}(S_1/S_{200})$ where S_1 is the single beam spectrum of unreacted POPC-NaCl and S_{200} is the single beam spectrum of POPC-NaCl reacted for 200 minutes.

Effect of varying OH concentration

The OH concentration was varied by varying the initial IPN concentration. The OH concentration at 2 s photolysis time, corresponding to the residence time in the chamber, was estimated using the gas phase kinetics model. Fig. 7 compares spectra of POPC-NaCl reacted for 200 min with 6.4×10^8 OH cm $^{-3}$ and 2.3×10^8 OH cm $^{-3}$. At the higher OH concentration, there was a greater loss of reactant =C-H and -CH $_2$ - groups and stronger absorptions due to product nitrate ions (1350 cm $^{-1}$) and organic nitrates (1630, 1280, and 860 cm $^{-1}$) for a given reaction time, as expected. The Acuchem model predicts the formation of higher NO $_2$ concentrations at the larger IPN and OH concentrations, leading to more NO $_3^-$ on the salt, as observed.

Kinetics

The loss rate of the peak due to =C-H can be used to measure the kinetics of addition of OH to the double bond in POPC. Because the IPN-N $_2$ -air is continually flowing through the sample and the illumination from the Xe arc lamp is constant, the steady-state OH concentration in the sample chamber is constant during the reaction, and delivery of OH to the surface should not be diffusion-limited. The initial rate of reaction of OH with double bonds in POPC is therefore

$$\left(\frac{d[\text{C}=\text{C}]}{dt}\right)_0 = -k_1[\text{POPC}]_0[\text{OH}]_0 \quad (\text{I})$$

where [C=C] is the concentration of double bonds (which is the same as the POPC concentration initially) and [OH] $_0$ is the steady-state OH concentration. Because the OH concentration is constant, the reaction is pseudo-first-order with respect to POPC. The integrated rate law is

$$\ln\left(\frac{[\text{C}=\text{C}]}{[\text{C}=\text{C}]_0}\right) = -k_1[\text{OH}]_0 t \quad (\text{II})$$

so that the rate constant k_1 can be obtained from the slope of a plot of $\ln([\text{C}=\text{C}]/[\text{C}=\text{C}]_0)$ vs. time and the known OH concentration in each experiment. Since absorbance is proportional to concentration, the absorbance at 3008 cm $^{-1}$ can be used in eqn (II), as shown for

Fig. 7 DRIFTS spectra of POPC-NaCl after reaction with 2.3×10^8 OH cm $^{-3}$ and 6.4×10^8 OH cm $^{-3}$, respectively, for 200 minutes. Spectra were normalized for the initial amount of phospholipid by dividing by the initial value of A_{2850} for each spectrum. Absorbance is calculated as $\log_{10}(S_1/S_{200})$ where S_1 is the single beam spectrum of unreacted POPC-NaCl and S_{200} is the single beam spectrum of POPC-NaCl reacted for 200 minutes.

Fig. 8 Natural log of absorbance divided by initial absorbance at 3008 cm⁻¹ due to the =C–H stretch (indicative of the amount of double bonds) in POPC versus time for typical experiments, used to calculate k_1 . Open circles are for $[OH] = 2.7 \times 10^8 \text{ cm}^{-3}$, and open squares are for $[OH] = 6.4 \times 10^8 \text{ cm}^{-3}$.

typical experiments in Fig. 8. The average value of k_1 determined from all experiments is $(3 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1s). This is approximately two orders of magnitude smaller than gas phase OH-alkene reactions.¹⁷ It is possible that as the *n*-hexane-ethanol mixture evaporates during the coating procedure, some of the phospholipid forms micelles or otherwise self-aggregates in competition with adsorption on NaCl. This would make some of the POPC less available for reaction, resulting in the assumed POPC surface concentration being overestimated and the value of k_1 underestimated. Since, the extent to which this occurs is unknown, we report the kinetics data as lower limits. Thus, $k_1 > (3 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1s), where the error is the statistical error and does not include the uncertainty in the OH concentrations which is primarily due to the uncertainty in the wall loss. Table 2 summarizes the kinetics data for each experiment.

