Products and kinetics of the reactions of an alkane monolayer and a terminal alkene monolayer with NO₃ radicals

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[1] The reactions of an alkanethiol and a terminal alkenethiol self-assembled monolayer with NO₃ radicals (in the presence of NO₂ and O₂) were studied. For the alkane monolayer, infrared (IR) spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirmed the formation of organonitrates (RONO₂). The observation of organonitrates is in contrast to the recent X-ray photoelectron spectroscopy (XPS) data, which showed very little nitrogen-containing surface species. The identification of organonitrates may help explain why significant volatilization of the organic chain was not observed in recent studies of alkane monolayer oxidation by NO₃ radicals. The reactive uptake coefficient (γ) of NO₃ on alkene monolayers determined in our study is higher than the values obtained in a recent study using liquid and solid alkene bulk films. A possible reason for this difference may be the location of the double bond at the interface. Using the γ value determined in our studies, we show that under conditions where NO₃ is high the lifetime of an alkene monolayer in the atmosphere may be short (approximately 20 min). XPS, IR, and ToF-SIMS were used to identify surface functional groups after the oxidation of the alkene monolayers by NO₃. The results are consistent with the formation of C-O, aldehyde/ketone, carboxylic groups, and nitrogen containing species.

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1. Introduction

[2] Field measurements have shown that organic material is abundant in the atmosphere, comprising 10–90% of the total fine particulate mass [Kanakidou *et al.*, 2005]. This organic material can be in the form of pure organic aerosol particles, or alternatively the organic substances can be mixed with inorganic material. In the latter case, the organic material can form coatings on the surface of aqueous particles [Ellison *et al.*, 1999; Gill *et al.*, 1983] or coatings adsorbed on the surface of solid particles, such as mineral dust [Usher *et al.*, 2003a].

[3] Recently the oxidation of condensed phase organic material by atmospheric radicals has attracted significant attention [Arens *et al.*, 2002; Bertram *et al.*, 2001; Bröske *et al.*, 2003; D'Andrea *et al.*, 2008; Docherty and Ziemann, 2006; Eliason *et al.*, 2004; Ellison *et al.*, 1999; Esteve *et al.*, 2003, 2004, 2006; George *et al.*, 2007; Gross and Bertram, 2008; Hearn *et al.*, 2007; Hearn and Smith, 2006; Hung *et al.*, 2005; Inazu *et al.*, 1997; Ishii *et al.*, 2000; Kahan *et al.*, 2006; Knopf *et al.*, 2006; Lai and Finlayson-Pitts, 1991; Lambe *et al.*, 2007; Mak *et al.*, 2007; McNeill *et al.*, 2007, 2008; Moise and Rudich, 2001; Moise *et al.*, 2002; Molina *et al.*, 2004; Perraudin *et al.*, 2005; Robinson *et al.*, 1995; Rudich, 2003; Rudich *et al.*, 2007; Vlasenko *et al.*,

2008; Wang *et al.*, 2000]. Field measurements suggest that this chemistry may change the composition of atmospheric particles [Robinson *et al.*, 2006]. Some studies suggest that these heterogeneous reactions can lead to rapid volatilization of organic particulate matter [McNeill *et al.*, 2008; Molina *et al.*, 2004; Vlasenko *et al.*, 2008]. The reactions may also be a significant sink for organic particles [Molina *et al.*, 2004] and a major source of volatile organic carbon (VOC) in the atmosphere [Ellison *et al.*, 1999; Kwan *et al.*, 2006]. Other studies suggest that under certain conditions these radical heterogeneous reactions may not be a significant source of VOC material [see, e.g., Docherty and Ziemann, 2006; George *et al.*, 2007; Hearn *et al.*, 2007; Knopf *et al.*, 2006; Moise and Rudich, 2001].

[4] Recently it has been suggested that radical-organic heterogeneous chemistry may vary significantly depending on the phase of the organic, the organic structure, oxygen concentration, and NO concentration [Ziemann, 2007]. These factors are expected to influence the relative importance of the different reaction pathways, and the importance of volatilization. More work with a range of experimental conditions is required to better understand the effect of these various factors on heterogeneous radical-organic chemistry so that laboratory results can accurately be extrapolated to the atmosphere.

[5] To improve the understanding of radical-organic heterogeneous chemistry, we have studied the reaction between NO₃ radicals (in the presence of O₂ and NO₂) and two types of organic self-assembled monolayers (SAMs). Studies with these surfaces enabled us to probe radical-organic reactions

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Figure 1. XPS results of NO₃ exposed ODT from Knopf *et al.* [2006]. (a) Atomic ratio of total oxygen, O, to total carbon, C_{total}, as a function of NO₃ exposure. (b) Atomic ratio of oxidized carbon, C_{ox}, to total carbon, C_{total}, as a function of NO₃ exposure. The bottom axis gives NO₃ exposure (atm sec) and the top axis gives total exposure time at 50 ppt NO₃ (days). Both *x* axes are valid for Figures 1a and 1b.

confined to the gas-surface interface, and separate surface and bulk processes [Rudich, 2003]. The results from these studies may provide insight into the reactivity of organics adsorbed on solid substrates such as mineral dust particles or urban surfaces [Diamond *et al.*, 2000; Donaldson *et al.*, 2005; Simpson *et al.*, 2006; Usher *et al.*, 2003a], and the reactivity of organic coatings on aqueous particles in the atmosphere [Ellison *et al.*, 1999]. These results may also provide insight into the reactivity of solid surfaces [Vieceli *et al.*, 2004]. The self-assembled monolayers we studied were an alkane monolayer (1-octadecanethiol C₁₈H₃₈S), referred to as ODT; and a terminal alkene monolayer (undec-10-ene-1-thiol, C₁₁H₂₂S), referred to as UDT. Differences in behavior between ODT and UDT can be attributed to the presence of the terminal double bond in UDT and not to the difference in chain length, since properties of hydrocarbon thiols on gold are thought to be independent of chain length for chains of more than 10 C atoms [Bain *et al.*, 1989].

[6] NO₃ radicals were chosen for these studies since NO₃ is an abundant radical in the troposphere with concentrations in the polluted nighttime of 60–300 ppt [Aldener *et al.*, 2006; Platt *et al.*, 1980; Stutz *et al.*, 2004] with measured extremes of up to 430 ppt [Finlayson-Pitts and Pitts, 2000]. Also it has recently been shown that reactions between NO₃ radicals and organic particles can be efficient and comparable in atmospheric importance to OH-organic heterogeneous reactions

under certain conditions [Gross and Bertram, 2008; Karagulian and Rossi, 2007; Knopf *et al.*, 2006; Mak *et al.*, 2007; Moise *et al.*, 2002].

[7] In our experiments, as mentioned above, the NO₃ reactions were performed in the presence of O₂ and NO₂ (NO₂ is a byproduct of the method of producing NO₃). This should complement several previous radical-organic heterogeneous studies which were carried out free of NO₂. An understanding of the effect of NO₂ concentrations may help explain some of the discrepancies in the literature on radical-organic heterogeneous reactions and they are expected to be of atmospheric relevance, since many atmospheric conditions have high NO₂ concentrations [Finlayson-Pitts and Pitts, 2000].

