LIGHT ALKYL NITRATES IN THE MARINE ENVIRONMENT

Aspmo, K[1]., van Ekeren J.S[2]. and Yttri, K.E[1].

Department for Chemical Analysis, Norwegian Institute for Air Research. P.O. Box 100, N-2027 Kjeller, Norway

Paul Scherrer Institute, Laboratory of Atmospheric Chemistry, CH-5232, Villigen PSI, Switzerland

Abstract

Alkyl nitrates are important constituents of the NO_y reservoir and have been observed in the troposphere in highly polluted urban areas as well as remote regions of the global troposphere. While the sources of light alkyl nitrates in urban areas are well known, the sources in remote marine air remain obscure. The finding that equatorial surface waters are super-saturated in both methyl nitrate ($MeONO_2$) and ethyl nitrate ($EtONO_2$) provides strong evidence that part of the ocean is a source of these short chain nitrates. At present one mechanism for production of alkyl nitrates in an aquatic system has been reported. In biological system no such mechanisms are known, and the suggestions put forward so far still remain speculative. Preliminary model calculations predict that the equatorial source might be a major contributor to the local reactive nitrogen reservoir and therefore plays a role in regulating the levels of tropospheric ozone in remote marine regions.

Introduction

Alkyl nitrates belong to the group of reactive nitrogen, denoted NO_y, which is defined as the sum of NO_x ($NO+NO_2$). NO_y is a product of the atmospheric oxidation of NO_x. The most important and abundant NO_y species is HNO_3. NO_y is considered to be a conserved quantity, in contrast to its constituent species. The distribution and speciation of NO_y controls the ozone formation and distribution in remote areas. In addition ozone is an important greenhouse gas and hydroxyl radical (OH) precursor. Alkyl nitrates can make up a significant fraction of the reactive nitrogen (20-80%, Shepson et al., 1993) in remote marine areas. Lately, direct measurements of alkyl nitrates by Chuck et al., (2002) has proven high concentrations of these compounds in equatorial seawater and in the air above, indicating a natural oceanic source.

In this report we will give an overview of the knowledge on alkyl nitrates in the remote marine atmosphere. We would like to investigate the importance of this source to the global NO_y concentration and its relevance to the formation of ozone.

Pathways for the production of alkyl nitrates

Alkyl nitrates can enter the atmosphere in different ways. Until recently the existence of alkyl nitrates in the atmosphere was explained by reaction of oxidised alkyls and nitrate in the presence of sunlight (Darnall et al., 1976).

Reaction 1a: $RO_2 + NO \rightarrow RO + NO_2$ (~95%)
Reaction 1b: $RO_2 + NO \xrightarrow{M} RONO_2$ (~5%)

$RO_2\cdot$ is an alkyl peroxy radical and $RONO_2$ is an alkyl nitrate. Reaction 1b is only significant in urban and polluted environments where the NO concentration is sufficiently high (Ballschmiter et al., 2002). Reaction favours alkyl species that have chains with more than 3 C-atoms.

Reaction 1a is the most probable pathway for peroxy radicals to react. The yield of $EtONO_2$ in reaction 1b in the atmosphere is less then 0.014 and for $MeONO_2$ it is considered to be close to zero.

Formation of alkyl nitrate, particularly $MeONO_2$, is favoured by another mechanism suggested by Simpson et al. (2002), where two alkyl peroxy radicals react to produce an alkoxy radical, which subsequently reacts with NO_2 to generate alkyl nitrates.

Reaction 2: $RO\cdot + NO_2 \rightarrow RONO_2$

Reaction 2 is favoured when concentrations of alkyl peroxy radicals are high and NO_x level is low. The first criterion is only fulfilled during biomass burning whereas low levels of NO_x are commonly found in remote marine areas.

Degradation of peroxyacetylnitrate (PAN) [$CH_3C(O)OONO_2$] is known to generate $MeONO_2$. However, PAN is present at quite low concentration in the marine boundary layer (2 pptv) (Seinfeld and Pandis, 1998).

Marine production

Equatorial surface waters are supersaturated in both methyl nitrate and ethyl nitrate (Chuck et al., 2002). This finding provides strong evidence that part of the ocean is a source of these short chain alkyl nitrates found in the atmosphere of remote marine areas.

