

Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations

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Received 31 December 2008; revised 26 March 2009; accepted 1 April 2009; published 6 June 2009.

[1] This paper presents determinations of reactive uptake coefficients for N₂O₅, $\gamma(\text{N}_2\text{O}_5)$, on aerosols from nighttime aircraft measurements of ozone, nitrogen oxides, and aerosol surface area on the NOAA P-3 during Second Texas Air Quality Study (TexAQS II). Determinations based on both the steady state approximation for NO₃ and N₂O₅ and a plume modeling approach yielded $\gamma(\text{N}_2\text{O}_5)$ substantially smaller than current parameterizations used for atmospheric modeling and generally in the range $0.5\text{--}6 \times 10^{-3}$. Dependence of $\gamma(\text{N}_2\text{O}_5)$ on variables such as relative humidity and aerosol composition was not apparent in the determinations, although there was considerable scatter in the data. Determinations were also inconsistent with current parameterizations of the rate coefficient for homogenous hydrolysis of N₂O₅ by water vapor, which may be as much as a factor of 10 too large. Nocturnal halogen activation via conversion of N₂O₅ to ClNO₂ on chloride aerosol was not determinable from these data, although limits based on laboratory parameterizations and maximum nonrefractory aerosol chloride content showed that this chemistry could have been comparable to direct production of HNO₃ in some cases.

Citation: Brown, S. S., et al. (2009), Reactive uptake coefficients for N₂O₅ determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations, *J. Geophys. Res.*, 114, D00F10, doi:10.1029/2008JD011679.

1. Introduction

[2] Hydrolysis of N₂O₅ is one of the most important reactions determining the atmospheric lifetime of NO_x against its conversion to soluble nitrate (NO₃[−]) [Dentener and Crutzen, 1993; Tie et al., 2003]. The reaction occurs principally in the dark because of the photochemical instability of the nitrate radical, NO₃, the precursor to N₂O₅. It provides a nonphotochemical route for conversion of NO_x to soluble nitrate that is competitive with photochemical reaction of OH with NO₂ [Jones and Seinfeld, 1983]. The hydrolysis reaction occurs rapidly by heterogeneous uptake

to aerosol [Mozurkewich and Calvert, 1988] but may also occur more slowly in the gas phase [Wahner et al., 1998a]. Accurate characterization of the rate of N₂O₅ hydrolysis is important to predictions of global tropospheric oxidant burdens [Bell et al., 2005; Evans and Jacob, 2005; Lamarque et al., 2005; Tie et al., 2001] and radiative forcing due to ozone and aerosol [Feng and Penner, 2007; Liao and Seinfeld, 2005]. Hydrolysis of N₂O₅ affects regional air quality through its roles in regulating the reactive nitrogen budget and photochemical ozone production [Riemer et al., 2003], spatial patterns of acid deposition [Calvert et al., 1985] and nitrate aerosol formation [Mathur et al., 2008; Schaap et al., 2004].

[3] Global and regional atmospheric chemistry models rely on parameterizations of the heterogeneous uptake coefficient, $\gamma(\text{N}_2\text{O}_5)$, that are based on laboratory measurements. Until recently, tropospheric models had typically used a large, constant value of $\gamma(\text{N}_2\text{O}_5) = 0.1$, independent of temperature, relative humidity or aerosol composition [Dentener and Crutzen, 1993; Tie et al., 2003]. More recent parameterizations have taken these variables into account on the basis of the availability of more detailed laboratory studies. Evans and Jacob [2005] developed a parameterization that incorporated relative humidity and temperature dependences of $\gamma(\text{N}_2\text{O}_5)$ on various aerosol types, including

