

Observations of the nitrate radical in the free troposphere at Izaña de Tenerife

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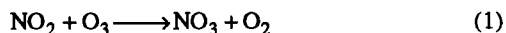
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Abstract. This paper reports direct measurements of the nitrate radical (NO_3) in the lower free troposphere. The measurements were carried out at Izaña de Tenerife (2300 m altitude) in the Canary Islands during May 1994, using the technique of differential optical absorption spectroscopy (DOAS). The average nighttime NO_3 concentration in very clean air from the mid-Atlantic was found to be 8 ppt, with a maximum observed concentration of about 20 ppt. Combining the NO_3 data with ancillary measurements of NO_2 and O_3 in a model shows that there are no important NO_3 scavengers in a part of the troposphere that is characterized by a very low relative humidity and aerosol particle count, and where the concentration of NO_2 is too small for significant quantities of N_2O_5 to form. On occasion, the presence of a trace concentration of NO or an organic species such as α -pinene is required to explain the observations. The lifetime of NO_3 at night was in excess of 2 hours, much longer than measured hitherto in the tropospheric boundary layer.

Introduction

Interest in the role of the NO_3 radical in atmospheric chemistry has been stimulated since the first spectroscopic detection of the species in the stratosphere [Noxon *et al.*, 1978] and later in the troposphere [Noxon *et al.*, 1980; Platt *et al.*, 1980]. As shown in Figure 1, NO_3 is formed in the atmosphere by the relatively slow reaction between NO_2 and O_3 ,

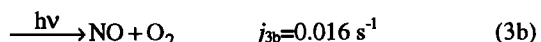


and then usually reaches an equilibrium with N_2O_5 :



Under typical atmospheric conditions this equilibrium is established on a timescale of about 1 min [Platt and Heintz, 1994], so that any loss of N_2O_5 effectively constitutes a loss of NO_3 . The concentrations of N_2O_5 and NO_3 are roughly equal for an NO_2 concentration of 1 ppb at 293 K [DeMore *et al.*, 1994].

Because of its strong absorption through most of the visible region of the solar spectrum, during the day, NO_3 is rapidly photolyzed via one of the following channels:

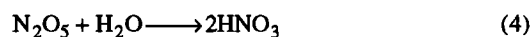


and is therefore estimated to have a lifetime of only about 5 s

[Orlando *et al.*, 1993]. Solomon *et al.* [1993] have estimated a lunar photolysis rate for NO_3 of $2.0 \times 10^{-7} \text{ s}^{-1}$, corresponding to a lifetime of 1400 hours, so that this process is only important in the sustained darkness of the polar winter night.

At nighttime, NO_3 can build up to significant concentrations and become an important oxidant of a wide variety of species (Figure 1). It is well established that NO_3 is highly reactive with certain unsaturated hydrocarbons including the butenes, monoterpenes and isoprene, as well as with reduced sulfur compounds such as dimethylsulfide (DMS) [Atkinson, 1991; Wayne *et al.*, 1991]. NO_3 also reacts rapidly with NO [DeMore *et al.*, 1994], although significant concentrations of NO will not exist at night in the presence of O_3 except adjacent to fresh emissions (for instance, 1 ppb of NO would be reduced to less than 1 ppt in about 10 min by 30 ppb of O_3).

In the absence of these reactive species, the homogeneous gas-phase removal of N_2O_5 by water vapor could be important:



However, laboratory measurements by Sverdrup *et al.* [1987] have yielded an upper limit to k_4 of only $2.7 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Since this upper limit was shown to be a function of the surface-to-volume ratio of the reactor vessel that was employed, even this very small upper limit is most likely constrained by the influence of heterogeneous wall processes [Sverdrup *et al.*, 1987]. Indeed, the accommodation coefficients of both N_2O_5 [DeMore *et al.*, 1994] and NO_3 [Rudich *et al.*, 1996] on moist surfaces have now been measured in the laboratory, and these heterogeneous reactions appear to be particularly important removal pathways in the marine boundary layer [Dentener and Crutzen, 1993; Yvon *et al.*, 1996].

Another possibility in the absence of reactive organic species is the self-reaction of NO_3 . However, the rate coefficient at 298

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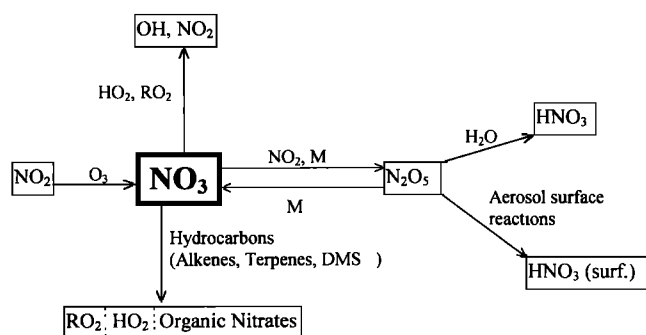


Figure 1. Schematic diagram of the nighttime chemistry of NO_3 .

k has been estimated to be $2.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Biggs *et al.*, 1993], and so this reaction does not play an important role in the atmosphere: at a relatively large nighttime concentration of 50 ppt, NO_3 would have a lifetime of about 1000 hours with respect to self-reaction. Johnston *et al.* [1986] proposed that the unimolecular decomposition of NO_3 is important in the atmosphere. However, a recent study by Davis *et al.* [1993] has shown that decomposition to $\text{NO}_2 + \text{O}$ is endothermic by 204 kJ mol^{-1} , and that there is a potential energy barrier of 198 kJ mol^{-1} for the process $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$. Hence, both pathways are negligibly slow at atmospheric temperatures.

Although the nitrate radical has long been recognized as a ubiquitous constituent in the nighttime polluted boundary layer [Harris *et al.*, 1983; Platt *et al.*, 1980, 1981, 1984; Smith *et al.*, 1995; Yvon *et al.*, 1996], there are very few observations of the radical in the free troposphere. Noxon [1983] measured NO_3 in the mid-Pacific troposphere at the Mauna Loa Observatory in Hawaii (altitude 3500 m). Optical absorption measurements of NO_3 and NO_2 were made along a 220-km path at altitudes between 2500 and 3500 m, extending toward the Moon or Sun, respectively. Concentrations of about 0.3 and 30 ppt for NO_3 and NO_2 were measured on three different nights [Noxon, 1983]. Thus, despite predictions that NO_3 should increase to only 2 or 3 times less than the concentration of NO_2 at the end of the night, the observed ratio was about 1% with no evidence of a growth in the NO_3 concentration [Noxon, 1983]. For instance, at a temperature of 285 K and with 40 ppb of O_3 present, 30–50% of the NO_2 present would have reacted with O_3 over the period of a 12-hour night [Noxon, 1983]. Furthermore, at the low NO_2 concentrations observed above Hawaii very little of the NO_3 would then form N_2O_5 . Hence the very low NO_3 concentrations that were observed led Noxon to conclude that an unknown scavenger of NO_3 was important even in clean air, and that the rate of scavenging ($1 \times 10^{-3} \text{ s}^{-1}$) was similar to that found previously in the Colorado Mountains [Noxon, 1983].