[8] The following research expands on our previous study of NO₃ radicals with ODT monolayers. In our previous study we used X-ray photoelectron spectroscopy (XPS) to investigate the oxidation of ODT monolayers [Knopf *et al.*, 2006]. Shown in Figure 1 are some of the results from this previous work [Knopf *et al.*, 2006]. The XPS data also show that less than 11% of the carbon chain was removed (i.e., volatilized) owing to NO₃ exposure. In addition, the XPS profiles were consistent with the formation of (1) C-O groups, (2) ketones or aldehydes, and (3) carboxylic acid groups. However, nitrogen species were not detected on the surface. As noted previously, nitrogen species (such as organonitrates) may have formed during the oxidation chemistry, but decomposed during the XPS measurements. In the following, we expand on our previous measurements by using infrared (IR) spectroscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to determine if surface nitrogen species do form during the oxidation of ODT monolayers by NO₃. This information is needed to determine if radical-organic reactions on monolayers are significantly different from the same reactions in the gas and liquid phase.

[9] In addition to studying reactions of an alkane monolayer, we also studied reactions of a terminal alkene monolayer. In this case, we performed detailed studies, since there have not been any previous studies of NO₃ radicals with alkene monolayers. Using a flow tube reactor, we measured the reactive uptake coefficient γ of NO₃ on the alkene monolayer as a function of NO₃ exposure. γ is defined as the fraction of collisions of the gas-phase reactant with the surface that leads to reactive uptake. These data were then used to determine how fast alkene surfaces and monolayers will be oxidized by NO₃ radicals in the atmosphere. We also carried out detailed surface-product studies. The results from these measurements were used to develop a mechanism for the NO₃-alkene monolayer reaction.

[10] Below we present the results for the alkane and alkene monolayers. We discuss reaction mechanisms for both monolayers. One of the main conclusions from these studies is that nitrogen containing species are significant products of the heterogeneous reactions studied.

2. Experimental Section

2.1. Chemicals

[11] Octadecanethiol (98%, C₁₈H₃₈S, ODT) was purchased from Sigma-Aldrich and used without further purification. Undec-10-ene-1-thiol (C₁₁H₂₂S, UDT) was synthesized according to the procedure described by Peanasky and

McCarley [1998]. NO₂ (99.5%) was purchased from Matheson, N₂ (99.999%), O₂ (99.993%) and He (99.999%) were purchased from Praxair. N₂O₅ was generated by reacting NO₂ with an excess amount of O₃ in a flow system as described by Schott and Davidson [1958]. The solid N₂O₅ crystals were stored at 197 K. NO₃ radicals were obtained by thermal conversion of gaseous N₂O₅ to NO₃ and NO₂ at 430 K in a Teflon-coated glass oven [Knopf *et al.*, 2006]. This dissociation of N₂O₅ was almost complete with residual N₂O₅ concentrations in the flow cell of approximately 1–3% of NO₃ concentrations.

2.2. Monolayer Preparation

[12] Monolayers were prepared on either gold coated silicon wafers for condensed phase product studies or a cylindrical gold coated tube for measurements of reactive uptake coefficients. These wafers and the cylindrical gold coated tube (inner diameter 1.91 cm, length 15 cm) were first cleaned in piranha solution (H₂SO₄ (96%)/H₂O₂ (30%) = 3:1), then rinsed with Millipore water (18 MΩ) and distilled ethanol. The wafers or the tubes were then immersed in a 1-mM solution of 1-octadecanethiol (ODT) or undecanethiol (UDT) in distilled ethanol for ≥24 h [Ishida *et al.*, 1997]. Subsequently, samples were cleaned in ethanol using an ultrasonic bath for 1 min and rinsed with Millipore water for approximately 3 min (5 min for gold tube). This cleaning procedure was repeated two more times. SAM coated gold surfaces were then dried under a stream of ultra-high-purity N₂.

2.3. Measurements of the Reactive Uptake Coefficient

[13] A temperature controlled, cylindrical flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS) was employed for measurements of the reactive uptake coefficient (γ) of NO₃ on alkene monolayers at 298 K. The inner wall of a gold coated tube was coated with a UDT SAM and inserted into the flow reactor. NO₃ radicals were added through a movable injector as previously described [Gross and Bertram, 2008; Knopf *et al.*, 2006; Mak *et al.*, 2007]. NO₃ concentrations of $(1\text{--}2) \times 10^{11}$ molecule cm⁻³ were used in the presence of O₂ $((1.1\text{--}1.3) \times 10^{16}$ molecule cm⁻³). The uncertainty in the NO₃ concentration was approximately ±40%. Helium was used as a carrier gas for NO₃. Total pressure in the flow reactor was 2.3–2.5 torr. NO₃ was detected at the exit of the flow cell using chemical ionization with I⁻ (obtained by passing trace amounts of CH₃I in N₂ through a ²¹⁰Po source). The NO₃ signal was monitored while the injector was pulled back at equal increments, exposing UDT surfaces to NO₃ radicals. Calculation procedures for the determination of γ from the depletion of the CIMS signal of the gas-phase reactant (here NO₃) during exposure to an organic surface have been described elsewhere [Knopf *et al.*, 2005].

2.4. Product Studies as a Function of Exposure

[14] The flow reactor was also used to expose SAMs on Au coated Si plates to NO₃ for subsequent XPS, IR, H₂O contact angle, and ToF-SIMS analysis. NO₃ exposure levels ranged from 0 to 9.06×10^{-5} atm sec (an exposure of 0–21 days at 50 ppt NO₃). Experiments were performed at 298 K, at a pressure of 2.3–2.7 torr, using NO₃ concentrations of $(1\text{--}5) \times 10^{11}$ molecule cm⁻³ and O₂ concentrations of $(1.1\text{--}1.6) \times 10^{16}$ molecule cm⁻³. Helium was used as carrier gas for NO₃.

XPS, IR and ToF-SIMS were then used to monitor the oxidation of the monolayer and identify surface products. H₂O contact angle measurements were used to determine the hydrophilicity of the monolayer.

[15] Note that in our experiments we were using relatively high NO₃ concentrations (approximately 1×10^{11} molecule cm⁻³), whereas in the atmosphere NO₃ concentrations are lower (roughly 1×10^9 molecule cm⁻³ depending on time and location). In order to extrapolate our results to the atmosphere, we assume that the only important parameter is total number of collisions between NO₃ radicals and the surface. This, however, requires verification in future experiments.

2.5. XPS, IR, ToF-SIMS, and Contact Angle Measurements

[16] XPS measurements were performed on a Leybold instrument using an achromatic Al K α X-ray source at a photon energy of 1486.6 eV and an electron take-off angle of 90°. Infrared measurements were performed with a Bruker grazing angle IR instrument in the wave number range 7000–500 cm⁻¹ (2048 scans per spectrum, 4 cm⁻¹ resolution). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was done using a Physical Electronics, PHI TRIFT II ToF-SIMS instrument with a 15 keV Ga⁺ primary ion beam (mass resolution ≥ 9000). The pulse duration was 5 ns with a current of 500 pA. Sample areas of 100 × 100 μm² were irradiated, total MS acquisition time was 10 min and negative ion spectra were obtained. The total ion dose was well below static limit. Contact angle estimates were obtained from camera images of a H₂O droplet (Millipore, 18 MΩ, static) on unreacted monolayers (ODT and UDT) and SAMs exposed to NO₃.