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sulfate, organic carbon, black carbon, sea salt and dust for use in the GEOS-CHEM model. Davis *et al.* [2008] incorporated relative humidity and temperature dependencies of $\gamma(\text{N}_2\text{O}_5)$ for a variety of inorganic aerosol types, including ammonium sulfate, bisulfate and nitrate, although omitting organic aerosol. The parameterization was intended for use in regional air quality models. Additional studies have examined specific effects of different aerosol types to demonstrate the implications of particular laboratory studies or to examine these effects in the context of regional models. Several studies have examined the suppression of $\gamma(\text{N}_2\text{O}_5)$ on nitrate aerosol (the so-called “nitrate effect”) [Hallquist *et al.*, 2003; Mentel *et al.*, 1999; Wahner *et al.*, 1998b]. Both Wahner *et al.* [1998b] and Riemer *et al.* [2003] parameterized this effect, with the latter applied to regional studies of NO_x, O₃ and aerosol. Organic coatings are known to lead to suppression of $\gamma(\text{N}_2\text{O}_5)$, and formalisms have been developed to describe this reduction due to condensation of organic aerosol on inorganic cores [Anttila *et al.*, 2006]. In addition to the heterogeneous hydrolysis, laboratory studies have examined the direct gas phase reaction of N₂O₅ with water vapor [Hjorth *et al.*, 1987; Mentel *et al.*, 1996; Tuazon *et al.*, 1983; Wahner *et al.*, 1998a], which can substantially increase the rate of N₂O₅ hydrolysis compared to heterogeneous uptake alone [e.g., Ambrose *et al.*, 2007]. Homogeneous N₂O₅ hydrolysis is part of the IUPAC recommendation for atmospheric modeling and is thus a standard input to models such as the Master Chemical Mechanism [Atkinson *et al.*, 2004].

[4] There are few studies that have directly tested the validity of parameterizations for heterogeneous N₂O₅ uptake coefficients, the rate coefficients for the homogeneous reaction, or the underlying laboratory data, based on atmospheric observations of N₂O₅. Surface level measurements of NO₃ by differential optical absorption spectroscopy (DOAS) and of NO₃ and N₂O₅ by in situ methods have generally shown evidence for rapid N₂O₅ hydrolysis [e.g., Aldener *et al.*, 2006; Allan *et al.*, 1999; Ambrose *et al.*, 2007; Apodaca *et al.*, 2008; Ayers and Simpson, 2006; Brown *et al.*, 2004; Geyer *et al.*, 2001; Heintz *et al.*, 1996; Martinez *et al.*, 2000; Platt *et al.*, 1984; Smith *et al.*, 1995; Vrekoussis *et al.*, 2007; Wood *et al.*, 2005]. Similar observations at higher elevation sites within the free troposphere or from vertical profiling by remote sensing have generally shown longer NO₃ lifetimes, perhaps indicating a lesser role for N₂O₅ hydrolysis [e.g., Allan *et al.*, 2002; Carslaw *et al.*, 1997; von Friedeburg *et al.*, 2002]. Recent aircraft measurements in the Northeast U.S. have shown evidence for large variability in $\gamma(\text{N}_2\text{O}_5)$ and have used in situ measurements of NO₃ and N₂O₅ to derive quantitative heterogeneous uptake coefficients for direct comparison to model parameterizations [Brown *et al.*, 2006a, 2006b]. However, the aircraft database is limited to only a single regional study and has to date demonstrated only the role of sulfate aerosol in promoting rapid N₂O₅ hydrolysis, with small values for other aerosol types. Recent direct measurements of N₂O₅ reactivity using a flow tube apparatus and aerosol sampled directly from ambient air have shown $\gamma(\text{N}_2\text{O}_5)$ smaller than parameterizations, with a positive dependence on both relative humidity and aerosol sulfate content (T. H. Bertram *et al.*, Direct observations of N₂O₅ reactivity: Insights on particulate water content and

implications for NO_x processing rates, submitted to *Geophysical Research Letters*, 2009).

[5] This paper presents nighttime aircraft measurements from the NOAA P-3 from the 2006 Second Texas Air Quality Study (TexAQS II) [Parrish *et al.*, 2009]. Similar to the previous aircraft study from the northeast United States, analysis of observed NO₃ and N₂O₅ in terms of a steady state between their production and loss provided a determination of heterogeneous N₂O₅ uptake coefficients. Further comparison of the data to model simulations of HNO₃ production corroborate the steady state analysis. The field determinations for $\gamma(\text{N}_2\text{O}_5)$ are compared to parameterizations for the uptake coefficients, and overall lifetimes of N₂O₅ are compared to tabulated rate coefficients for homogeneous hydrolysis. In general, the results show smaller uptake coefficients and longer N₂O₅ lifetimes than the tabulation and indicate the potential for errors in the representation of nighttime nitrogen oxide chemistry in current models.

