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Alkyl nitrate photochemical production rates in North Pacific seawater

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ABSTRACT

Low molecular weight alkyl nitrates are produced in surface seawater from the photochemically initiated reaction of NO with organic peroxy radicals. In this study, methyl, ethyl, isopropyl, and n-propyl nitrate photochemical production rates were determined from shipboard incubation experiments. Surface water samples from a variety of different North Pacific water masses were irradiated in sunlight, with and without added nitrite. Production was observed in some, but not all unmodified waters. Production rates increased with increasing addition of nitrite. The relative rates of production of C₁, C₂, and C₃ alkyl nitrates were roughly constant in all production experiments, and similar to the concentration ratios in ambient waters. This constancy most likely reflects consistency in the ratios of the various organic peroxy radicals involved in the reaction ROO+NO. Alkyl nitrate production rates at 1 μM nitrite concentrations generally did not vary markedly by water type, indicating that distribution of nitrite, not organic matter may control photochemical alkyl nitrate formation in the oceans. At higher nitrite levels, differences in production rates may reflect variations in the concentration or reactivity of dissolved organics.

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1. Introduction

Tropospheric ozone is an important greenhouse gas and hydroxyl radical (OH) precursor. The formation and distribution of ozone in the troposphere is affected by the distribution and speciation of reactive odd nitrogen (NO_y) in the troposphere (Ridley and Atlas, 1999). Atmospheric alkyl nitrates can account for up to 80% of NO_y in the marine boundary layer (Jones et al., 1999; Talbot et al., 2000). These compounds undergo photolysis and reaction with OH to generate NO_x, leading to the production of tropospheric ozone (Clemmshaw et al., 1997; Talukdar et al., 1997a,b).

Several studies in the remote marine troposphere indicate that the oceans are a likely source of alkyl nitrates to the troposphere (Atlas et al., 1992; Blake et al., 2003; Fischer et al., 2002; Swanson et al., 2004). Shipboard measurements have shown supersaturation of methyl and ethyl nitrate in the Atlantic and methyl, ethyl, and propyl nitrate in the Pacific, indicating that the tropical oceans are a net source of alkyl nitrates to the atmosphere (Chuck et al., 2002; Dahl et al., 2005). Global atmospheric chemistry simulations based on these results show that oceanic alkyl nitrate emission is equivalent to 0.35 Tg of N per year, which contributes roughly 3% to the global oxidative capacity of the troposphere (Neu et al., 2008).

Relatively little is known about the source of alkyl nitrates in seawater. It has been proposed that the free radical reaction of alkyl peroxy radicals and NO could produce alkyl nitrates in the aqueous

phase via the following reaction (Dahl et al., 2003; Moore and Blough, 2002; Padmaja and Huie, 1993).

The free radical formation of alkyl nitrates in solution was observed in benzene (Shelton and Kopcaewski, 1967) and in water (Padmaja and Huie, 1993). This reaction has previously been observed during photochemical experiments with seawater (Dahl et al., 2003; Moore and Blough, 2002). In seawater, NO can be produced from the photolysis of nitrite (Zafiriou and MacFarland, 1981; Zafiriou and True, 1979b).

The photolysis of CDOM can produce carbon-centered radicals, which react with dissolved oxygen to form ROO radicals (Blough, 1997; Kieber and Blough, 1990; Zika, 1987).

The ROO and NO radicals can then react to produce alkyl nitrates, with a high yield as shown by Dahl et al. (2003).

Photochemical incubation studies with seawater in the laboratory have shown alkyl nitrate production at rates sufficient to account for surface ocean concentrations of methyl and ethyl nitrate observed in the Atlantic Ocean (Chuck et al., 2002; Dahl et al., 2003). Alkyl nitrate production in seawater is increased by the addition of nitrite (Dahl et al., 2003; Moore and Blough, 2002). Dahl et al. (2003) found that

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Fig. 1. Cruise track for PHASE-1. The symbols indicate locations of sample collection for incubation experiments. ○ Warm pool samples; □ High chlorophyll samples; △ Gyre samples; ◇ North of Hawaii samples.

alkyl nitrate production increased linearly with increasing nitrite, for nitrite levels up to a few μM . At higher nitrite levels, the nitrite dependency decreases, suggesting that peroxy radicals, rather than NO , become limiting.

This study presents evidence of photochemically initiated free-radical formation of alkyl nitrates in seawater from shipboard incubations in the North Pacific Ocean. The measurements were conducted during the PHASE-1 cruise aboard the R/V *Wecoma* along a track from Guam to Honolulu, HI and then to Newport, OR from May 22–July 1, 2004. The cruise track with incubation sampling locations is plotted in Fig. 1. Related measurements of alkyl nitrate saturation state and oceanic depth profiles were reported by Dahl et al. (2005; 2007).