More recently, considerably higher concentrations of NO_3 in the free troposphere have been retrieved from slant column measurements using lunar spectra during sunrise [Smith *et al.*, 1993]. NO_3 concentrations of $(7\text{--}8) \times 10^7 \text{ molecules cm}^{-3}$ ($\approx 4\text{--}5$ ppt) were observed at an altitude of around 3 km over Fritz Peak (Colorado) during summer. Finally, Penkett *et al.* [1993] proposed the presence of NO_3 to explain the observed ratio of hydrocarbons in the free troposphere at high latitudes. During winter, branched chain alkanes are removed more rapidly than straight chain alkanes, which could be explained by an NO_3 concentration of about 20 ppt during a period when the OH chemistry is less dominant [Penkett *et al.*, 1993].

Thus recent work indicates that NO_3 is a more important species in the free troposphere than originally suggested by Noxon [1983]. The aim of the present study was to make direct measurements of NO_3 in the free troposphere, as part of a wider study of the oxidising capacity of this part of the atmosphere. The nighttime measurements of NO_3 reported here were complemented by daytime measurements of OH, which are described in an accompanying paper [Armerding *et al.*, this issue].

The Field Campaign

The field campaign was carried out at Izaña de Tenerife in the Canary Islands ($28^\circ 18' \text{N}$ and $16^\circ 29' \text{W}$) in May 1994. Figure 2 is a map showing the proximity of the Canary Islands to the African coast, and a schematic diagram of Tenerife. There are two observatories situated at Izaña, which lies on a mountain platform at an altitude of 2376 m above sea level, 400 km west of Africa. Izaña Atmospheric Watch (GAW-WMO) station is a Tropospheric Ozone Research (TOR) station, as well as a baseline station belonging to the World Meteorological Organisation's worldwide Background Air Pollution Monitoring Network. Measurements of CO_2 , CH_4 , O_3 and meteorological parameters have been made on a continuous basis since June 1984. The station is operated by the Instituto Nacional de Meteorología (Santa Cruz de Tenerife), and it is the only continuously operating station in the southern part of the North Atlantic. About a kilometer away, the Solar Observatory (Instituto de Astrofísica de Canarias) makes observations of solar events.

The meteorological station is located on a natural volcanic platform (Montaña de Izaña) in the middle of the mountainous ridge that runs from the base of the volcanic cone of the Pico del Teide (3717 m) to the northeast side of the island (Figure 2). The vegetation surrounding the station is sparse, and the ground is loosely covered with light volcanic material. A lush pine forest covers most of the island between an altitude of 1200 and 2000 m above sea level and a laurel forest continues downward. The road leading to the observatory is closed to public traffic and is used only by workers at the two observatories, a nearby television station and a small military camp several hundred meters away.

A predominant feature of the meteorology of Tenerife is the presence of a subsidence inversion below the elevation of the meteorological station [Schmitt *et al.*, 1988]. The lower air mass is cooler and more moist than the dry, warm, upper layer. The inversion acts as an effective lid to prevent polluted air, arising from the activities of the 300,000 inhabitants of the island, reaching the clean air aloft. The inversion remains intact for 90% of the time in the summer and 70% in the winter [Schmitt *et al.*, 1988]. For most nights during May, the station existed well above the level of the inversion. The strong solar irradiance during the day causes a local upslope wind system to be set into motion, whereby air is transported from lower altitudes (though still above the inversion) to the station. This leads to lower concentrations of O_3 and CO_2 and markedly higher concentrations of NO, NO_2 , NO_x , PAN, and nonmethane hydrocarbons (NMHC) during these conditions [Schmitt *et al.*, 1988]. The influence of orography becomes lower during the night, and a downslope wind system is generally set in place, bringing free tropospheric air to the station. During the spring and early summer the nighttime O_3 levels increase to a maximum of 55–60 ppb, and there is good evidence that the