Taking place in the atmosphere, reaction 1b is not likely to explain the concentrations of light chain alkyl nitrates in remote marine atmosphere. However, reaction 1b can take place in the seawater column as well (Dahl et al., 2003).. In seawater alkyl peroxy radicals are produced photochemicaly from photolysis of coloured dissolved organic matter (CDOM), whereas NO is produced from photolysis of nitrite (NO_2^-). Both NO_2^- and CDOM are naturally present in the ocean. Reaction 1b has been investigated in laboratory studies by Dahl et al. (2003). They showed that the yield of the reaction in seawater is significantly higher than in the gas phase.

The reaction rates observed in the natural water experiments of Dahl et al. (2003) indicates quite strongly that photochemical production of alkyl nitrates can reach concentrations that are environmentally significant. It takes no more than 5 hours of sunlight to produce a mixing layer of 75 m when the production is taking place in the upper ten meters of equatorial surface water[1].

The concentration of $MeONO_2$ in the marine boundary layer over the Atlantic equatorial region was found to be a factor ~3 higher than for $EtONO_3$ (Blake et al., 2003). However, in the water column $EtONO_2$ seems to be equal to or even higher than $MeONO_3$. This can be explained by the difference in mass flux from the ocean to the atmosphere calculated by

---

[1] Ethyl nitrate in equatorial surface seawater with concentration of~ 3.3×10^{-15} mol cm^{-3} and production rate of ethyl nitrate of 2×10^{-19} mol cm^{-3} s^{-1} (Dahl et al., 2003).

Chuck et al. (2003), showing that the flux of $MeONO_3$ is a factor ~ 5 larger than $EtONO_2$. This work calculated the Henry constants[2] for both $MeONO_2$ and $EtONO_2$ and found that they had a very low solubility in seawater, adding strength to the theory that the ocean is a source of light alkyl nitrates.

The yield of $EtONO_2$ in seawater based on photochemical production (reaction 1b) is assumed to be higher than for $MeONO_2$ (Dahl et al., 2003). There are strong indications that the yield increases with increasing length of the alkyl chain (Dahl et al., 2003). A possible explanation may be that shorter chained peroxy radicals are more abundant in the water column. However, we have not found any literature confirming that shorter chained peroxy radicals are favoured in the photochemical production of peroxy radicals in seawater. (Stefan: is this a better sentence?)

Assuming short chain peroxy radicals being the most ubiquitous in seawater and the fact that short chain alkyl nitrates have the highest fluxes supports the fact that concentrations of alkyl nitrates (n = 1-4) in the marine boundary layer is internally rated as followed (Blake et al., 2003):

$$MeONO_2 > EtONO_2 > 2\text{-}PrONO_2 > 2\text{-}BuONO_2$$

Where $PrONO_2$ is 2-propyl nitrate and $BuONO_2$ is 2-butyl nitrate

Biological sources

In addition to the photochemical production of alkyl nitrate in surface seawater, biological sources could be responsible for the formation of the alkyl nitrates. In fact there are indications put forward by Chuck et al. (2002) that several biological sources may contribute to the levels of alkyl nitrates in the remote marine atmospheric environment. The reason for this suggestion is the correlation between $MeON_2$, $EtONO_2$ and the concentration of chlorophyll in seawater. This indicates that some kind of biological activity may be involved in the mechanisms. The use of chlorophyll as an indicator of biological activity is a very general approach and is by no mean suitable for determining what kind of species being responsible for the formation of light alkyl nitrates. No further information has been found in the literature concerning this potential source.

Concentrations of alkyl nitrates in the surface waters are highly correlated, potentially indicating a common source. Looking at oceanic depth profiles (Chuck et al., 2003) and vertical profiles of light alkyl nitrates in the atmosphere, (Blake et al., 2003a; Blake et al., 2003b) indications of different mechanisms emerge, suggesting different types of water supporting various mechanisms of synthesis.

For the regions close to equator high concentrations of $EtONO_2$ were found at deep water in opposite to $MeONO_2$, which declines at deeper waters (Chuck et al.2002). This finding was suggested by the authors to be due to bacterial and/or algae processes. No further explanation for this hypothesis was presented other than that there was a similarity between the depth profile of NO_3^- and $EtONO_2$, suggesting that NO_3^- may play a part in the formation of $EtONO_2$.