2. Experimental

Net photochemical production rates of C_1 – C_3 alkyl nitrates in seawater were determined by monitoring the change in alkyl nitrates levels in seawater samples incubated in natural sunlight. The incubations were carried out in a flowing seawater incubator on deck (30 cm water depth). Filtered and unfiltered seawater samples were collected for incubation from the surface to 20 m using Niskin bottles. Filtered samples were gravity filtered directly from the Niskin bottles using a $0.2 \mu\text{m}$ inline filter (Whatman Polycap AS $0.2 \mu\text{m}$).

Seawater samples were divided into 4–7 aliquots of 250 mL each. The nitrite concentration of the samples was increased up to $12 \mu\text{M}$ by

Fig. 2. Methyl and ethyl nitrate production rates determined for waters at ambient nitrite concentrations with methyl nitrate on the left and ethyl nitrate on the right. The error bars are 1σ , calculated using the least squares regression of alkyl nitrate calibration curves. There was no clear difference between filtered and unfiltered samples. Incubations with negative production rates (i.e., loss) include both filtered and unfiltered samples.

addition of up to 500 μL of 1–2 mM nitrite stock solution (ACS reagent grade sodium nitrite 99.6%). One aliquot was not spiked and remained at ambient nitrite concentration. The samples were drawn into 100 mL Pyrex glass syringes fitted with polycarbonate stopcocks. Light incubation syringes were placed in the deck incubator and dark controls were carried out in the laboratory using the laboratory seawater for temperature regulation. Integrating radiation sensors (IMET) were used to determine the average solar irradiance during the incubations. Incubations were typically 5–7 h in duration to maximize exposure to daytime sunlight. A few samples were spiked with nitrate instead of nitrite to observe the affect of increased nitrate concentrations using the procedure described above.

Alkyl nitrate concentrations were determined before and after incubation using purge and trap gas chromatography with a mass spectrometer for detection. Nitrite concentrations were determined prior to incubation using a continuous flow analyzer based on a colorimetric, spectrophotometric technique with a detection limit of 0.8 μM ($\pm 6\%$) (Dahl, 2005). The production rates were calculated from the change in alkyl nitrates over the incubation time and normalized to an irradiance intensity of 1000 W m^{-2} , as follows:

$$P_{\text{RONO}_2} = \frac{[\text{RONO}_2]_f - [\text{RONO}_2]_i}{t} \cdot \frac{1000}{I}$$

where I is the average PAR (400–700 nm) intensity, and t is incubation time. The normalization is meant to take into account day to day variation in light intensity due to cloud cover or precipitation.

The detection limit for production rate measurements was limited by the sensitivity of the GC–MS system ($\text{DL} = \sim 200 \pm 50$ fmoles for ethyl nitrate). For ethyl nitrate, the difference in the concentrations before and after incubation had to be at least 3 pM, corresponding to a production rate of ~ 0.5 pM/h for a 6 h incubation.

Two filtered and one unfiltered seawater samples were used to determine if alkyl nitrate production varied by time of day. For these samples, alkyl nitrates were measured hourly throughout the incubations, yielding four production rate measurements over a 6–8 h period. These production rates were normalized and did not vary significantly by time of day and indicate that a four or more hour long incubation is an accurate determination of average production rate.

There are several reasons why the production rates measured in this experiments may not be identical to *in situ* rates in the water column. One is the use of Pyrex syringes, which attenuate UV light ($\sim 70\%$ and $\sim 20\%$ transmittance at 300 and 270 nm, respectively). This should cause 1) a small reduction in the photolysis rate of nitrite ($<10\%$), and hence the production of NO, and 2) a reduction in photolysis of CDOM, and hence in the production rate or chemical composition of organic peroxy radicals. In addition, no attempt was made to mimic light intensities or spectra at various depths in the water column.

3. Results and discussion

The waters used in the experiments were divided into four water types based on a combination of depth profile data, location, and similarity in production rates. The four water types are Warm Pool, High Chlorophyll, Gyre, and North of Hawaii. The characteristics of the water masses were described in detail by Dahl et al. (2007) and the location and type of each water are shown on Fig. 1.