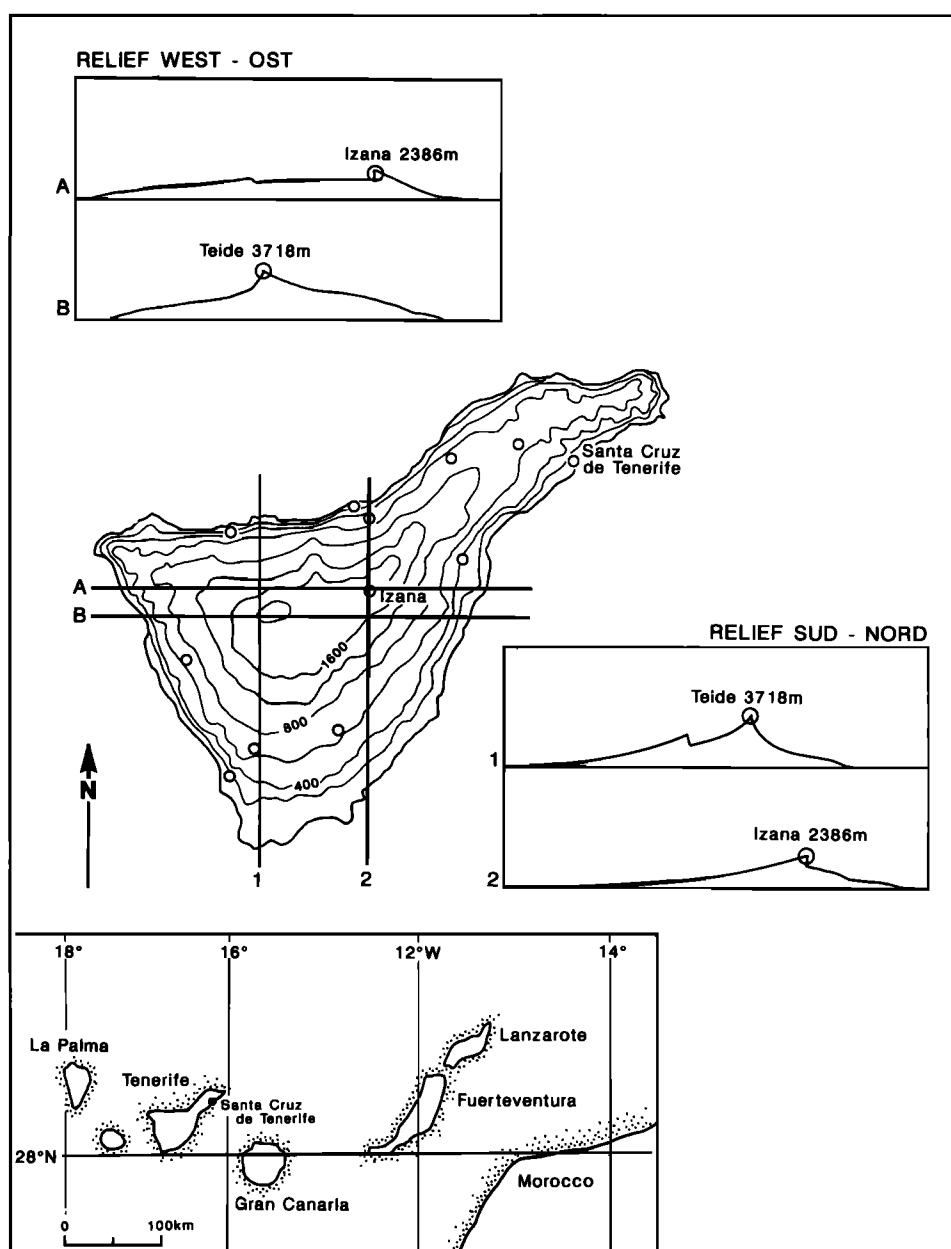


Figure 2. Contour plot of Tenerife, indicating the site of the meteorological station at Izaña, which is situated at an altitude of 2376 m. The insets show the relief of the island along north-south and east-west axes, and the location of the Canary Islands with respect to the African coast.

source of this O_3 -rich air is the upper troposphere or lower stratosphere [Prospero et al., 1995].

The synoptic situation in the Canaries is dominated by the subtropical anticyclone that generally blocks meridional transport to the south and is usually situated over the Azores, NW of the station [Sancho et al., 1992]. A complex transport situation is caused by changes in position and horizontal structure of the anticyclone. Two main circulation features coexist in this region, which have limited interaction with each other. One is produced by trade winds that tend to be well established in the mixed boundary layer, especially during summer. Above the inversion layer, in the free troposphere, the atmospheric circulation is quite different, consisting of subsident air masses which typically originate from the north-central or western North Atlantic ocean. A 5-year study of isentropic

trajectories at 305–315 K by E. Cuevas et al. (Tropospheric ozone over the eastern North Atlantic subtropical region: Connections with dynamic processes, submitted to *Journal of Geophysical Research*, 1996; hereafter referred to as submitted paper) has revealed the following statistics for the month of May: for 2% of the month, low trajectories from the Sahara sector give rise to hazy conditions; 22% of the time, air masses originate over Europe; and for 68% of the month the trajectories originate in the North Atlantic (north-west sector), mostly from levels higher than 4 km.

Experimental

During the campaign, the concentration of NO_3 was measured by differential optical absorption spectroscopy (DOAS), a

technique that has been reviewed recently [Platt, 1994; Plane and Smith, 1995]. The concentration of a trace species is monitored by its characteristic absorption of UV/visible light over an optical path length of several kilometers [Platt and Perner, 1983]. For this study, the instrument was situated in a small out-building 50 m from the meteorological station. Unlike our previous design with two separate telescopes [Plane and Nien, 1992], the instrument employed here has coaxial transmitting and receiving telescopes which utilize different concentric sections of the same 30-cm-diameter primary mirror, in a Newtonian configuration. This is achieved with an additional secondary mirror, as shown in Figure 3. The transmitter is powered by a 450-W xenon arc lamp and uses the front secondary and the outside of the primary mirror to create an outgoing beam in the shape of an annulus. A retro-reflector then folds the light beam and displaces part of it to the inside of the annulus: this part of the return beam arrives at the inner portion of the primary mirror and is directed by the rear secondary mirror into a quartz optical fiber (600 μm diameter, 5-m length). The received light is then dispersed by a 0.5-m Czerny-Turner spectrometer onto a 1024 element diode array. The recorded spectra are about 35 nm in width with a resolution of 0.6 nm. During this campaign, the retro-reflector was situated 974 m away and 105 m below the observatory on a concrete platform (2271 m above sea level), giving a total path length of 1.98 km and an angle of declination of 6° . The average height of the light beam above the ground was 30 m.

The spectral deconvolution routine has been described in detail previously [Plane and Nien, 1992; Plane and Smith, 1995]. By means of a system of optical shutters, the instrument is able to record separately the lamp spectrum transmitted through the atmosphere, any scattered sunlight component, and the unattenuated spectrum of the xenon lamp. A processed atmospheric absorption spectrum is then produced by removing the scattered light and the xenon lamp structure from the transmitted light spectrum. The processed spectrum is then converted into a differential optical density spectrum, to which a set of appropriate molecular absorption cross sections are fitted by a least squares routine employing singular value decomposition [Press *et al.*, 1986]. The sources of the reference cross sections are NO_2 in the 345 to 380-nm wavelength region from Schneider *et al.* [1987], O_3 in the 310 to 345-nm region from Daumont *et al.* [1992], and NO_3 in the 645 to 680-nm region from the recommendation of DeMore *et al.* [1994] which is based on the measurements of Ravishankara and Mauldin [1986], Sander [1986] and Canosa-Mas *et al.* [1987]. In the case of NO_3 , the broad absorption peak at 662 nm is partially obscured by the (311) vibrational overtone band of H_2O . This H_2O band was removed from the nighttime spectrum by taking a daytime reference spectrum about an hour before sunset or an hour after sunrise, when the NO_3 concentration would have been negligible because of its rapid photolysis (reaction 3). The instrument was usually run automatically, recording an atmospheric spectrum every 10 min.