2. Field Measurements and Nighttime Aircraft Data

[6] There were four night flights during TexAQS II, three of which flew late enough into the night to be suitable for determination of $\gamma(\text{N}_2\text{O}_5)$ by the steady state analysis (section 3). Table 1 lists the trace gas and aerosol measurements relevant to this analysis. The instrument for measurement of NO₃ and N₂O₅ was a four-channel cavity ring-down spectrometer that detects NO₃ by 662-nm optical extinction in an ambient temperature channel and the sum of NO₃ and N₂O₅ in a second 662-nm channel with a heated inlet to convert N₂O₅ to NO₃ [Dubé *et al.*, 2006]. Inlet transmission efficiencies were calibrated via reaction of NO₃ with NO to give NO₂, which was measured in two additional 532-nm cavity ring-down channel according to the method of Fuchs *et al.* [2008]. Figures 1 and 2 show flight tracks and data for the night flights of 8 and 12 October 2006, the two flights on which the majority of $\gamma(\text{N}_2\text{O}_5)$ determinations were obtained. The flight tracks are color and size coded according to NO₃ and numbered according to the NO_x plumes analyzed to determine $\gamma(\text{N}_2\text{O}_5)$. Time series in Figures 1 and 2 show the data for O₃, NO₂, NO₃, N₂O₅ and aircraft altitude plotted against the time since sunset.

3. Determination of $\gamma(\text{N}_2\text{O}_5)$ From Steady State Analysis

[7] Steady state lifetimes for NO₃ and N₂O₅ are a standard analysis tool used to assess the reactivity of these compounds [Platt *et al.*, 1984]. The assumption of steady state regards NO₃ and N₂O₅ as reactive intermediates produced from the oxidation of NO₂ by O₃ and lost via oxidation (NO₃) or hydrolysis (N₂O₅) reactions.

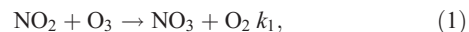
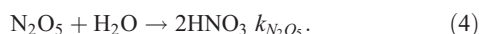


Table 1. Instruments Used for Analysis of N₂O₅ Uptake Coefficients

Measurement/Technique	Accuracy	Frequency	Reference
NO ₃ , N ₂ O ₅ /CRDS ^a	20%	1 Hz	<i>Dubé et al.</i> [2006]
NO, NO ₂ , O ₃ /chemiluminescence	3–8%	1 Hz	<i>Ryerson et al.</i> [1999, 2000]
HNO ₃ /CIMS ^b	15%	1 Hz	<i>Neuman et al.</i> [2002]
Aerosol surface area density/particle counters ^c	25%	1 Hz	<i>Brock et al.</i> [2003], <i>Wilson et al.</i> [2004]
Aerosol composition/AMS ^d	30%	0.1 Hz	<i>Bahreini et al.</i> [2003, also submitted manuscript, 2009]
Speciated VOC/can samples ^e	5–10%	80/flight	<i>Schauffler et al.</i> [1999]

^aCavity ring-down spectroscopy.^bChemical ionization mass spectrometry.

^cMeasurements at 7% RH were corrected to ambient conditions using a parameterization for hygroscopic growth based on the measured change in extinction between dry and ambient relative humidity using a cavity ring-down aerosol extinction spectrometer [Baynard et al., 2007]. The surface area correction factor, $SA_{\text{correction}}$, was $SA_{\text{correction}} = (1 + 5.9672 \times 10^{-6} RH^{2.0868} + 3.4005 \times 10^{-5} RH^{2.1255})^2$. For RH < 75% the correction factors for surface area were <1.8, and the combined uncertainty of the measurement and the growth correction was 25% based on the deviation of Mie scattering calculations with observed RH dependence of aerosol extinction. Above 75% RH the uncertainties due to the hygroscopic growth became substantially larger.

^dCompact time of flight aerosol mass spectrometer.^eAnalyzed by GC-MS.

Here, k_1 and K_{eq} are the bimolecular rate coefficients and temperature-dependent equilibrium constants for reactions (1) and (2), respectively, and k_{NO_3} and $k_{\text{N}_2\text{O}_5}$ are the total first-order rate coefficients for loss of NO₃ and N₂O₅ in reactions (3) and (4). Sinks for NO₃ in reaction (3) are represented as VOC oxidation reactions, although the total sink for NO₃ may also include heterogeneous loss to aerosol. Photolysis of NO₃ was unimportant for nighttime aircraft sampling; aside from a few specific instances (not analyzed here), reaction of NO₃ with NO was also generally unimportant. Hydrolysis of N₂O₅ in reaction (4) may include both homogeneous and heterogeneous reactions, as discussed further below. Heterogeneous uptake of N₂O₅ may also lead to additional products, such as ClNO₂, that will be considered explicitly in section 7.