From collision theory, the reaction probability (γ) is related to the rate constant by

$$\frac{\#C=C}{\text{cm}^2 \text{ s}} = \gamma [OH]_0 \sqrt{\frac{RT}{2\pi M_{OH}}} \quad (\text{III})$$

where R is the gas constant, T is the temperature (K), and M_{OH} is the molar mass of OH.¹⁷ By combining eqn (I) and (III), the

reaction probability can be calculated. Assuming a surface concentration of POPC of $1.6 \times 10^{14} \text{ molecules cm}^{-2}$ and using the lower limit value of k_1 above, a reaction probability for reaction of OH with the double bond in POPC of $\gamma^{\text{add}} > (4 \pm 1) \times 10^{-3}$ (1s) is obtained.

The OH radical can also abstract from the saturated portions of the alkyl chain (overwhelmingly the $-\text{CH}_2-$ groups), leading to a decrease in their infrared absorption bands as is observed (Fig. 3b). However, $-\text{CH}_2-$ (and $-\text{CH}_3$) groups can also be lost due to scission of the C=C bond (Scheme 2) if the end fragment forms a volatile product that is pumped away in the gas stream. A significant contribution from the latter mechanism would be expected based on the observation of a number of multifunctional products from addition to the double bond followed by bond scission (Fig. 2b and Scheme 2). The rate of loss of $-\text{CH}_2-$ groups from POPC therefore should be larger than that from DPPC, which has the same number of $-\text{CH}_2-$ groups. However, the initial rates of $-\text{CH}_2-$ decay were indistinguishable, within experimental error, in the two systems. This could arise if the products of bond scission remain adsorbed to the salt surface. While nonanal, for example, is quite volatile and likely to be pumped away,^{29,41} species such as 2-hydroxydecanal (Scheme 2) may be retained to a larger extent on the salt surface.

To test this possibility, a sample of POPC–NaCl was exposed to commercially available 1-undecanol (C₁₁ alcohol, calculated⁴⁹ vapor pressure is $7 \times 10^{-6} \text{ atm}$ at 295 K) and the spectrum recorded. Pumping for three hours did not result in changes in the spectrum, indicating the alcohol remained adsorbed on the salt. Given that the calculated vapor pressure of 2-hydroxydecanal ($9 \times 10^{-7} \text{ atm}$) is even lower than that of 1-undecanol, it is also not expected to be pumped from the sample. Similarly, the organic nitrate 2-nitrooxydecanal (Scheme 2) has a sufficiently low calculated vapor pressure ($9 \times 10^{-7} \text{ atm}$)⁴⁹ that it and similar products may remain on the salt. Thus, the lack of difference in the rates of $-\text{CH}_2-$ decay for POPC and DPPC is likely due to retention of many of the multifunctional products of C=C scission on the salt.

The relative importance of addition to the C=C bond compared to abstraction from $-\text{CH}_2-$ groups can be estimated

Table 2 Lower limits for rate constants and reaction probabilities for POPC–NaCl and DPPC–NaCl + OH

	A_{2850}	[IPN] (10^{16} cm^{-3})	$[OH]^a$ (10^8 cm^{-3})	k_1 ($10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) ^b	$\gamma^{\text{addition } b}$
POPC–NaCl	0.233	0.19	1.7	3.8	4×10^{-3}
	0.184	0.30	2.3	3.6	4×10^{-3}
	0.172	0.37	2.7	2.7	3×10^{-3}
	0.176	8.0	6.4	3.5	4×10^{-3}
	0.254	8.1	6.4	2.2	2×10^{-3}
	0.246	9.1	6.4	2.0	2×10^{-3}
	0.179	11	6.4	5.7	6×10^{-3}
			Average	$(3 \pm 1) (1s)^b$	$(4 \pm 1) \times 10^{-3} (1s)^b$
				k_2 ($10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) ^b	$\gamma^{\text{abstraction } b}$
DPPC–NaCl	0.187	0.24	2.0	8.7	9×10^{-4}
	0.206	0.27	2.2	5.9	6×10^{-4}
	0.191	0.23	2.0	7.2	8×10^{-4}
			Average	$(7 \pm 1) (1s)^b$	$(8 \pm 1) \times 10^{-4} (1s)^b$