3. Results and Discussion

3.1. Reaction of NO₃ With an Octadecanethiol (ODT) Monolayer

3.1.1. IR Spectroscopy

[17] Grazing angle IR measurements were performed on ODT SAMs that had been exposed to NO₃ radicals. Listed in Table 1 are possible nitrogen species that may form during the NO₃ chemistry (in the presence of O₂ and NO₂) and the corresponding IR transition frequencies. For our analysis we only focused on the IR regions from 3000 to 2800 cm⁻¹ and 1700 to 1200 cm⁻¹. The 3000–2800 cm⁻¹ region corresponds to the C-H stretching region. The 1700–1200 cm⁻¹ region covers a frequency range where several of the possible nitrogen species have transitions. We did not include in this analysis the regions above 3000 cm⁻¹, between 2800 and 1700 cm⁻¹ and below 1200 cm⁻¹ because assigning the baseline in these regions was often difficult and subjective owing to large baseline fluctuations, low peak intensities, and interference by water vapor peaks in some areas. Shown in Figure 2 are typical results. NO₃ exposures used in this study were 3.6×10^{-5} atm sec, which is equal to 50 ppt for 8.4 days. 50 ppt (24 h average) corresponds roughly to polluted conditions. On the basis of the XPS data shown in Figure 1 the amount of carbon oxidation with this exposure was about 20%. The spectrum shown in Figure 2 corresponds to $(I_{\text{unoxidized}} - I_{\text{oxidized}})/I_{\text{unoxidized}}$, where I_{oxidized} and $I_{\text{unoxidized}}$ correspond to the intensity of the reflected light from the oxidized and unoxidized film, respectively. The results from

Figure 2. ODT IR spectrum calculated from an ODT sample exposed to 3.6×10^{-5} atm sec of NO₃ and an unoxidized ODT SAM as reference sample (see text). Negative peaks correspond to features only present or more prominent in the unexposed ODT SAM; positive peaks show features only present or more prominent in the exposed ODT SAM.

Figure 2 show first that the NO₃ reaction led to the disappearance of the CH₃ and CH₂ groups, which is consistent with the oxidation of the organic chain. Figure 2 also shows the appearance of new peaks at 1645 and 1283 cm⁻¹ after exposure to NO₃. The presence of these peaks is consistent with the formation of organonitrates (RONO₂) (see Table 1). Organonitro (RNO₂) groups, peroxy nitrates (ROONO₂) and peroxyacylnitrate surface species were not identified in the IR data. Peroxy nitrates and peroxyacylnitrates are expected to have a short lifetime. Hence, these species may have been lost when transferring the substrates to the analytical instruments for surface analysis.

[18] The observation of organonitrate peaks in the IR spectrum is in contrast to the XPS data by Knopf *et al.* [2006],

which showed very little N(1s) signal. This suggests that the organonitrates decomposed during the XPS measurements. To investigate this further we exposed an ODT monolayer to NO₃ (exposure level = 9.06×10^{-5} atm sec). Then we recorded an IR spectrum of the sample, followed by an XPS spectrum, followed by another IR spectrum. In the first IR spectrum negative peaks in the region from 3000 to 2800 cm⁻¹ were observed owing to the disappearance of CH₃ and CH₂ surface species, and positive peaks at 1645 cm⁻¹ and 1283 cm⁻¹ were observed due to the formation of alkyl nitrates, similar to Figure 2. However, in the second IR spectrum (after the XPS measurements) the 1645 cm⁻¹ and 1283 cm⁻¹ peaks were strongly diminished in intensity, while features for CH₃ and CH₂ remained unchanged. This provides further support that the N-containing functional groups decomposed during XPS analysis. In general, XPS is considered nondestructive, but some damage to sensitive material has been reported before [Laibinis *et al.*, 1991; Ulman, 1995; Wasserman *et al.*, 1989]. A comparison between the average bond energies shows that O-N bonds (201 kJ mol⁻¹) are much weaker than C-O (358 kJ mol⁻¹) or C=O (799 kJ mol⁻¹) [Ebbing, 1993] and therefore organonitrates should be much more prone to decomposition in XPS than the other functional groups expected in our experiments. Alcohols, carbonyl and carboxyl groups have been analyzed successfully by XPS in the past [Briggs and Beamson, 1992; Dicke *et al.*, 2002; Wang *et al.*, 2005] and are not expected to decompose owing to the bond strengths.

3.1.2. ToF-SIMS Measurements

[19] ToF-SIMS measurements were also carried out to further confirm the formation of nitrate functional groups. Figure 3 shows negative ion ToF-SIMS spectra of an ODT monolayer prior to exposure to NO₃ (Figure 3a) and after exposure to NO₃ (Figure 3b). For these studies an exposure of 5.4×10^{-5} atm sec (equivalent to 50 ppt NO₃ for 12.6 days) was used. On the basis of the XPS data shown in Figure 1, approximately 35% of the carbon is oxidized with this exposure.

[20] The Figure 3a spectrum, recorded before NO₃ exposure, shows mostly Au_xS_y clusters and low molecular weight

Table 1. Peak Assignment for IR Spectroscopy of Different Nitrogen Containing Species^a

Assignment	Peak Position (cm ⁻¹)	Reference
RNO ₂	1580–1540	Allen <i>et al.</i> [1994], Hung <i>et al.</i> [2005], Jang and Kamens [2001], Lai and Finlayson-Pitts [1991], Tuazon <i>et al.</i> [1999], Williams and Fleming [1989]
	1390–1340	[Hung <i>et al.</i> [2005], Jang and Kamens [2001], Tuazon <i>et al.</i> [1999], Williams and Fleming [1989]
RONO ₂	1666–1600	[Allen <i>et al.</i> [1994], Alvarado <i>et al.</i> [1999], Atkinson <i>et al.</i> [1998], Hallquist <i>et al.</i> [1999], Hung <i>et al.</i> [2005], Jang and Kamens [2001], Lai and Finlayson-Pitts [1991], Palen <i>et al.</i> [1992], Tuazon <i>et al.</i> [1999], Williams and Fleming [1989]
	1286–1250	Allen <i>et al.</i> [1994], Alvarado <i>et al.</i> [1999], Atkinson <i>et al.</i> [1998], Cassanelli <i>et al.</i> [2006], Hallquist <i>et al.</i> [1999], Hung <i>et al.</i> [2005], Palen <i>et al.</i> [1992], Tuazon <i>et al.</i> [1999], Williams and Fleming [1989]
	862–843	Allen <i>et al.</i> [1994], Alvarado <i>et al.</i> [1999], Atkinson <i>et al.</i> [1998], Cassanelli <i>et al.</i> [2006], Hallquist <i>et al.</i> [1999], Hung <i>et al.</i> [2005], Palen <i>et al.</i> [1992], Tuazon <i>et al.</i> [1999]
	1724–1721	Hallquist <i>et al.</i> [1999], Tuazon <i>et al.</i> [1999]
ROONO ₂	1298–1296	Hallquist <i>et al.</i> [1999], Hung <i>et al.</i> [2005], Tuazon <i>et al.</i> [1999]
	797–789	Hallquist <i>et al.</i> [1999], Tuazon <i>et al.</i> [1999]
PAN	1842–1830	Allen <i>et al.</i> [2005], Atkinson <i>et al.</i> [1998]
	1741–1738	Allen <i>et al.</i> [2005], Atkinson <i>et al.</i> [1998]
	1302–1300	Allen <i>et al.</i> [2005], Atkinson <i>et al.</i> [1998]
	794	Allen <i>et al.</i> [2005], Atkinson <i>et al.</i> [1998]

^aR, alkyl chain; PAN, peroxyacetylnitrate. Typical ranges of wave numbers (cm⁻¹) and references are provided.