[8] The steady state lifetimes of NO₃, N₂O₅ and their sum (NO₃ + N₂O₅), τ_{NO_3} , $\tau_{\text{N}_2\text{O}_5}$ and τ_{sum} , are the ratios of the observed concentrations to the NO₃ production rate from reaction (1), $P(\text{NO}_3) = k_1[\text{O}_3][\text{NO}_2]$. The inverse lifetimes, also referred to as the loss frequencies [Geyer and Platt, 2002], can be related to the total first-order sink rate coefficients in reactions (3) and (4), k_{NO_3} and $k_{\text{N}_2\text{O}_5}$ [Brown et al., 2006b, 2003; Heintz et al., 1996].

$$\tau_{\text{NO}_3}^{-1} \equiv \frac{k_1[\text{O}_3][\text{NO}_2]}{[\text{NO}_3]} \approx k_{\text{NO}_3} + K_{\text{eq}}[\text{NO}_2]k_{\text{N}_2\text{O}_5}, \quad (5)$$

$$\tau_{\text{N}_2\text{O}_5}^{-1} \equiv \frac{k_1[\text{O}_3][\text{NO}_2]}{[\text{N}_2\text{O}_5]} \approx k_{\text{N}_2\text{O}_5} + \frac{k_{\text{NO}_3}}{K_{\text{eq}}[\text{NO}_2]}, \quad (6)$$

$$\tau_{\text{sum}}^{-1} \equiv \frac{k_1[\text{O}_3][\text{NO}_2]}{[\text{NO}_3] + [\text{N}_2\text{O}_5]} \approx \frac{k_{\text{NO}_3} + K_{\text{eq}}[\text{NO}_2]k_{\text{N}_2\text{O}_5}}{1 + K_{\text{eq}}[\text{NO}_2]}. \quad (7)$$

Here the approximate equalities indicate the steady state approximation (see below). The linear relationships between $\tau_{\text{NO}_3}^{-1}$ and $K_{\text{eq}}[\text{NO}_2]$ in equation (5) and $\tau_{\text{N}_2\text{O}_5}^{-1}$ and $1/K_{\text{eq}}[\text{NO}_2]$ in equation (6) allow for individual determination of the two sink rate coefficients as the slopes and intercepts of the inverse lifetimes as a function of the unitless weighting factor, $K_{\text{eq}}[\text{NO}_2]$, which is equal to the ratio of N₂O₅ to NO₃ at equilibrium. The relationship between this weighting factor and τ_{sum} in equation (7) is not linear but can be similarly fit to determine k_{NO_3} and $k_{\text{N}_2\text{O}_5}$. All three equations contain identical information so that they can be used in combination for consistency, or separately if, for example, one of the instrument channels produced higher quality or more reliable data than another (not generally the case for the measurements described here).

[9] Nighttime aircraft transects of NO₂-containing pollution plumes within the residual daytime boundary layer (i.e., below the mixing height from the preceding day, but above the nocturnal boundary layer) provide data that are well-suited to this analysis. The plume transects sample a range in NO₂ and therefore in the weighting factor, $K_{\text{eq}}[\text{NO}_2]$, allowing for robust fits to equations (5)–(7). In contrast to surface sampling, aircraft transects also provide nearly instantaneous (several minutes at most) snapshots of individual plumes that are not influenced by chemical evolution within the duration of the measurement. Finally, plumes within the residual layer at night are commonly decoupled from surface level emissions and are therefore more likely to have had sufficient time to achieve steady state in the absence of recent NO_x input.

[10] Determination of the individual sink rate coefficient for N₂O₅ provides a measurement of the uptake coefficient, $\gamma(\text{N}_2\text{O}_5)$ if the aerosol surface area density (S_A) is known (see Table 1) and if N₂O₅ hydrolysis occurs exclusively by heterogeneous uptake to aerosol rather than in the gas phase.

$$k_{\text{N}_2\text{O}_5} = \frac{1}{4} \bar{c} \gamma(\text{N}_2\text{O}_5) S_A \quad (8)$$