---

[2] H $MeONO_2 = 0.0087$ M atm^{-1} and H $EtONO_2 = 0{,}034$ M atm^{-1} (T = 298K)

Discussion

Recently it has been discovered that alkyl nitrates have a primary (oceanic) source in addition to the secondary sources. Secondary products are generated from photochemical oxidation of hydrocarbons in the presence of NO_x. Primary and secondary sources show distinct differences in the concentrations of the compounds, making them useful as indicators of air mass origin and age in combination with back trajectories. Measurements in regions of high oceanic emissions show that $MeONO_2$ and $EtONO_2$ mixing ratios are dominating (Atlas *et al.*, 1997 and Blake *et al.*, 2003b), in contrast to photochemically produced alkyl nitrates where the heavier alkyl nitrates are favoured (Roberts, 1990). Longer-chain alkyl nitrates are lost by photochemical degradation, leaving 2-butyl nitrate as the dominant alkyl nitrate in fresh urban environments. Alkyl nitrates are emitted by biomass burning as well, making the total picture more complicated. Mixing ratios of $MeONO_2$ exceeded 500 pptv for all stages of the burning (Simpson *et al.*, 2002), whereas mixing ratios of C2-C4 alkyl nitrates are relatively more important during smouldering. The mixing ratio of $MeONO_2$ in remote marine areas ranges between 5-50 pptv (Chuck et al., 2002, Simpson et al., 2002). For the longer alkyl nitrates the mixing ratio decreases with increasing chain length. The study by Simpson et al. was done in northern Australia, but it is believed that biomass burning contributes significantly to the alkyl nitrates on a global scale. The lifetime of the $MeONO_2$ and $EtONO_2$ are calculated to be between 5 and 25 days (Chuck *et al.*, 2002), implying that plumes with high concentrations of alkyl nitrates originates from biomass burning could be observed in the remote marine atmosphere. This could also explain why Chuck *et al.*, 2002 observed higher concentrations (approximately a factor 10) over the eastern part of the southern Atlantic ocean, compared with lower concentrations over a more westerly transsect, which might be due to eastern dominating wind direction in equatorial regions.

The concentration of $MeONO_2$ and $EtONO_2$ in the marine boundary layer has its highest concentration close to the equator. In the Southern Hemisphere (>10°S) of the Pacific Ocean concentration of both compounds are considerably lower than that found close to equator however, almost a factor 2 higher than in the Northern Hemisphere (>10°N). For $PrONO_2$ and $BuONO_2$ the trend in concentrations are the opposites for that of $MeONO_2$ and $EtONO_2$, as the concentrations increase with northern latitudes. Photochemical production of $MeONO_2$ and $EtONO_2$ could be a plausible explanation. Enhanced levels of $MeONO_2$ and $EtONO_2$ are only found in a very narrow band around the equator, indicating that the position of the sun is very sensitive to alkyl production in water. Light penetrates significantly deeper down into the water layer when the light is coming in perpendicular to the surface. In October, when the measurements took place, this was clearly the case.

Not only the photochemical production of alkyl nitrates plays a role, the mentioned correlation with chlorophyll points towards a production mechanism from biological processes. Up to now it is highly speculative how these biological organisms are producing alkyl nitrates.

Alkyl nitrates are believed to play a substantial role in regulating the ozone concentrations in remote equatorial marine areas, although the mechanism is lacking in the literature.

Reaction 3: $NO_2 + h\nu \rightarrow O(^3P) + NO$
Reaction 4: $O(^3P) + O_2 \rightarrow O_3$
Reaction 5: $NO + HO_2/RO_2 \rightarrow NO_2 + OH/RO$
Reaction 6: $RO_2 + RO_2 \rightarrow 2RO + O_2$
Reaction 7: $RO_2 + HO_2 \rightarrow ROOH + O_2$

In the troposphere the concentration of NO_x controls the production of ozone. When the concentration of NO becomes below a certain level (50 pptv) reaction 6 and 7 competes with reaction 5 which eventually leads to reduced ozon production. This does not invole alkyl nitrates. On the other hand, alkyl nitrates make up to 80% of the total NO_y reservoir, which makes them not insignificant. We suggest the following mechanism for the alkyl nitrate induced reduction of tropospheric ozon production:

Reaction 6: $RO_2 + RO_2 \rightarrow 2RO + O_2$
Reaction 2: $RO\cdot + NO_2 \rightarrow RONO_2$

In this way NO_2 can not contribute to ozon production according to reaction 3 and 4.