Figure 3. Negative ion ToF-SIMS spectra of ODT on gold in the m/z 1–700 region. (a) Spectrum was obtained on an ODT sample without NO₃ exposure. (b) Spectrum was obtained after an NO₃ exposure of 5.4×10^{-5} atm sec (equivalent to 50 ppt NO₃ for 12.6 days).

fragments of the alkanethiol chains (C⁻, CH⁻, C₂H⁻, S⁻, SH⁻), but also characteristic peaks for ODT. These peaks included the whole molecule of ODT and are labeled “MS” in Figure 3 with “M” meaning C₁₈H₃₇. The observed peaks agreed well with those observed in previous ToF-SIMS measurements of alkanethiol SAMs on gold performed by *Offord et al.* [1994], *Sun and Gardella* [2002], and *Sohn et al.* [2004].

[21] Comparisons of ODT spectra in Figures 3a and 3b showed that after NO₃ exposure, peaks characteristic of the unoxidized hydrocarbon SAMs (C⁻, CH⁻, C₂H⁻, S⁻, SH⁻, H₂AuMS⁻, and Au₂MS⁻) decreased or disappeared. New peaks of high intensities formed in the m/z region < 100 amu, which can be attributed to O⁻, OH⁻, NO₂⁻, NO₃⁻, SO₃⁻, and HSO₄⁻. Furthermore, a large number of additional peaks emerged in the m/z region > 100 amu, but with smaller intensities. These are most likely due to oxidized ODT molecules that subsequently fragmented during the sputtering process. Owing to the high number of possible fragments in these long chain hydrocarbons, the wide variety of different oxidation levels and the variety of different oxidation products, it was not possible to identify these products unambiguously.

[22] The identification of NO₂⁻ and NO₃⁻ peaks in ToF-SIMS confirmed the formation of nitrogen containing species on the surface, and these peaks are also consistent with the formation of organonitrates, which fragment to NO₂⁻ and NO₃⁻ during the sputtering process.

[23] The combined evidence for the presence of organonitrates found in IR and ToF-SIMS clearly showed that these compounds were formed during reaction of ODT with NO₃ but were not stable in XPS analysis.

[24] The Figure 3b spectrum also shows peaks due to SO₃⁻ and HSO₄⁻. Oxidized sulfur likely results from oxidation of the sulfur group in the monolayer by NO₃ at large exposures. This is consistent with previous XPS results that also showed oxidation of the sulfur group at NO₃ exposures greater than 3×10^{-5} atm sec [*Knopf et al.*, 2006].

3.1.3. Contact Angle Measurements

[25] Contact angles of H₂O droplets on unexposed and NO₃ exposed ODT monolayers were obtained using camera images. The initial contact angle determined for ODT before NO₃ exposure was $101^\circ \pm 4^\circ$ (error represents one standard deviation). Reported literature values for different long chain alkane monolayers (C₈–C₁₈) range from 93° to 119° [*Bain et al.*, 1989; *Bertram et al.*, 2001; *Dubowski et al.*, 2004; *Inman*

Figure 4. Proposed reaction mechanism for an alkane surface with NO₃ in the presence of NO₂ and O₂ based on gas-phase chemistry.

et al., 2004; Offord *et al.*, 1994; Owens *et al.*, 2004; Paz *et al.*, 1992; Robinson *et al.*, 1995; Rudich *et al.*, 2000; Thomas *et al.*, 2001; Wasserman *et al.*, 1989]. These numbers show that our contact angle for ODT is in general agreement with literature values.

[26] ODT samples were exposed to 9.06×10^{-5} atm sec NO₃ (equivalent to 50 ppt for 21 days). This exposure can be seen as an extreme limit of aerosol exposure under polluted conditions. After this exposure, the contact angle on ODT was $60^\circ \pm 6^\circ$, a decrease by approximately 41° . This result is consistent with the monolayers becoming more hydrophilic owing to oxidation. Previous studies investigating changes in H₂O contact angles (θ) on hydrocarbon monolayers (C₈–C₂₀) after exposure to gas-phase reactants reported a very broad range of data for alkanes: after F radical exposure $\theta = 82^\circ$ [Robinson *et al.*, 1995], after O₃ exposure $\theta = 71^\circ$ and 99° [Owens *et al.*, 2004; Thomas *et al.*, 2001], after OH exposure $\theta = 10^\circ$ [Bertram *et al.*, 2001], and after O exposure $\theta = \sim 35$ – 45° [Paz *et al.*, 1992]. Part of the variability is likely due to the different exposure levels used in these experiments and also to different condensed phase products formed (e.g., hydroxyl groups versus carbonyl groups).

[27] To put our values in an atmospheric context, we converted our contact angle results into cloud condensation nucleation activities. On the basis of data presented by Pruppacher and Klett [1997], an insoluble 200 nm (diameter) particle with $\theta = 101^\circ$ will have a critical supersaturation ($S_{\text{crit}} = RH - 100\%$) for water nucleation of $> 150\%$. In contrast, an insoluble 200 nm particle with $\theta = 60^\circ$ will have a critical supersaturation of approximately 100%. This shows that the oxidation by NO₃ radicals can decrease the critical supersaturation required for water nucleation. However, even after oxidation, the S_{crit} is still much larger than S_{crit} for water soluble particles. For example, S_{crit} for a

200 nm ammonium sulfate particle is less than 0.1% [Seinfeld and Pandis, 2006]. Also, typical values of supersaturations found in clouds are between about 0.2 and 2% [Finlayson-Pitts and Pitts, 2000].

3.1.4. Proposed Reaction Mechanism

[28] Shown in Figure 4 is the proposed mechanism for oxidation of an alkane monolayer by NO₃ radicals in the presence of O₂ and NO₂ based on gas-phase chemistry. We use this as a starting point to discuss the previous XPS data from Knopf *et al.* [2006] and the current IR and ToF-SIMS data.

[29] As a reminder, XPS showed limited volatilization (i.e., loss of the carbon chain), and the formation of (1) C–O groups, (2) ketones or aldehydes, and (3) carboxylic groups. The IR spectra and ToF-SIMS showed the formation of organonitrates.