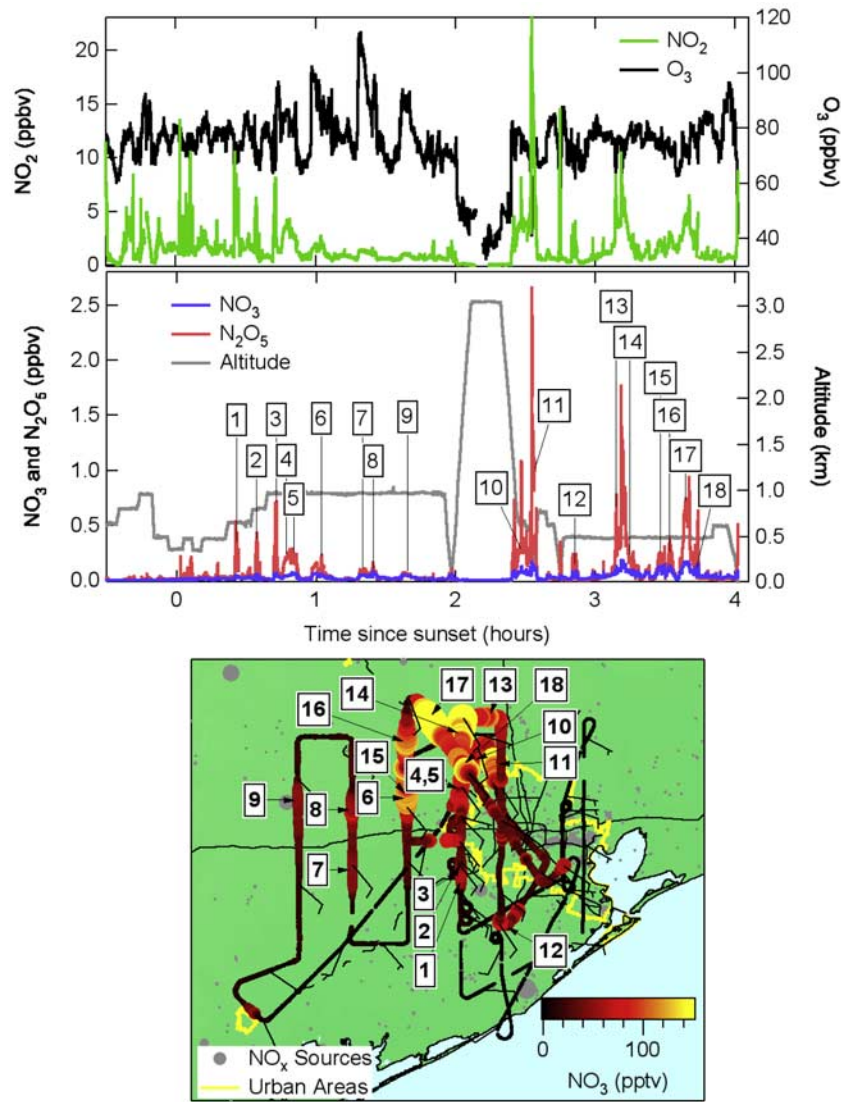


Figure 1. (top) Mixing ratios of O₃, NO₂, NO₃, N₂O₅, and aircraft altitude plotted as a function of time since sunset (defined as solar zenith angle of 90°) for the 8 October 2006 flight. (bottom) Map of the Houston area (urban boundary outlined in yellow) with the P-3 flight track superimposed. The flight track is color- and size-coded by NO₃ mixing ratio. The numbers in the top and bottom plots are the individual NO_x plumes analyzed to determine $\gamma(\text{N}_2\text{O}_5)$ values.

Here, $\bar{c}$ is the mean molecular speed of N₂O₅ from gas kinetic theory. Equation (8) is valid for submicron aerosol, which constituted the majority (>96%) of the aerosol surface area during the TexAQS campaign, and for small uptake coefficients (<0.1) such that gas phase diffusion to the particle surface does not limit the uptake rate [Fuchs and Stagnin, 1970]. There are two principal uncertainties in this method for determining $\gamma(\text{N}_2\text{O}_5)$. The first is the time required for the approach to steady state, as described in more detail below. The second is potential covariance between the independent variable, $K_{eq}[\text{NO}_2]$ in equations (5)–(7), and the sink rate coefficients, k_{NO_3} and $k_{\text{N}_2\text{O}_5}$. These covariances arise from correlation between NO₂ and either reactive VOC (influencing k_{NO_3}) or aerosol surface area (influencing $k_{\text{N}_2\text{O}_5}$). The latter is a particular concern for determinations of $\gamma(\text{N}_2\text{O}_5)$ in this study since aerosol surface area was frequently correlated with NO₂ in night-

time plumes sampled during TexAQS II. Substitution of equation (8) into equations (5)–(7) yields a different set of equations that accounts for this covariance.