3.1. Incubations at ambient nitrite levels

Without added nitrite, the alkyl nitrate production rates for filtered and unfiltered seawater samples were typically near or below the detection limit of the technique of ~ 0.5 pM/h (Fig. 2). Error bars for all production rates were calculated using least squares analysis of the alkyl nitrate calibration curves. Negative production rates (i.e., losses) were found in a few cases, indicating significant loss of alkyl nitrates during the incubation. These samples included methyl nitrate light incubation at station 15, and ethyl nitrate dark incubations at station 17. Presumably, the lack of alkyl nitrate production at ambient nitrite levels in the light incubations reflects loss of alkyl nitrates during the experiment, because these experiments measure net, rather than gross,

production. These experiments are the first observations of significant loss rates in light or dark incubations at ambient nitrite levels. No significant differences in production or loss rates at ambient nitrite levels were seen between filtered and unfiltered samples. Negative production rates were observed in both filtered and unfiltered samples. The most negative rate observed for ~ 60 pM/h for ethyl nitrate was observed in a filtered sample. Alkyl nitrates are believed to be fairly stable chemically in seawater, with estimated degradation rates on the order of months to years from chloride substitution and hydrolysis (Dahl et al., 2007). It is not possible to a priori determine if these losses are due to bacterial degradation or some other mechanism without further study.

3.2. Incubations with added nitrite

With the addition of nitrite (1–10 μM), alkyl nitrate photochemical production rates were observed in most water types at rates well above the detection limit of the technique. Plots of production rate as a function of nitrite for representative incubations the high chlorophyll, gyre, and north of Hawaii samples are shown in Fig. 3. Warm pool production rates were very low and could not be shown on the scale used in these plots. These samples exhibited quite different behavior. The production rates in the high chlorophyll waters near the equator increased linearly with nitrite up to 1–2 μM . Above

Fig. 3. Photochemical alkyl nitrate production rates in representative samples from high chlorophyll (St. 17 unfiltered), gyre (St. 25 unfiltered), north of Hawaii (St. 27 filtered) regions. Production rates are shown as a function of nitrite concentration prior to incubation. Note that left y-axis applies to ethyl and propyl-nitrates, and the right y-axis applies to methyl nitrate. Methyl nitrate production was not determined in the gyre waters due to an interfering peak in the chromatogram.

Fig. 4. Production rates of alkyl nitrates at determined at each station at an average nitrite concentration of 1.2 ± 0.2 M. Methyl nitrate production was not determined for stations 21, 23, and 25. The water masses are separated by dotted lines and indicated by WP (warm pool), HC (high chlorophyll), GY (gyre), and NH (north of Hawaii).

this nitrite concentration there was a decrease in slope, most likely as the production started to “saturate” with increasing nitrite. The production rate in the gyre water sample increased linearly up to about $2 \mu\text{M}$ nitrite, and leveled-off at higher nitrite levels. The production rate in the sample collected north of Hawaii continued to increase with additional nitrite up to $8 \mu\text{M}$ nitrite for methyl nitrate; however, the slope of C_2 – C_3 production rate vs. nitrite decreased slightly between 2 and $4 \mu\text{M}$. Dahl et al. (2003) observed similar behavior and speculated that the decrease in slope at higher nitrite levels is due to limitation of alkyl nitrate production by something other than NO. Presumably the nitrite level at which “saturation” occurs is a function of the photochemical production rate of alkyl peroxy radicals.

The magnitude of the production rates in the nitrite addition experiments varied between water types. To provide a consistent basis for comparison, production rates at $\sim 1 \mu\text{M}$ nitrite were compared (Fig. 4). Warm Pool waters exhibited the lowest production rates (0.6 ± 1.5 pM/h average) for ethyl nitrate. High Chlorophyll waters had average production rates of 26.1 ± 8.3 pM/h for ethyl nitrate. Gyre water production rates were higher at nitrite levels $> 2 \mu\text{M}$ than the previous water samples, but for $\sim 1 \mu\text{M}$ nitrite, the average ethyl nitrate production rate was 21.3 ± 9.1 . This suggests greater variability in the Gyre samples compared to the other water masses. The average ethyl nitrate production rate measured North of Hawaii at $\sim 1 \mu\text{M}$ was 30.0 ± 5.8 . The ambient alkyl nitrate concentrations at the stations sampled for production rates are shown in Fig. 5. The highest ambient concentrations (400–600 pM) were observed in the Equatorial waters and the lowest (< 20 pM) were observed in the Gyre waters (Dahl et al., 2007).

A few experiments were conducted to determine the dependence of alkyl nitrate production rates on nitrate concentration. In these experiments, seawater samples were spiked with nitrate to concentrations of up to $17 \mu\text{M}$. The addition of nitrate did

not significantly increase alkyl nitrate production. This is reasonable, because the photolysis of nitrate is considerably slower than that of nitrite (Jankowski et al., 1999; Zafriou and True, 1979a,b). Nitrate photolysis results in the formation of nitrite and NO_2 , which require further photolysis or reaction to produce NO (Loeager and Sehested, 1993; Schwartz, 1984). Presumably, alkyl nitrate production would occur on the time scale of these experiments, if higher levels of nitrate were used.