[30] The initial reaction step (1) in the oxidation process is the abstraction of a hydrogen atom from a methyl or methylene group of the alkyl chain to form HNO₃ and an alkyl radical. The second reaction step is the transformation of an alkyl radical into a peroxy radical in the presence of O₂ [Atkinson, 1997]. In the presence of NO₂, peroxy nitrates may form which may subsequently thermally decompose back to the reactants (step 3) [Atkinson, 1997]. Hence peroxy nitrates represent a temporary reservoir of NO₂. The peroxy radical can also react with NO₃ to form an alkoxy radical, NO₂, and O₂ (step 5). Alternatively, the peroxy radical can undergo self reaction, leading to the formation of alkoxy radicals and O₂ (step 5) or an alcohol and carbonyl (step 4) [Atkinson, 1997]. If the alkoxy radical forms, it can decompose by scission of a C–C bond (step 8), or can undergo isomerization to form a hydroxyl alkyl radical (step 9). Alternatively the alkoxy radical can react with NO₂ to form alkylnitrates (step 6) or react with O₂ to form ketones or aldehydes (step 7) [Atkinson, 1997].

[31] The XPS data suggest that decomposition by scission of a C–C bond is of minor importance (step 8). The presence of C–O, ketones, and aldehydes can be explained by step 4, step 7 or step 9. Carboxylic functional groups observed in XPS spectra are probably due to C(=O)O formed in secondary reactions, for example, oxidation of aldehydes to acids (as reported by George *et al.* [2007]). The new results in this manuscript (based on IR and ToF-SIMS data) show that organic nitrates are also a significant product of the heterogeneous oxidation. Organonitrates can be formed by step 6. Alternatively it has been suggested that organoperoxy nitrates can decompose in the condensed phase to form organonitrates or carbonyls [Docherty and Ziemann, 2006]. This pathway (not shown in Figure 4) may also be important in our monolayer studies for the production of organonitrates.

[32] The identification of organonitrates in our oxidation studies may be important for a few reasons: first, the formation of organonitrates in our experiment may explain why we did not see significant decomposition of the carbon chains in our recent studies with NO₃ radicals. In our previous study we showed that NO₃ (in the presence of O₂ and NO₂) does not rapidly decompose an alkane monolayer by scission of a C–C bond: even under extremely polluted conditions, the maximum loss of the organic layer was only 10% [Knopf *et al.*, 2006]. This is consistent with our current studies that show that the formation of organonitrates is a significant pathway. Formation of organonitrates removes RO₂ and/or RO species

from the system, and hence will reduce the importance of the decomposition channel. Possibly this is one of the differences between our work with NO₃ and alkane monolayers and the recent studies with OH and alkane SAMs where significant decomposition was observed.

[33] Second, the results suggest that perhaps under certain atmospheric conditions, radical-organic reactions may be a source of condensed phase organonitrates. It is well known that condensation of gas phase species is an important source of condensed phase organonitrates. Also another possible source of particle-bound organonitrates is condensed phase photochemistry [Karagulian *et al.*, 2008]. Perhaps under certain conditions of high NO₃ and NO₂ concentrations the formation of condensed phase organonitrates by radical-organic reactions may also contribute. Field measurements exploring this topic would be interesting.

[34] Third, our results may have implications for condensed phase OH-organic reactions as well. Under many atmospheric conditions, NO₂ concentrations are high. Perhaps for these situations, organonitrates will also form by a similar mechanism to the mechanism in our experiments (either RO + NO₂ or RO₂ + NO₂ to form RO₂NO₂ followed by decomposition to RONO₂) and limit the importance of the decomposition channel (step 8 in Figure 4) in the OH-organic reaction. However, Molina *et al.* [2004] studied the oxidation of an alkane monolayer by OH in the presence of NO_x/O₂/H₂O in various proportions and they observed significant decomposition of the monolayer. This suggests that the OH-organic reaction mechanism is less susceptible to the presence of NO₂.

3.2. Reaction of NO₃ With Undecenethiol (UDT): A Terminal Alkene SAM

3.2.1. Reactive Uptake Coefficient of NO₃ on an Unoxidized UDT SAM

[35] The γ value for a UDT SAM was determined to be 3.4×10^{-2} ($+ 4.4 \times 10^{-2}/-1.8 \times 10^{-2}$) (the uncertainty reported corresponds to the 95% confidence interval and an uncertainty in the diffusion coefficients of NO₃ in He and O₂ of 15%). In comparison, the value determined for ODT was $(8.8 \pm 1.0) \times 10^{-4}$ [Knopf *et al.*, 2006], a factor of approximately 39 less. This enhancement of UDT reactivity compared to ODT reactivity is in agreement with the enhancement observed for reaction rate constants of different gas-phase reactions of alkanes and alkenes with NO₃. For example $k_{\text{propene}}/k_{\text{propane}} = 18$, $k_{1\text{-butene}}/k_{n\text{-butane}} = 305$, $k_{\text{cyclohexene}}/k_{\text{cyclohexane}} = 237$, where k represents different gas-phase rate constants for NO₃ reactions [Atkinson, 1997; Finlayson-Pitts and Pitts, 2000].

[36] The γ value of the terminal alkene UDT obtained in this study is higher than the values obtained by Moise *et al.* [2002] using liquid and solid alkene bulk films. Moise *et al.* [2002] measured $(1.6 \pm 0.3) \times 10^{-3}$ and $(1.4 \pm 0.1) \times 10^{-3}$ for liquid and solid 1-octadecene films; $(2.3 \pm 0.9) \times 10^{-3}$ and $(1.8 \pm 0.3) \times 10^{-3}$ for liquid and solid 1-hexadecene films; $(5.8 \pm 2.0) \times 10^{-3}$ and $(5.2 \pm 2.0) \times 10^{-3}$ for liquid and solid 7-tetradecene films, respectively. A possible reason for this difference may be the location of the double bond at the interface. In our experiments the double bond is located at the outermost two carbon atoms and is probably more easily accessible by NO₃ radicals than double bonds in a liquid or bulk solid. Vieceli *et al.* [2004], recently studied

the structure of liquid 1-tetradecene (C₁₄ alkene with a terminal double bond) and a 1-octenethiol SAM using molecular dynamics simulations. They showed that at the air-liquid interface the molecular orientation becomes perpendicular to the interface normal rather than random. Also these authors reported the percentage of the total accessible surface area that is due to double bonds as 28.5 and 99.7% for liquid 1-tetradecene and the terminal-alkene SAM, respectively. This trend is consistent with the difference observed between our study and the studies by Moise *et al.* [2002].

[37] Another possible reason for the difference between our results and the results by Moise *et al.* [2002] may be the NO₃ concentrations used in the different experiments. Moise *et al.* [2002] used a slightly higher concentration of NO₃. They also used a rotating flow reactor which replenishes the surfaces of the liquid and prevents the surface from being rapidly oxidized.