The finding that the ocean is a potential strong source of reactive nitrogen is new, and is important for the understanding of the total reactive nitrogen reservoir. This reservoir is believed to be rather constant, only the relative concentration of the single species from the reservoir changes from place to place. A great gap in nitrogen knowledge has been closed by the discovery of ocean as an alkyl nitrate source.

References:

Atlas, E., W. Pollock, J. Greenberg, L. Heidt, and A. M. Thompson, 1993: Alkyl Nitrates, Nonmethane Hydrocarbons, and Halocarbon Gases over the Equatorial Pacific-Ocean During Saga-3. *J. Geophys. Res.-Atmos.*, **98,** 16933-16947.

Atlas, E., F. Flocke, S. Schauffler, V. Stroud, D. Blake, and F. S. Rowland, 1997: Evidence for marine sources of atmospheric alkyl nitrates: Measurements over the tropical Pacific Ocean during PEM-tropics. *Eos Trans. AGU*, **78(46),** Fall Meet. Suppl., F115.

Ballschmiter, K., 2002: Atmospheric chemistry: A marine source for alkyl nitrates. *Science*, **297,** 1127-1128.

Blake, N. J., D. R. Blake, A. L. Swanson, E. Atlas, F. Flocke, and F. S. Rowland, 2003a: Latitudinal, vertical, and seasonal variations of C-1-C-4 alkyl nitrates in the troposphere over the Pacific Ocean during PEM- Tropics A and B: Oceanic and continental sources. *J. Geophys. Res.-Atmos.*, **108,** art. no.-8242.

Blake, N. J., D. R. Blake, B. C. Sive, A. S. Katzenstein, S. Meinardi, O. W. Wingenter, E. L. Atlas, F. Flocke, B. A. Ridley, and F. S. Rowland, 2003b: The seasonal evolution of NMHCs and light alkyl nitrates at middle to high northern latitudes during TOPSE. *J. Geophys. Res.-Atmos.*, **108,** art. no.-8359.

Chuck, A. L., S. M. Turner, and P. S. Liss, 2002: Direct evidence of a Marine Source of C1 and C2 alkyl nitrates. *Science*, **297,** 1151-1154.

Dahl, E. E., E. S. Saltzman, and W. J. de Bruyn, 2003: The aqueous phase yield of alkyl nitrates from ROO+NO: Implications for photochemical production in seawater. *Geophys. Res. Lett.*, **30,** art. no.-1271.

Darnall, K. R., W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N. Pitts, 1976: Importance of Ro2+No in Alkyl Nitrate Formation from C4-C6 Alkane Photooxidations under Simulated Atmospheric Conditions. *J. Phys. Chem.*, **80,** 1948-1950.

Neff, J. C., E. A. Holland, F. J. Dentener, W. H. McDowell, and K. M. Russell, 2002: The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle? *Biogeochemistry*, **57,** 99-136.

Roberts, J. M., 1990: The Atmospheric Chemistry of Organic Nitrates. *Atmospheric Environment Part a-General Topics*, **24,** 243-287.

Shepson, P. B., K. G. Anlauf, J. W. Bottenheim, H. A. Wiebe, N. Gao, K. Muthuramu, and G. I. Mackay, 1993: Alkyl Nitrates and Their Contribution to Reactive Nitrogen at a Rural Site in Ontario. *Atmospheric Environment Part a-General Topics*, **27,** 749-757.

Simpson, I. J., S. Meinardi, D. R. Blake, N. J. Blake, F. S. Rowland, E. Atlas, and F. Flocke, 2002: A biomass burning source of C-1-C-4 alkyl nitrates. *Geophys. Res. Lett.*, **29,** art. no.-2168.

Talbot, R. W., J. E. Dibb, E. M. Scheuer, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, D. R. Blake, N. J. Blake, E. Atlas, and F. Flocke, 2000: Tropospheric reactive odd nitrogen over the South Pacific in austral springtime. *J. Geophys. Res.-Atmos.*, **105,** 6681-6694.