3.3. Relative rates of production of the C_1 – C_3 alkyl nitrates

Cross plots of the observed production rates at all concentrations of nitrite are shown in Fig. 6. The relative ratios of methyl, isopropyl, and n-propyl nitrate to ethyl nitrate production were 6.9 ± 1.2 , 0.1 ± 0.0 , and 0.2 ± 0.0 respectively. All correlations were positive and significant at a 95% confidence interval. The relative production rates of C_1 – C_3 alkyl nitrates did not vary significantly by water mass type, a surprising observation given the complicated nature of radical chemistry in seawater. The observed production rate ratios of methyl and ethyl nitrate in the incubation experiments (~ 7) were similar to the ambient concentration ratios (~ 6) observed near the equator during the same study (Dahl et al., 2007). The production rate ratios of isopropyl and n-propyl nitrate to ethyl nitrate (0.1 and 0.2 respectively) were also similar to concentration ratios (0.2 and 0.1 respectively). This similarity could indicate that the photochemical production is the major of alkyl nitrates in this region. The concentration ratios of methyl to ethyl nitrate were significantly different north of the equatorial region (i.e. north of 9°N) (Dahl et al., 2007). Photochemical production outside the upwelling region is likely to be slow, given the lack of available nitrite for NO formation. If alkyl nitrate production cannot occur due to the availability of precursors such as nitrite, it is possible that the different ambient concentration ratios reflect other production mechanisms or losses (chemical, biological etc.) of alkyl nitrates. The loss rates of alkyl nitrates in seawater are unknown and it is therefore not possible to estimate how loss rates could affect the relative concentrations of levels of the alkyl nitrates. Dahl et al. (2007) estimated that the lifetime of alkyl nitrates in 25 – 30°C waters is ~ 1 year based on hydrolysis rates and chloride substitution.

Little is known about the abundance of various alkyl peroxy radicals in seawater (Blough, 1997). We can use the relative formation rates of the various alkyl nitrates observed in these experiments to assess the relative production rates of their precursor alkyl peroxy radicals. Using the incubation results and yields of $\text{ROO} + \text{NO}$ derived from laboratory experiments (Dahl et al., 2003), we estimate the relative formation rates of methyl, ethyl, isopropyl, and n-propyl peroxy radicals to be 21, 1, 0.1, and 0.7 respectively. Zafriou and Dister (1991) used NO loss rates as a means of estimating total free radical formation rates in seawater. That measurement largely reflects the production of O_2 , rather than organic free radicals. Some work has been done on the measurement of carbon centered radicals in seawater (Kieber and Blough, 1990), but measurements or estimates of alkyl peroxy radical production have not been published.

4. Conclusions

Alkyl nitrate production rates were measured as a function of nitrite concentration in a variety of surface waters of the Equatorial and North Pacific Ocean. These studies confirm and extend earlier results suggesting that oceanic surface waters have significant potential for photochemical formation of alkyl nitrates. The incubation

Fig. 5. Ambient alkyl nitrate concentrations determined in water samples taken prior to the incubation samples. No ambient alkyl nitrate concentrations were determined after station 25. The water masses are separated by dotted lines and indicated by WP (warm pool), HC (high chlorophyll), and GY (gyre).

Fig. 6. Cross plots of methyl, isopropyl, and n-propyl nitrate production versus ethyl nitrate production during the study. The correlations significant at the 95% confidence interval.

experiments demonstrate that the presence of nitrite is required in order for this potential to be realized. Nitrite presumably acts as a photolytic source of NO, which acts as a scavenger for C₁–C₃ alkyl peroxy radicals. This study suggests that for nitrite levels up to several μ M, NO appears to limit alkyl nitrate production.

This and previous studies have noted that equatorial Pacific waters have alkyl nitrate levels orders of magnitude larger than those in the adjacent north Pacific gyre. The incubation results show that the two waters have similar alkyl nitrate production potentials, i.e. similar production rates at similar nitrite levels. This argues against differences in the photochemical reactivity of the dissolved organic matter as factor controlling the alkyl nitrate distribution. We propose that the difference in alkyl nitrate levels between the two environments is controlled primarily by the nitrite levels and the extent to which the nitrite distribution overlaps with the photic zone. A rigorous test of this hypothesis will require high precision measurements of nitrite, and *in situ* incubations in quartz flasks at various depths in the water columns of both environments.

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