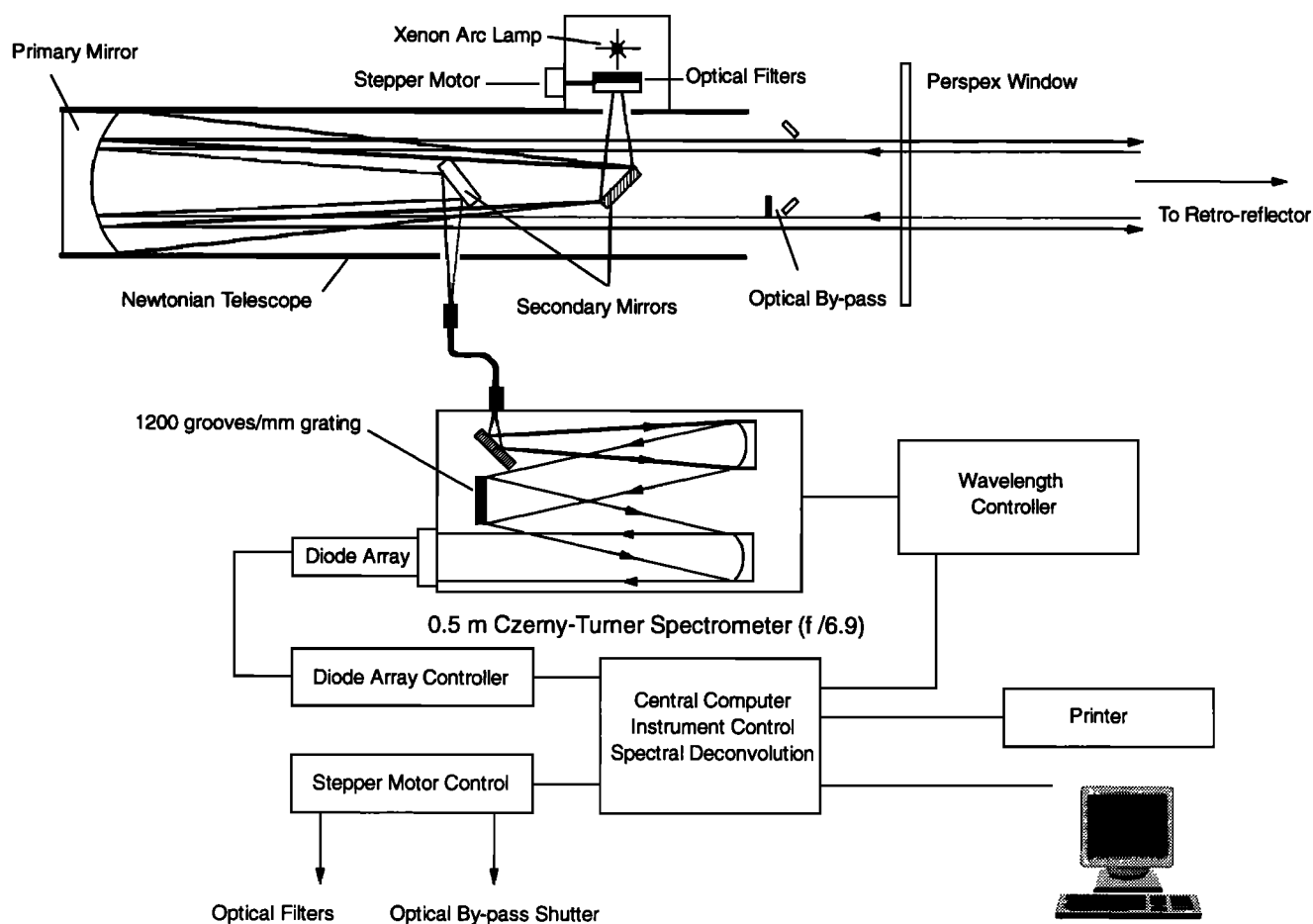


Figure 3. Schematic diagram of the differential optical absorption spectrometer used in the campaign at Izaña.

The measurements of NO_3 at the Izaña site presented two challenges. First, the topography of the location dictated the relatively short path length that had to be used in this study (1.98 km). Although the shorter path length resulted in a brighter return signal, this was offset by the reduced absorption obtained over the shorter path [Plane and Smith, 1995]. Second, the relative humidity (RH) at the site decreased substantially during the night, often to less than 5%, compared with daytime values of 10–20%. Thus the absolute H_2O concentration giving rise to the (311) vibrational overtone band was much larger during the day than at night. Some of the rotational lines in this band become saturated when making optical absorption measurements over a path length of several kilometers in the boundary layer, so that the band is no longer in the Beer-Lambert absorption regime (S. Aliwell and R.L. Jones, University of Cambridge, personal communication, 1996). Fortunately, over the relatively short path length and drier atmosphere in this study the column density of H_2O was $\leq 10^{22}$ molecule cm^{-2} , which is at the margin of where this deviation from Beer-Lambert behavior becomes significant (J. Harder, National Oceanic and Atmospheric Administration, Boulder, personal communication, 1996).

Ancillary data for the campaign were provided by the staff of the meteorological station. The meteorological instruments, a sun photometer, and two dust samplers were located above a platform on the top of the station building. An air inlet for the majority of measurements at the station was situated 2.5 m

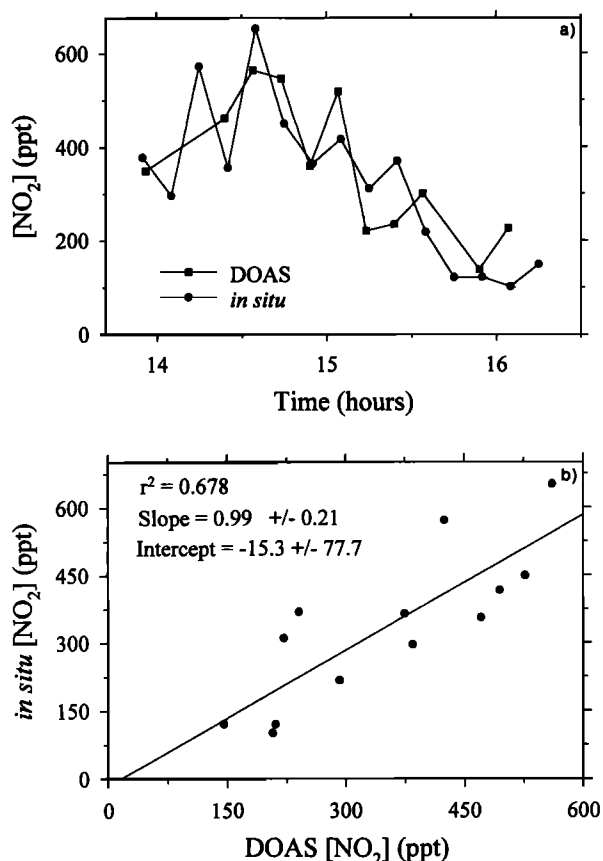


Figure 4. Results of an NO_2 comparison between the DOAS instrument and an in situ instrument (Eco Physics PLC 760) at the meteorological station on May 5, 1994: (a) time profile of the NO_2 concentration; (b) correlation plot.