[38] Table 2 shows a summary of studies on heterogeneous reactions of different gas-phase oxidants with terminal alkene monolayers. Reactive uptake coefficients, γ , and average atmospheric concentrations for each oxidant are reported. Direct comparison of γ values for each oxidant is of minor atmospheric relevance since the concentration of each oxidant is different in the atmosphere. Therefore the last column in Table 2 shows the product of γ and the average atmospheric concentrations of the gas-phase oxidants. These numbers are more relevant parameters for assessing the importance of the various gas-phase species to atmospheric oxidation since the number of molecules lost to an organic surface should be proportional to $\gamma \times \text{concentration}$. The most important process will generally be the process with the largest $\gamma \times [\text{reactant concentration}]$ and therefore the highest oxidative power. The abundance of NO₃ in the atmosphere is highly variable, with a high spatial and seasonal variability. For these calculations we use NO₃ concentrations of 50 ppt and 5 ppt to roughly represent polluted urban and rural conditions [Atkinson *et al.*, 1986; Finlayson-Pitts and Pitts, 2000; Geyer *et al.*, 2001]. However, keep in mind NO₃ concentrations vary significantly in urban and rural conditions. As can be seen from Table 2, the oxidative power of NO₃ is significantly higher than that of OH, Cl, and Br. Only O₃ is of equal importance to NO₃ owing to its much higher tropospheric concentrations.

[39] Using the reactive uptake coefficient determined in this study and the equation presented by Gross and Bertram [2008] and Moise and Rudich [2001], we can calculate an average lifetime of an alkene monolayer at the interface of an aerosol particle in the atmosphere. Assuming an NO₃ concentration of 50 ppt, we obtain a value of 22.6 min. This shows that the lifetime is short in polluted environments and that in regions where NO₃ concentrations are high, surface concentrations of alkenes are expected to be low. A similar conclusion was reached by Moise and Rudich [2001] using reactive uptake coefficients determined on bulk liquid and solid alkene films.

3.2.2. Measurements of the Reactive Uptake of NO₃ as a Function of Exposure Time

[40] Measurements of the reactive uptake coefficient as a function of time were carried out to determine if the surfaces were catalytic (i.e., a reaction takes place at the surface but the surface is not an active participant) or if the reaction rate

Table 2. Reactive Uptake Coefficients of Different Gas-Phase Oxidants on Terminal Alkene Monolayers, Average Atmospheric Concentrations of the Gas-Phase Species, and Calculated Oxidative Power^a

Oxidant	Surface	γ	[Oxidant]	$\gamma \times [\text{Oxidant}]$
NO ₃	terminal C ₁₁ alkene ^b	0.034	1.2×10^9	4.1×10^7
			1.2×10^8	4.1×10^6
OH	terminal C ₃ alkene ^c	0.6	1×10^6	6×10^5
Cl	terminal C ₈ alkene ^d	0.1–1	1×10^4	$1 \times 10^3 - 1 \times 10^4$
Br	terminal C ₈ alkene ^d	0.05	1×10^6	5×10^4
O ₃	terminal C ₃ and C ₈ alkenes ^e	$9 \times 10^{-6} - 3 \times 10^{-4}$	2.5×10^{12}	$2.3 \times 10^7 - 7.5 \times 10^8$

^aNotation: γ , reactive uptake coefficients; [oxidant]/molecule cm⁻³, average atmospheric concentrations of the gas-phase species; and $\gamma \times [\text{oxidant}]$, calculated oxidative power. For NO₃ radicals, calculations have been performed for both high NO₃ concentrations (50 ppt) and low concentrations (5 ppt) to represent approximately a range of concentrations encountered in the atmosphere owing to spatial and seasonal fluctuations.

^bThis study.

^cBertram *et al.* [2001].

^dMoise and Rudich [2001].

^eDubowski *et al.* [2004], Moise and Rudich [2000], and Usher *et al.* [2003b].

decreased with time owing to oxidation of the monolayer. For these measurements an NO₃ concentration of 1.0×10^{11} molecule cm⁻³ was used. The change in γ with exposure to NO₃ is shown in Figure 5. The initial fast uptake coefficient is most likely due to a fast reaction with the double bond. Once the double bond was oxidized, the uptake coefficient reached a value consistent with the uptake on an alkane monolayer. The exposure at which the reactive uptake reached a near steady state value is consistent with the time it would take to oxidize all the alkene functional groups on the surface, based on calculations presented by Bertram *et al.* [2001].

[41] Next XPS, IR and ToF-SIMS studies of the reaction of NO₃ with alkene monolayers are presented. The purpose of these measurements is to identify surface products and determine the mechanism for the oxidation of the double bond. All these experiments were carried out using exposures less than 2×10^{-5} atm sec, which is significantly less than the exposures used in our previous alkane SAM studies. As shown in Figure 1, an alkane monolayer is hardly oxidized at exposures less than 2×10^{-5} atm sec. Using these low exposure levels, the reaction should be mostly confined to the double bond.

3.2.3. X-ray Photoelectron Spectroscopy

[42] XPS measurements of alkene monolayers were carried out as a function of NO₃ exposure (ranging from 0 to 1.8×10^{-5} atm sec, equivalent to 0 – 4.2 days at 50 ppt NO₃). Figure 6 shows the C(1s) region of the XPS spectra obtained using three different NO₃ exposures ranging from 0 to 9.1×10^{-6} atm sec (equivalent to 50 ppt for 50 h). For the unexposed sample only one peak at 285 eV was observed. This peak is due to vinyl or methylene functional groups. After exposure to NO₃, the main peak at about 285 eV remained, but a shoulder was observed at higher energies within the C(1s) region indicating the oxidation of the organic surface. We fit the total C(1s) region with four overlapping Gaussian-Lorentzian peaks, similar to our previous studies of alkane monolayers. The peaks used in the fit were centered at approx. 285 eV, 286.5 eV, 288 eV, and 289.5 eV. The peaks at energies above 285 eV represent oxidized C species (consistent with C-O, aldehyde/ketone, and carboxylic groups, respectively).

[43] To determine the fraction of carbon oxidized as a function of exposure time, we calculated the atomic ratio of oxidized carbon (C_{ox}, three peaks at higher binding energy) to the total carbon peak area (C_{total}). Figure 7c shows these

ratios for NO₃ exposures of 0– 1.8×10^{-5} atm sec. The error bars (which represent $\pm 2\sigma$) were derived from four different UDT SAMs on gold-coated Si wafers exposed to the same amount of NO₃. As can be seen, after exposures of only 2.0×10^{-7} atm sec (equivalent to 1.1 h at 50 ppt NO₃), approximately 12% of the C(1s) signal corresponded to oxidized carbon.

[44] Figure 7b shows the increase in O(1s) due to increasing NO₃ exposure. The trend observed is qualitatively the same as for C_{ox}/C_{total} in Figure 7c. As with C_{ox}/C_{total}, it is observed that for O/C after longer exposures (1.2×10^{-6} – 1.8×10^{-5} atm sec) the reaction slowed down and O/C increased with a smaller slope than in the initial stage of oxidation.