$$\tau_{\text{NO}_3}^{-1} \approx k_{\text{NO}_3} + \frac{1}{4} \bar{c} S_A K_{eq}[\text{NO}_2] \gamma(\text{N}_2\text{O}_5) \quad (9)$$

$$\tau_{\text{N}_2\text{O}_5}^{-1} K_{eq}[\text{NO}_2] \approx k_{\text{NO}_3} + \frac{1}{4} \bar{c} S_A K_{eq}[\text{NO}_2] \gamma(\text{N}_2\text{O}_5) \quad (10)$$

$$\tau_{\text{Sum}}^{-1} (1 + K_{eq}[\text{NO}_2]) \approx k_{\text{NO}_3} + \frac{1}{4} \bar{c} S_A K_{eq}[\text{NO}_2] \gamma(\text{N}_2\text{O}_5) \quad (11)$$

The independent variable in equations (9)–(11) is $\bar{c} S_A K_{eq}[\text{NO}_2]/4$, and the quantities on the left-hand sides

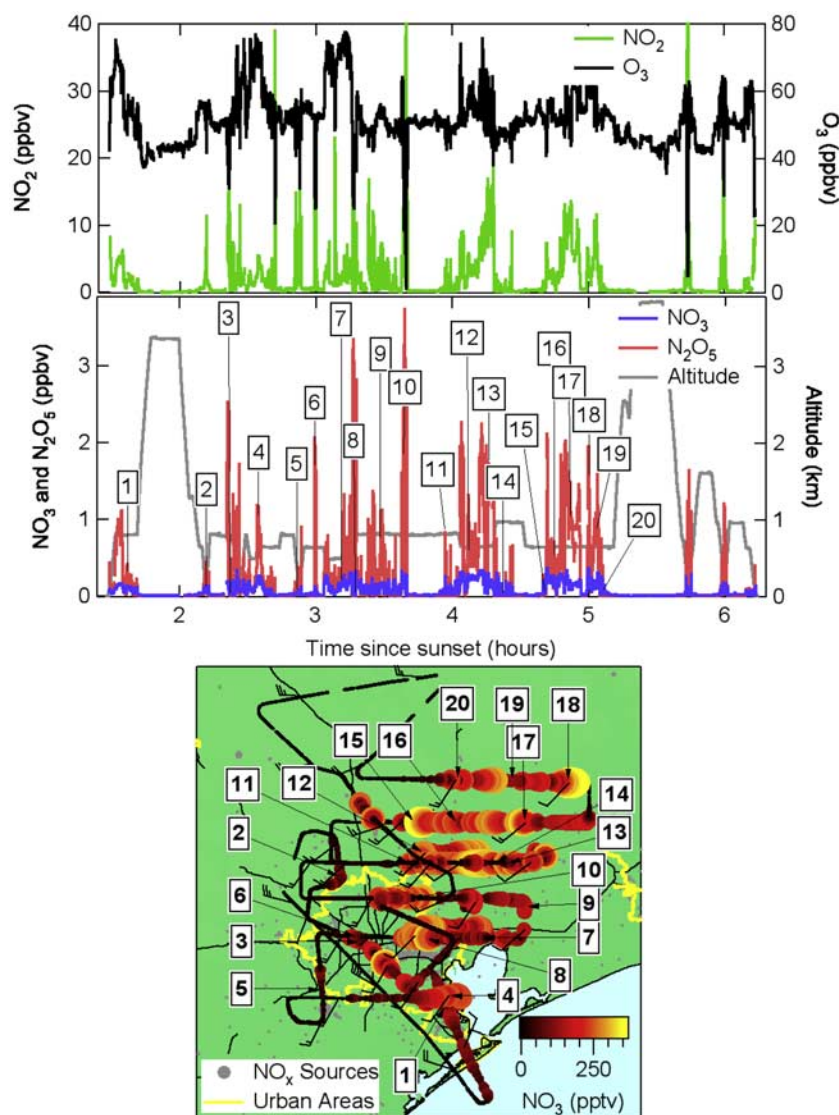


Figure 2. Same as Figure 1 but for the 12 October 2006 flight.

have been multiplied by the appropriate weighting factor to make the right-hand sides identical. Fits to equations (9)–(11) not only account for covariance between NO_2 and S_A , but also yield $\gamma(\text{N}_2\text{O}_5)$ directly as the slope of a linear fit.