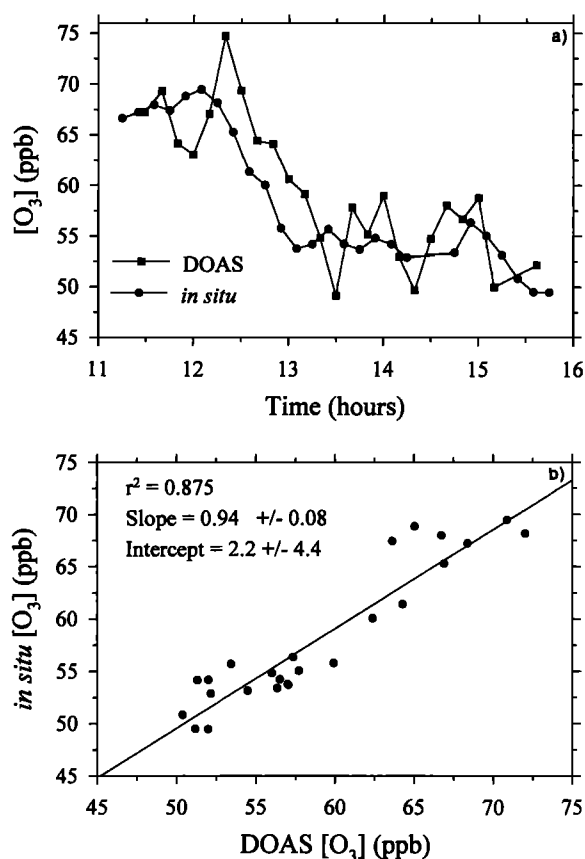


Figure 5. Results of an O_3 comparison between the DOAS instrument and an in situ instrument (Dasibi 1008 AH) at the meteorological station on May 11, 1994: (a) time profile of the O_3 concentration; (b) correlation plot.

above the observation platform, i.e. a total height of 13 m above the ground. Species that were monitored included O_3 (Dasibi 1008 AH), condensation nuclei (General Electric CNC2), NO_2 (Eco Physics PLC 760, detection limit approximately 30 ppt), NO (Eco Physics CLD 770 AL, detection limit of 20 ppt), NO_x (Gold convertor operated at 300 °C), PAN (automatic GC-ECD system) and NMHC (automated GC-FID system). Unfortunately, measurements of NO_2 and NO were only available at the meteorological station from May 1–5, after which the instruments were moved to the solar observatory and only provided intermittent data for the remainder of the campaign. Meteorological soundings were made using a radiosonde with temperature, pressure, and relative humidity sensors (Vaisala RS-80).

Results

In addition to observing NO_3 at night, the DOAS instrument was used during daytime to measure NO_2 and O_3 in order to compare with the in situ (point sampling) instruments at the meteorological station. Figures 4 and 5 illustrate the NO_2 and O_3 comparisons, respectively. In both cases there is satisfactory agreement between the long-path and in situ instruments, even in the case of NO_2 concentrations down to the DOAS detection limit of about 100 ppt over this path length [Plane and Smith, 1995]. The correlation plots in Figures 4b and 5b have slopes very close to unity, although there is some scatter, particularly in

the NO_2 plot. This is most probably because the instruments sampled different air masses (the DOAS beam was on average 80 m below the in situ air intake). The site is prone to upslope wind conditions during the day owing to the strong solar irradiance [Schmitt *et al.*, 1988]; these winds transport pollution from lower altitudes, and variability in O_3 , CO_2 , and water vapor has been noted previously [Schmitt *et al.*, 1988; Comes *et al.*, 1995; E. Cuevas *et al.*, submitted paper, 1996].

Figure 6 is a time profile of the NO_3 concentration from May 4-5. The error bars assigned to each measurement illustrate the standard error of the least squares fit of the NO_3 reference cross section to the atmospheric spectrum. This fit is performed over 450 points in the wavelength interval 655-667 nm [Plane and Smith, 1995]. The uncertainty is thus about ± 5 ppt, which is about a factor of 4 larger than in our previous studies, which employed path lengths 2-2.5 times longer to measure NO_3 in boundary layer environments where there was little diurnal variation in RH [Smith *et al.*, 1995; Yvon *et al.*, 1996].

Discussion

Measurements of NO_3 were made on a total of 17 nights during the campaign. However, during 10 of these nights the NO_2 instrument at the solar observatory was not operating, and on a further three nights the DOAS light beam was obscured by clouds around the retro-reflector (this problem arose because the meteorological station was located on a mountain ridge (Figure 2) with the retro-reflector 105 m below the observatory). We have therefore selected four nights of NO_3 measurements for detailed study. Isentropic trajectories, calculated backward for 10 days at about the pressure level of Izaña, showed that on three of these nights the air at the observatory had come directly from the Atlantic, either west or northwest of the island (J.T. Merrill, University of Rhode Island, personal communication, 1996). On May 4-5, the air originated in the mid-Atlantic and passed over southern Spain and West Africa before reaching the site. However, the NO_x concentration and aerosol count are indistinguishable from the other three nights, and so this fourth night has been included for consideration.

Figure 7 shows all the NO_3 measurements made on these nights, together with the hourly averages and standard

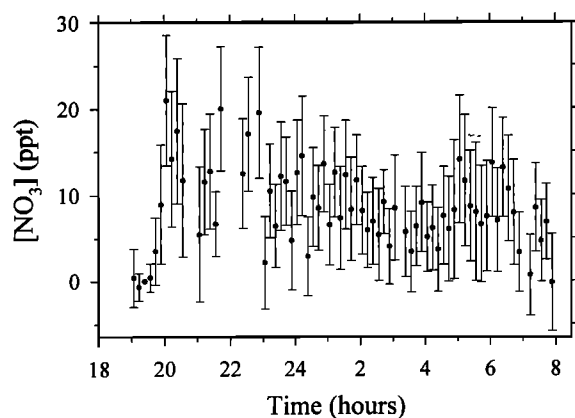


Figure 6. A time profile of the NO_3 concentration measured over the night of May 4-5, 1994 at Izaña. The error bars indicate the statistical uncertainty in the fit of the reference NO_3 absorption cross section to the processed atmospheric optical density spectrum.