[45] We also exposed the monolayers to O₂ and NO₂, in the absence of NO₃. After exposure to just these species (using concentrations greater than those used in the NO₃ experiments) the C_{ox}/C_{total} atomic ratio and O/C atomic ratio were

Figure 5. Changes in the reactive uptake coefficient γ with increasing NO₃ exposure of a UDT SAM. Bottom x axis corresponds to actual time of the experiment (min) (at an NO₃ concentration of 1.0×10^{11} molecule cm⁻³), and top x axis shows the corresponding total NO₃ exposure time (hours) of the SAM at an atmospheric concentration of 50 ppt.

Figure 6. XPS spectra of the C(1s) region for a UDT monolayer (top) before exposure to NO₃ (0 atm sec) and after exposures of (middle) 1.2×10^{-6} atm sec (equivalent to 50 ppt for 6.7 h) and (bottom) 9.1×10^{-5} atm sec (equivalent to 50 ppt for 50 h).

within the error limits for the unexposed sample shown in Figure 7.

[46] To assess the amount of decomposition of the UDT SAM, we plotted the atomic ratio of the total integrated C(1s) signal to the total Au(4f) signal intensity (C/Au) (Figure 7d). No significant changes of this ratio could be observed within experimental certainty. However, owing to the large uncertainties, we can only conclude that less than 21% of the surface volatilized during the longest exposure experiments. As detachment of the carbon chain is also possible owing to oxidation of the sulfur head group, 21% should be considered an upper limit to the amount of carbon loss due to C-C bond scission.

[47] Monitoring the S(2p) signal of UDT SAMs after exposure to NO₃ showed only unoxidized sulfur (peak maximum at 163.1 ± 0.2 eV) for exposures $\leq 1.2 \times 10^{-6}$ atm sec and both unoxidized sulfur (peak maximum at 163.1 ± 0.2 eV) and oxidized sulfur (peak maximum at 168.0 ± 0.2 eV) for exposures $\geq 9.1 \times 10^{-6}$ atm sec.

[48] N(1s) signals were below detection limit in all measurements of exposed and unexposed UDT SAMs. However, the nitrogen species may have formed during the oxidation chemistry but decomposed during XPS measurements, similar to the alkane monolayer experiments. To determine if nitrogen species were formed in these reactions, we carried out IR and ToF-SIMS measurements (see below).

[49] To investigate the behavior of UDT after long exposures to NO₃ radicals, we also performed a few experiments with large NO₃ exposures. After an exposure of 4.5×10^{-5} atm sec the monolayers reached oxidized C fractions ($C_{\text{ox}}/C_{\text{total}}$) of 0.37%, and an O/C ratio of 0.42% (data not

Figure 7. Summary of processing study and XPS results for UDT. (a) Changes in γ with increasing NO₃ exposure. Changes in atomic ratios obtained in XPS as a function of NO₃ exposure for (b) atomic ratio of total oxygen, O, to total carbon, C; (c) atomic ratio of oxidized carbon, C_{ox} , to total carbon, C_{total} ; and (d) atomic ratio of total carbon, C_{total} , to total gold, Au. The two scales on the top and bottom x axes are valid for Figures 7a–7d and provide information on NO₃ exposure levels in atm sec (bottom axis) and in total exposure time (hours) at an atmospheric NO₃ concentration of 50 ppt (top axis).

Figure 8. UDT IR spectrum calculated from an UDT sample exposed to 1.21×10^{-6} atm sec of NO₃ (50 ppt for 6.7 h) and an unoxidized UDT SAM as reference sample (see text). Negative peaks correspond to features only present or more prominent in the unexposed UDT SAM; positive peaks show features only present or more prominent in the exposed UDT SAM.

shown). These values are similar to the values obtained on ODT monolayers after long NO₃ exposures.

3.2.4. IR Spectroscopy

[50] First, spectra were taken of an unexposed UDT sample with perdeuterated ODT as reference to confirm the presence of methylene groups in the original UDT SAMs (data not shown). Then IR measurements were performed on samples that had been exposed to NO₃. For this analysis we only focused on the IR regions from 3000 to 2800 cm⁻¹ and 1370 to 1200 cm⁻¹. The wavelength range used in these experiments is slightly smaller than the range used in the alkane monolayers experiments. This is because the signal to noise is smaller in the alkene experiments owing to the low NO₃ exposures and smaller degree of oxidation of the films. The spectrum shown in Figure 8 was obtained the same way as Figure 2 for ODT. An exposure level of 1.21×10^{-6} atm sec (50 ppt for 6.7 h) was used in this experiment. As with ODT, NO₃ exposure of UDT resulted in negative peaks in the range 3000–2800 cm⁻¹ due to the decrease of the symmetric and asymmetric stretching modes of CH₂. At this short exposure to NO₃ we do not expect significant oxidation of the methylene groups in UDT. As peak intensities depend on the orientation of the different vibrational modes [Ulman, 1991], we assume that the negative peaks appearing in the region of 3000–2800 cm⁻¹ are due to increased disorder within the monolayer due to reaction of the double bond. This is consistent with results by Moise and Rudich [2001] who observed almost complete disappearance of the CH₂ stretching peaks in IR, while XPS indicated only a 20% reduction in total carbon and a significant fraction of remaining unoxidized C(1s). The IR spectra clearly showed the formation of a peak at 1281 cm⁻¹. On the basis of Table 1, this could be due to an

organonitrate, organoperoxyntate, or peroxyacylnitrate. It seems unlikely that the identified surface species are organoperoxyntates or peroxyacylnitrate, since these species typically have a short lifetime and are expected to decompose while the substrates are transferred to the IR spectrometer for analysis, as discussed above. We can conclude that nitrogen species are formed, contrary to the conclusion one may reach from the XPS data.

3.2.5. ToF-SIMS Measurements

[51] Shown in Figure 9 are negative ion ToF-SIMS spectra for UDT before (Figure 9a) and after exposure to NO₃ (Figure 9b). As with ODT, spectra before NO₃ exposure showed Au_xS_y clusters, low molecular weight fragments of the monolayer chains (C⁻, CH⁻, C₂H⁻, S⁻, SH⁻), and characteristic peaks for the whole UDT molecule. These peaks are labeled M, which indicates C₁₁H₂₁. All peaks characteristic of the unoxidized hydrocarbon SAMs decreased or disappeared upon NO₃ exposure (C⁻, CH⁻, C₂H⁻, S⁻, SH⁻, MS⁻, and Au(MS)₂⁻). New peaks of high intensities formed especially in the m/z region < 100, which could be attributed to O⁻, OH⁻, NO₂⁻, NO₃⁻, SO₃⁻, and HSO₄⁻. As with ODT, peaks for NO₂⁻ and NO₃⁻ led us to conclude that nitrogen containing functional groups formed during the oxidation of UDT by NO₃, but decomposed during XPS measurements.

[52] Again, as with ODT, NO₃ exposed UDT SAMs showed peaks of SO₃⁻ and SO₄⁻. This is consistent with the appearance of a S(2p) peak of oxidized sulfur in XPS spectra of UDT exposed to $\geq 9.1 \times 10^{-6}$ atm sec.