[11] Figures 3 and 4 show example data and fits for single plumes from the 8 and 12 October 2006 flights. The plume in Figure 3 was sampled to the northwest of Houston, 3.7 h after local sunset on 8 October (plume 18 in Figure 1). A calculated backward trajectory (R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Tracker) Model, 2003, <http://www.arl.noaa.gov/ready/hysplit4.html>) placed the air mass near the Houston ship channel 4–5 h prior to sampling. Figure 3 shows plots of the steady state lifetimes according to equations (9)–(11) and the best fit values of $\gamma(\text{N}_2\text{O}_5)$ and k_{NO_3} (listed on Figure 3 as an inverse). The lower left-hand graph shows the time series for the observed NO_3 and N_2O_5 in the plume and the calculated NO_3 and N_2O_5 from the average values of the parameters from the top graphs. As the lower right graph shows, there was a significant correlation between the aerosol surface area and $K_{\text{eq}}[\text{NO}_2]$, such that fits to

equations (9)–(11) were superior to fits to equations (5)–(7) for determination of $\gamma(\text{N}_2\text{O}_5)$. The steady state $\gamma(\text{N}_2\text{O}_5)$ was 0.0028. The relative humidity was 67%, and the aerosol composition was 54% organic (by mass), with the inorganic component fully neutralized as ammonium sulfate and ammonium nitrate. Similar aerosol types gave small $\gamma(\text{N}_2\text{O}_5)$ values in our previous study in the northeast United States [Brown *et al.*, 2006b]. In spite of the small $\gamma(\text{N}_2\text{O}_5)$, there was sufficient aerosol surface area in this plume to limit the N_2O_5 lifetime to roughly 2 h, still allowing for significant production of HNO_3 (see below).

[12] Figure 4 shows a similar set of example plots from the 12 October flight for a plume sampled to the northeast of Houston (plume 18 in Figure 2) 5 h after sunset. The transport time for industrial NO_x sources in the Houston ship channel to the point of sampling was 6 h. As in the previous example, the parameters derived from these fits reproduced the observed data in the lower left-hand plot, with $\gamma(\text{N}_2\text{O}_5)$ values in the range 0.0010–0.0013. Correlations between aerosol surface area and $K_{\text{eq}}[\text{NO}_2]$ were also evident in this plume. The relative humidity on this transect

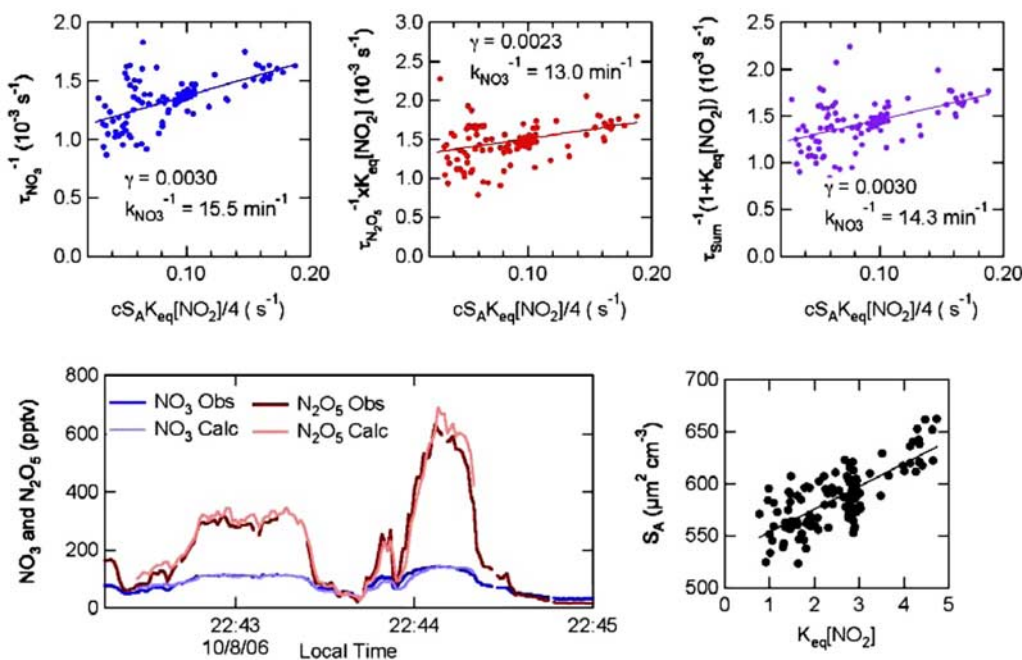


Figure 3. (top) Inverse NO₃ and N₂O₅ steady state lifetimes and of the summed lifetime of NO₃ and N₂O₅ according to equations (9)–(11), for a single NO_x plume intercepted on the 8 October 2006 flight. The text on the plots gives the best fit values of $\gamma(\text{N}_2\text{O}_5)$ and k_{NO_3} for each fit. (bottom left) Time series of NO₃ and N₂O₅ mixing ratios for this plume and the calculated time series for these data using the average of the fitted parameters from the top plots. (bottom right) Aerosol surface area density against $K_{\text{eq}}[\text{NO}_2]$ showing the covariance between these quantities (see text).