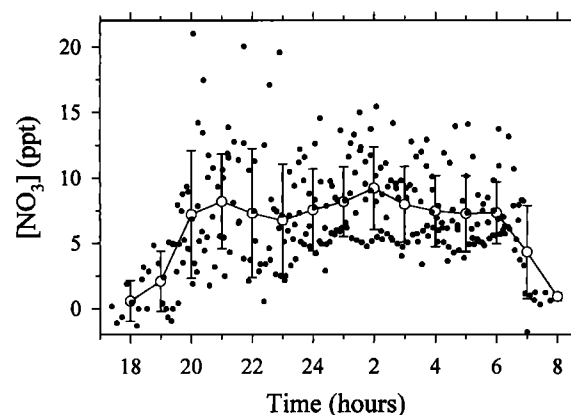


Figure 7. Solid circles indicate the NO_3 concentration plotted as a function of time from measurements during four nights at Izaña: May 1-2, 4-5, 22-23, and 23-24, 1994. Note that the NO_3 profiles from the first three of these nights are plotted separately in Figures 8, 6, and 9, respectively. Open circles show the hourly average NO_3 concentrations with their standard deviations.

deviations. Shortly after sunset (about 1940 hours) the NO_3 concentration increased to an average value of about 8 ppt over most of night, before a rapid decrease at sunrise (about 0620 hours). Two nights of data are shown in more detail in Figures 8 and 9. In each figure, the upper panel illustrates the NO_3 concentration plotted as a 30-min moving average, together with

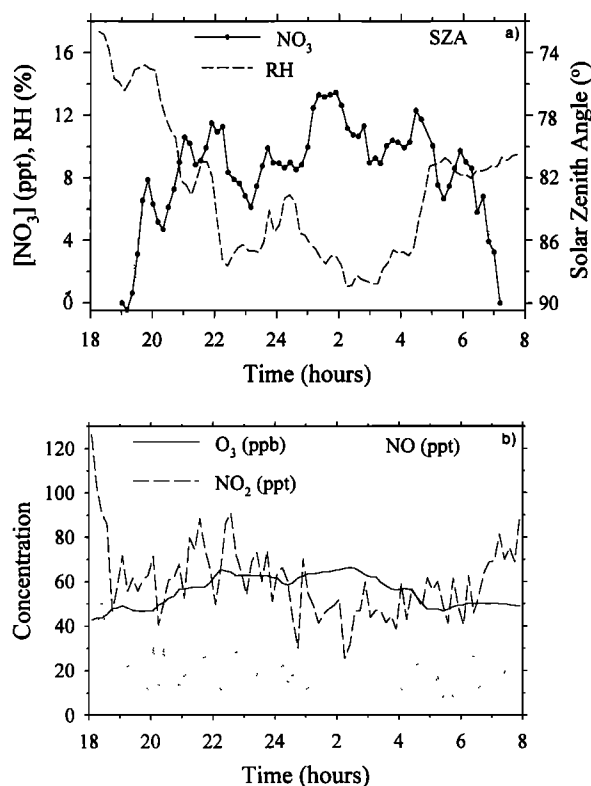


Figure 8. Time profiles of measurements from the night of May 1-2, 1994, at Izaña: (a) the concentration of NO_3 plotted as a 30-min moving average, the relative humidity, and the solar zenith angle; (b) the concentrations of NO_2 , NO , and O_3 . Sunset was at 1936 and sunrise at 0630 hours GMT.

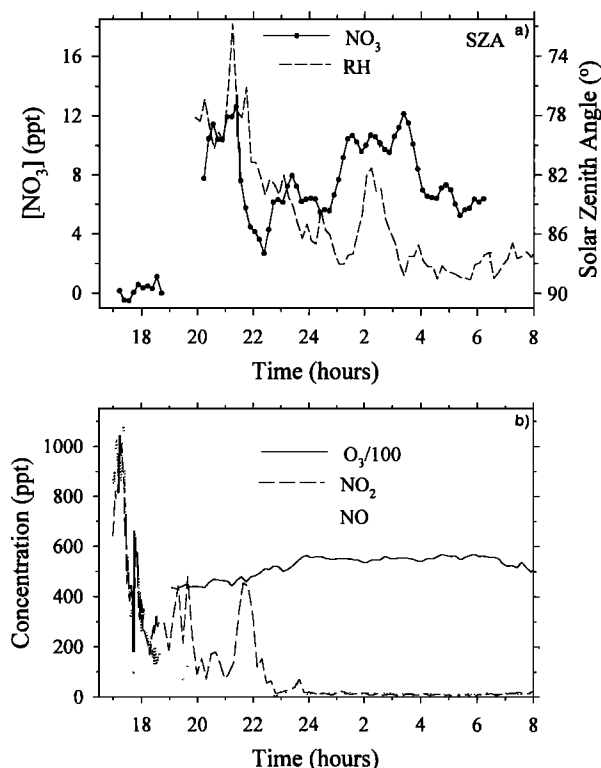


Figure 9. Time profiles of measurements from the night of May 22-23, 1994, at Izaña: (a) the concentration of NO_3 plotted as a 30-min moving average, the relative humidity, and the solar zenith angle; (b) the concentrations of NO_2 , NO , and O_3 . Sunset was at 1948 and sunrise at 0616 hours GMT.

a plot of the solar zenith angle and the RH. The lower panel shows the concentrations of NO_2 , NO , and O_3 that were measured by the in situ instruments. All of the times are GMT (1 hour behind local time). The results from the night of May 1-2 (Figure 8) show the clear relationship between the solar zenith angle and NO_3 concentration (sunset was at 1936 hours and sunrise at 0630 hours). Interestingly, the rapid decrease in the concentration of NO_3 at sunrise (from about 10 to less than 2 ppt) due to photolysis is associated with an increase in the NO_2 concentration over the same time period of about 20 ppt.

Figure 8a shows a very striking negative correlation between NO_3 and RH, where the very small values of RH of only 1-2% between 0200 and 0330 hours on this night are associated with the largest NO_3 concentrations. Such a negative correlation might be expected because of the heterogeneous loss of NO_3 and N_2O_5 that occurs on particle surfaces at higher relative humidities [Platt *et al.*, 1984; Rudich *et al.*, 1996]. However, mineral and sea-salt particles typically deliquesce only when the RH is above 40% and, in any case, the aerosol counts were very low, ranging from only 300 to 500 cm^{-3} . Furthermore, there is a reasonably strong positive correlation between O_3 and NO_3 . Hence a more likely explanation for the negative correlation with RH is that during the night there is subsidence from aloft of free tropospheric air that is relatively rich in O_3 (and NO_3) but depleted in water vapor. Overall, NO_2 appears to decay gradually over the night, perhaps because of conversion to NO_3 , although the subsiding air may also have become progressively cleaner.

Figure 9 illustrates somewhat different behavior on the night of May 22-23. After sunset (1948 hours), there is a rapid

increase in NO_3 to a peak of about 12 ppt just before 2200 hours, before a sharp decrease to about 3 ppt. This correlates with the pulse of NO_2 shown in Figure 9b (the large concentrations of NO_2 and NO before sunset were caused by a forest fire about 17 km to the NW). For the remainder of the night the NO_3 then averaged about 8 ppt. Although not clear on the scale of Figure 9b, there is again an increase in NO_2 shortly after sunrise of about 10 ppt.