^a Calculated using Acuchem, see text for details. ^b Lower limits as discussed in text.

if it is assumed that the rate constants for abstraction are the same for DPPC and POPC. Using a similar approach to that in eqn (II) for the loss of $-\text{CH}_2-$ in DPPC gives an average rate constant (k_2) for abstraction, $k_2 = (7 \pm 1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1s), corresponding to a reaction probability of $\gamma^{\text{abst}} = (8 \pm 1) \times 10^{-4}$ (Table 2); these again are lower limits due to the possibility of aggregation of the phospholipid on the surface as discussed above. Using the value of $k_1 = (3 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for addition of OH to the POPC double bond, the percentage of the reaction that occurs initially by addition is $\sim 80\%$. This can be compared to what would be expected for a gas phase reaction using the structure–reactivity relationships of Atkinson.^{50,51} The ratio of rate constants for addition of OH to a *cis*-C=C bond compared to abstraction of a secondary C–H (with two neighboring $-\text{CH}_2-$ groups) is 40. With 28 $-\text{CH}_2-$ groups and two $-\text{CH}_3$ groups total in the oleoyl and palmitoyl chains of POPC, one might expect addition to the double bond to account for 60% of the reaction. This is within experimental error of the DRIFTS measurements, suggesting that oxidation at a gas–solid interface does not significantly change the branching ratio for addition *versus* abstraction.

Atmospheric implications

Based on these studies, the lifetime of POPC with respect to both OH addition and hydrogen abstraction would be < 6 days at an atmospherically relevant OH concentration of $5 \times 10^6 \text{ radicals cm}^{-3}$. The lifetime of DPPC where only hydrogen abstraction can occur would be much longer, < 32 days. These lifetimes are much longer than the 6 hour lifetime predicted for the reaction of POPC with 100 ppb O_3 .⁴³

In the atmosphere, sea-salt aerosol particles can potentially experience both bottom-up and top-down oxidation. Initially, only top down oxidation will occur in freshly generated particles that don't contain species such as NO_2^- or NO_3^- that can be photolyzed to yield oxidants. Bottom-up oxidation will begin to occur if these species form in the particles *via* NO_x reactions with the halide ions^{20,52} and are subsequently photolyzed.^{53–58} With an OH concentration of $5 \times 10^6 \text{ radicals cm}^{-3}$ and a reaction probability of $> 4 \times 10^{-3}$, the rate of reactive OH uptake would be $> 3 \times 10^8 \text{ radicals s}^{-1} \text{ per cm}^2$ of surface. For particles containing 1% NaNO_3 on the surface, the upper limit to the production rate of OH from photolysis of NO_3^- on July 1 at a solar zenith angle of 0° would be $2 \times 10^6 \text{ radicals s}^{-1} \text{ per cm}^2$ of surface, assuming the previously calculated photolysis rate constant²⁴ for NO_3^- of $3.9 \times 10^{-7} \text{ s}^{-1}$. Even if every OH produced this way reacted with an organic molecule, oxidation from the bottom up would not be competitive with top-down oxidation. The products in both these top-down and the previous bottom-up studies^{23,24} include organic nitrates. These species can serve as reservoirs for oxides of nitrogen that can decompose to release NO_x back into the atmosphere^{59,60} far from where they were formed.¹⁷

Acknowledgements

This work was supported by the National Science Foundation (Grant No. 0836735 and 1207112). The authors would like to

thank James N. Pitts Jr. for helpful discussions and comments on the manuscript, and John Greaves, Beniam Berhane, Véronique Perraud, Carla Waring-Kidd, and Noriko Nishino for helpful discussions.

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