3.2.6. Contact Angle Measurements

[53] The initial contact angle determined before NO₃ exposure was $92^\circ \pm 5^\circ$ for UDT (number given here is the average value and standard deviation). Literature values for monolayers of terminal alkenes (C₈–C₁₉) were reported at 89° – 107° [Bain et al., 1989; Bertram et al., 2001; Dubowski et al., 2004; Robinson et al., 1995; Rudich et al., 2000; Thomas et al., 2001; Wasserman et al., 1989]. The large contact angles observed for the unoxidized monolayers indicate the presence of well-ordered SAMs in this study. NO₃ exposure of UDT samples was 9.06×10^{-5} atm sec (equivalent to 50 ppt NO₃ for 3 weeks). After this exposure, the contact angle on UDT had decreased to $59^\circ \pm 6^\circ$, a decrease of 33° . This gives further support that the monolayers were oxidized leading to a more hydrophilic surface. Previous studies investigating changes in H₂O contact angles on hydrocarbon monolayers (C₈–C₁₉) after exposure to gas-phase reactants reported the following data for terminal alkene monolayers: after F radical exposure $\theta = 75^\circ$ [Robinson et al., 1995], and after O₃ exposure $\theta = 74^\circ$ and $\sim 70^\circ$ [Dubowski et al., 2004; Thomas et al., 2001].

3.2.7. Proposed Reaction Mechanism

[54] Shown in Figure 10 is the proposed mechanism for oxidation of an alkene monolayer by NO₃ radicals in the presence of O₂ and NO₂ based on gas-phase chemistry [Atkinson, 1991; Atkinson, 1997, 2000; Berndt and Böge, 1995; Gong et al., 2005; Kwok et al., 1996; Noda et al., 2000; Tuazon et al., 1999]. The gas-phase reaction of NO₃ with alkenes is assumed to proceed via addition of NO₃ to the C–C double bond (Figure 10, step 1). This leads to a C–ONO₂ functional group on one of the two C atoms of the double bond and leaves an alkyl radical at the other C atom.

Figure 9. Negative ion ToF-SIMS spectra of UDT on gold in the m/z 1–600 region. (a) Spectrum was obtained on a UDT sample without NO₃ exposure. (b) Spectrum was obtained after an NO₃ exposure of 9.1×10^{-6} atm s (equivalent to 50 ppt for 50 h).

This radical compound is expected to react further with O₂ to an alkylperoxy radical (RO₂, step 2) [Finlayson-Pitts and Pitts, 2000].

[55] Reactions of the RO₂ radical are believed to occur in the same way as those of the RO₂ in the alkane reaction scheme (Figure 4), except that the neighboring C atom contains an ONO₂ functional group. An additional difference is the fact that the scission channel leads to the elimination of NO₂ and the formation of two aldehydes (step 9).

[56] Not shown in Figure 10 are additional reactions that the alkyl nitrate radical may undergo at low pressures in competition with step 2. When the nitrate radical adds to the double bond, an excited state results. If this excited state is not collisionally stabilized, it can decompose to NO₂ and an aldehyde or ketone or alternatively eliminate NO₂ and form an epoxide that reacts further to a carbonyl [Atkinson, 1991; Dlugokencky and Howard, 1989]. The importance of these steps on a surface however is unclear.

[57] As a reminder, the XPS results are consistent with the formation of C–O, C=O, and C(=O)O functional groups. IR and ToF-SIMS analysis showed the formation of nitrogen-containing species, likely organonitrates. Scission of the carbon chain at the double bond could not be confirmed, but could not be ruled out either. The formation of C–O and C=O functional groups could be explained by step 4, the

Russell mechanism. Formation of C–O could also be explained by step 7, and the formation of C=O could also be explained by steps 8 and 9. Carboxylic functional groups determined using XPS were probably formed in secondary reactions, for example, oxidation of aldehydes [George *et al.*, 2007].

[58] Our experiments are the first to investigate heterogeneous reactions between radicals and alkene monolayers in the presence of O₂ and NO₂, so our product analysis should be helpful for understanding this heterogeneous mechanism. D'Andrea *et al.* [2008] investigated the reaction between OH and an alkene monolayer, but in the absence of NO₂ and O₂, so the results are not directly comparable. In addition, both Hung *et al.* [2005] and Docherty and Ziemann [2006] studied the reaction between NO₃ (in the presence of O₂ and NO₂) and liquid alkene particles. Hung *et al.* [2005] observed organonitrate, peroxyxynitrate, organonitrite, and carbonyl functional groups using infrared spectroscopy and high molecular weight products were also observed using LC-MS. Docherty and Ziemann [2006], using mass spectrometry, identified hydroxyl nitrates, carbonyl nitrates, dinitrates, hydroxydinitrates, and possibly more highly nitrated products. It is interesting to note that several of the functional groups identified in these previous liquid reactions were also identified in our current monolayer studies. It therefore appears

Figure 10. Proposed reaction mechanism for an alkene surface with NO₃ in the presence of NO₂ and O₂ based on gas-phase chemistry.

that the reaction pathways for the alkene monolayers are similar to the reaction pathways for the liquid, although the relative importance of the different channels may differ.

[59] Also, when studying the reaction between NO₃ and liquid alkene particles, *Docherty and Ziemann* [2006] observed substantial organonitrate formation after the double bond was completely reacted, which was attributed to either the reaction of N₂O₅ with a hydroxyl group or H-atom abstraction. This latter explanation is consistent with the alkane monolayer results we presented above.

4. Conclusions and Atmospheric Implications

[60] For the alkane SAM, IR spectroscopy and ToF-SIMS confirmed the formation of organonitrates (RONO₂). The observation of organonitrates is in contrast to the XPS data by *Knopf et al.* [2006], which showed very little N(1s) signal. The formation of organonitrates in our experiment may explain why we did not see significant decomposition of the carbon chains in our recent studies with NO₃ radicals. Formation of organonitrates removes alkyl peroxy (RO₂) and/or alkoxy (RO) species from the system, and hence will reduce the importance of the decomposition channel. Possibly this is one of the differences between our work with NO₃ and alkane monolayers and some of the recent studies with OH and alkane SAMs where significant decomposition was observed. In the case of alkene SAMs, the γ value of the terminal alkene UDT obtained in this study is higher than the values obtained by *Moise et al.* [2002] using liquid and solid alkene bulk films. A possible reason for this difference may be the location of the double bond at the interface. Using the γ value determined in our studies, we show that oxidation of an

alkene monolayer by NO₃ can be significantly more important than oxidation by OH, Cl, and Br in the atmosphere. Only O₃ is of equal importance to NO₃ owing to its much higher tropospheric concentration. We also used our γ value for the alkene SAM to show that the lifetime of an alkene monolayer in the atmosphere will be short (approximately 23 min) assuming an NO₃ concentration of 50 ppt.

[61] XPS, IR and ToF-SIMS were used to identify surface functional groups after the oxidation of the alkene monolayers by NO₃. The results are consistent with the formation of C-O, aldehyde/ketone, carboxylic groups, and nitrogen species. It is interesting to note that several of the functional groups identified in previous studies of NO₃ radicals (in the presence of O₂ and NO₂) with liquid alkene films were also identified in our current monolayer studies.

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