During these four nights at Izaña, characterized by very clean air, the usual scavengers of NO_3 (see Introduction) were absent. The RH at night was always below 20% and often below 10%, so that heterogeneous loss can be discounted. Among potentially significant gas-phase removal processes, reaction with NO was unlikely since the concentration was below the detection limit (20 ppt), as expected in the absence of fresh sources of NO . Although the concentrations of various hydrocarbons were periodically monitored during the campaign, these measurements were mostly of alkanes which react very slowly with NO_3 [Wayne *et al.*, 1991]. Nevertheless, some indication is given by the nighttime concentrations of ethene and propene, which were generally below 25 ppt, and isoprene, which was usually below 5 ppt.

For these reasons, NO_3 would be expected to have a particularly long lifetime. The lifetime, $\tau(\text{NO}_3)$, is a useful parameter for interpreting field measurements of the radical [Platt *et al.*, 1984; Smith *et al.*, 1995] and is defined by assuming that NO_3 exists in steady state between production by reaction (1) and removal by the sum of the loss processes:

$$\tau(\text{NO}_3) \geq \frac{[\text{NO}_3]}{k_1[\text{NO}_2][\text{O}_3]} \quad (5)$$

In fact, in this study $\tau(\text{NO}_3)$ is usually a lower limit to the radical lifetime because the rates of production and removal of NO_3 were so slow that steady state was not in fact achieved (see below). Averaging the NO_3 , NO_2 and O_3 measurements from 30 min after sunset to 30 min before sunrise on May 1-2 (Figure 7) produces an average $\tau(\text{NO}_3)$ of 2 hours. On the other three nights where the NO_2 concentrations were smaller and therefore less reliable, $\tau(\text{NO}_3)$ appears to be considerably longer than 2 hours. These lifetimes are much longer than those that have been reported in the tropospheric boundary layer [Platt *et al.*, 1984; Platt and Janssen, 1995; Smith *et al.*, 1995].

The air flow patterns at Izaña are known to be complex, with the upslope conditions established during the day reversing at sunset to form downslope winds during the night. These downslope winds transport air from aloft to the altitude of the observatory. In order to model the nighttime production of NO_3 we have therefore constructed a simple transport model containing the chemistry listed in Table 1 (note that heterogeneous loss of NO_3 or N_2O_5 is assumed to be negligible). At time t during the night, the measured O_3 and NO_2 concentrations were used to estimate backward in time the NO_2 concentration that would have existed at sunset. This assumes that the NO_2 and O_3 sampled at time t have remained in a discrete air parcel of constant temperature since sunset, and that the oxidation of NO_2 was irreversible. The model was then run without allowing for any losses of NO_3 by reaction with organic species, in order to estimate the maximum NO_3 concentration that could have built up between sunset and time t . This procedure was repeated for all the measurements of NO_3 over the course of the night.

Table 1. Chemical Reactions in the Simple Transport Model

Reaction	Rate Coefficient, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$1.2 \times 10^{13} \exp\{-(2450 \pm 150)/T\}^a$
$\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$k_0 = 2.2 \times 10^{-30} (T/300)^{4.3} \text{ cm}^6$ $k_{\text{rec}}^b \left\{ \begin{array}{l} k_{\text{rec}} = 1.5 \times 10^{-12} (T/300)^{0.5} \\ k_{\text{rec}} / 2.7 \times 10^{-27} \exp\{(11000 \pm 500)/T\}^a \end{array} \right.$
$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	
$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	$4.5 \times 10^{-14} \exp\{-1260/T\}^a$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	see text
$\text{NO}_3 + \text{HC} \rightarrow \text{products}$	when $\text{HC} = \alpha\text{-pinene}$, $k = 1.2 \times 10^{-12} \exp(490/T)^c$

^a DeMore *et al.* (1994).^b For details of how to calculate k_{rec} , refer to DeMore *et al.* (1994).^c Wayne *et al.* (1991).

Comparisons of the model predictions with the observations for the nights of May 1-2 and May 22-23 are shown in Figures 10 and 11, respectively. Two contrasting pictures emerge: the modeled NO_3 concentrations in Figure 10 are generally much larger than those observed, while in Figure 11, apart from a large peak at 2200 hours caused by a spike of NO_2 (Figure 9b), there is very satisfactory agreement. The NO_2 concentration is too small after midnight for the equilibrium between NO_3 and N_2O_5 (reactions (2)) to be attained. A significant difference between these nights is that the average wind speed on the night of May 1-2 was 15 m s^{-1} , compared to only 3 m s^{-1} on May 22-23 when the downslope wind system was probably very well established. During the earlier night the strong winds may well have mixed air containing traces of organic species from below the height of the observatory. To demonstrate this effect, a small sink provided by 1 or 2 ppt of α -pinene has been added to the model, producing good agreement with the observations over most of the night (Figure 9). Note that a similar sink for NO_3 would be provided by only 0.2 ppt of NO , if a local (perhaps biogenic) source of NO were present.

The data from the night of May 1-2 can also be used to investigate the effectiveness of the homogeneous gas-phase reaction between N_2O_5 and H_2O (reaction (4)). Estimating the concentration of H_2O from the measured RH and air temperature during the night, Figure 12 illustrates that k_4 would have to be about $5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in order to produce satisfactory

agreement between the modeled and observed NO_3 time profiles. However, this value of k_4 is more than 2 orders of magnitude larger than the upper limit derived in the laboratory study of Sverdrup *et al.* [1987], and so reaction (4) cannot provide the required sink on this night.

Inspection of Figures 10-12 reveals that the observed buildup of NO_3 after sunset is more rapid than predicted by the model. A possible reason for this is illustrated in Figure 13, which shows the temperature and RH data from a sounding profile taken at 2125 hours (2 hours after sunset) on the night of May 1-2. Both the RH and temperature profiles show an inversion just at the altitude of the observatory (2376 m). Since the DOAS light beam measuring NO_3 was between 30 and 135 m lower than the sampling point for NO_2 at the meteorological station, the NO_3 was probably formed during the first part of the night in air contaminated by boundary layer pollution, i.e., with larger concentrations of NO_2 than those measured higher up the ridge and employed in the model calculations. Indeed, this inversion was often noticed during the late afternoon, when clouds covered the retro-reflector while the meteorological station and the building housing the DOAS instrument were in bright sunlight.

Conclusions

An average nighttime NO_3 concentration of 8 ppt (maximum 20 ppt) has been observed in the free troposphere at Izaña de

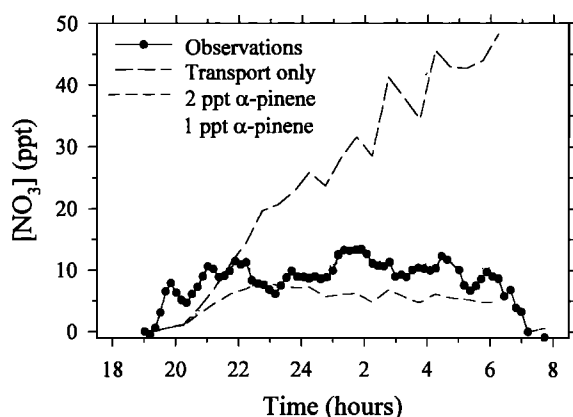


Figure 10. Time profiles of NO_3 from May 1-2, 1994, showing the observed concentrations and model predictions using the NO_2 and O_3 measurements in Figure 8b extrapolated back to sunset (see text), for the cases of no hydrocarbon sinks (i.e., transport only), and 1 or 2 ppt of α -pinene.

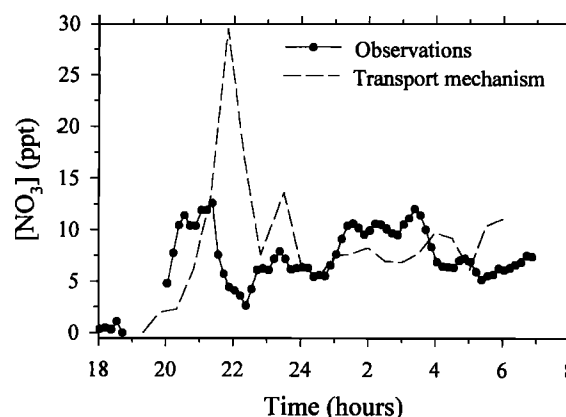


Figure 11. Time profiles of NO_3 from May 22-23, 1994, showing the observed concentrations and model predictions using the NO_2 and O_3 measurements in Figure 9b extrapolated back to sunset (see text).

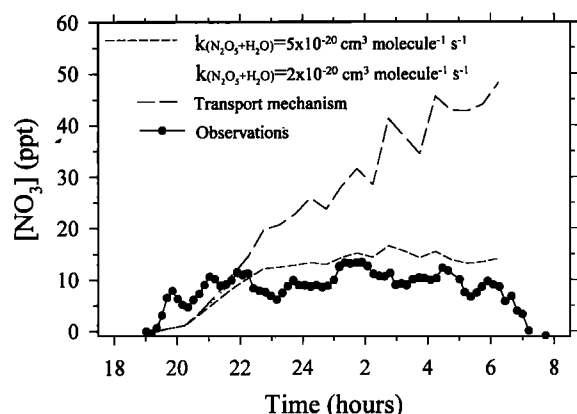


Figure 12. Time profiles of NO_3 from May 1-2, 1994, showing the observed concentrations and model predictions using the NO_2 and O_3 measurements in Figure 8b extrapolated back to sunset (see text), for the cases of no sinks for NO_3 or N_2O_5 (i.e., transport only), and with trial values for the rate coefficient $k(\text{N}_2\text{O}_5 + \text{H}_2\text{O})$.

Tenerife (2300 m) during early summer. The range of concentrations is in good agreement with previous measurements made by Smith *et al.* [1993] using a remote sensing technique above Fritz Peak (Colorado) in summer. The results are also in sensible accord with the NO_3 concentration proposed by Penkett *et al.* [1993] to explain the observed ratio of hydrocarbons in the free troposphere at high latitudes.

The lifetime of NO_3 was found to be in excess of 2 hours, much longer than has been reported from observations in the tropospheric boundary layer. The absence of significant scavengers is expected because of the low RH and aerosol count, and the small concentrations of reactive organic species. A simple model demonstrates that close to 50% of the NO_2 is converted to NO_3 during a 10-hour night, and the NO_3 essentially builds up over the course of the night because the NO_2 concentration is too small to produce significant levels of N_2O_5 . Thus NO_3 appears to act as a nighttime reservoir for NO_2 . Apart from requiring a small NO_3 sink from a trace species such as α -pinene or NO to model one night of observations, the good

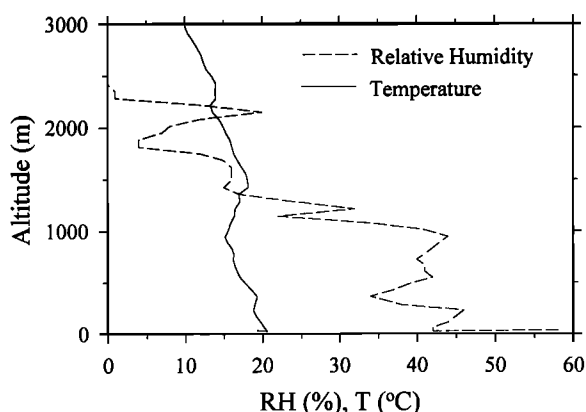


Figure 13. Temperature and relative humidity data from a sounding profile taken at 2125 on the night of May 1-2. Both the relative humidity and temperature profiles demonstrate the presence of an inversion at about the altitude of the meteorological station (2376 m).

agreement between model and observation confirms that there are no significant scavengers for NO_3 in the lower free troposphere.

This conclusion is not in agreement with the result of Noxon [1983], who found that the ratio of NO_3 to NO_2 was only about 1%. However, Solomon *et al.* [1989] have proposed that Noxon underestimated the NO_3 concentration by using too narrow a wavelength range for the optical absorption measurements, so that the water vapor absorption bands were not completely removed from his spectra. Further evidence for this comes from Noxon's observation that the scavenging rate of NO_3 was the same in the boundary layer of the Colorado Rocky Mountains as in the free troposphere over the Pacific Ocean. While the rapid scavenging in Colorado can easily be explained by the abundance of biogenic hydrocarbons emitted from the pine forests around Fritz Peak, such a large source is unlikely to have existed at the Mauna Loa site.

Finally, the absence of scavenging mechanisms in the free troposphere indicates that NO_3 should be an important oxidant of reactive hydrocarbons under conditions where the impact of OH is reduced, namely, at high latitudes during winter. The significance of this result is now being investigated by means of a three-dimensional global tropospheric model (T. Berntsen and I.S.A. Isaksen, manuscript in preparation, 1996).

Acknowledgments. This work was supported by the European Commission (contract EV5V-CT93-0321). We thank the Natural Environment Research Council for a studentship (N.C.) and the staff of the Observatorio de Vigilancia Atmosférica de Izaña for their hospitality and assistance in deploying the DOAS instrument.

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(Received April 2, 1996; revised October 28, 1996; accepted October 28, 1996).