was 59%, and the submicron aerosol composition was 60% organic with a neutralized ammonium sulfate/ammonium nitrate inorganic fraction. Lifetimes for N₂O₅ were generally longer on the 12 October flight than on 8 October, consistent with the larger measured aerosol surface area and relative humidity on 8 October. There was no significant

difference in average uptake coefficients between the two flights, however.

[13] Table 2 gives all of the $\gamma(\text{N}_2\text{O}_5)$ values from the three TexAQS II night flights. These determined $\gamma(\text{N}_2\text{O}_5)$ are mainly from the steady state analysis described above, assuming that all hydrolysis is attributable to heterogeneous

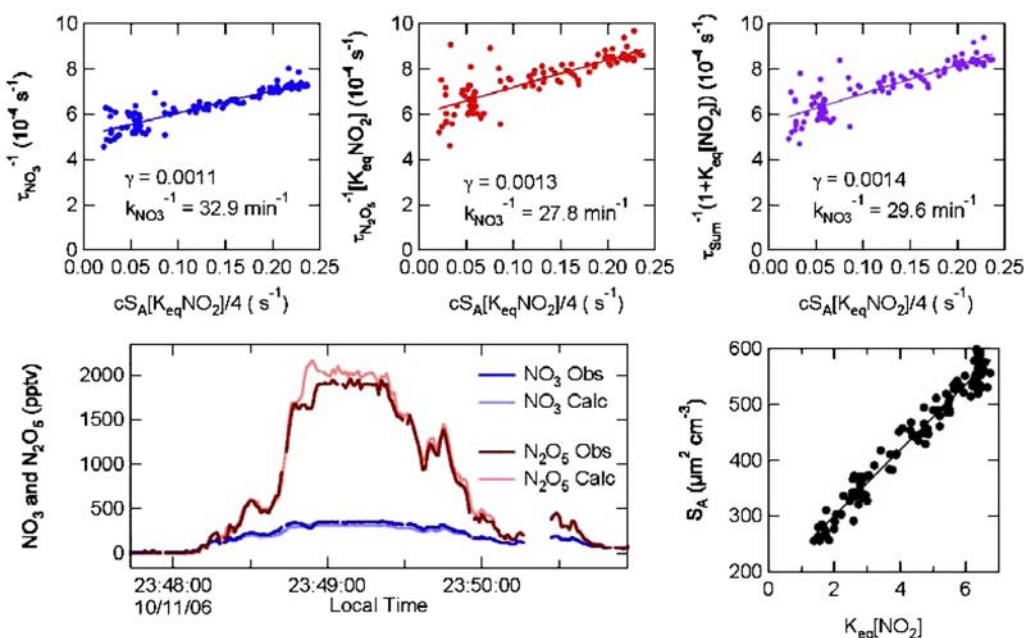


Figure 4. Same as Figure 3 but for a plume intercepted on the 12 October 2006 flight.

Table 2. N₂O₅ Uptake Coefficient Determinations From Three Night Flights

Plume Number	$\gamma(\text{N}_2\text{O}_5)^a$	RH (%)	Organic Mass/Total Mass	$\text{NO}_3^-/(\text{NO}_3^- + \text{SO}_4^{2-})$	T (K)
<i>8 October</i>					
6	0.0059	65	0.59	0.12	292.2
7	0.0025	67	0.53	0.07	292.2
8	0.0022	55	0.65	0.15	292.5
9	0.0024	59	0.50	0.06	292.4
10	0.0030	68	0.59	0.13	294.0
11	0.0050	67	0.58	0.14	296.4
14	0.0038	66	0.56	0.11	295.4
16	0.0009	68	0.55	0.10	295.3
17	0.0015	68	0.57	0.14	295.2
18	0.0028	67	0.51	0.06	295.4
Median	0.0025	67	0.56	0.11	294.0
Avg $\pm 2\sigma$	0.003 ± 0.002	65 ± 9	0.56 ± 0.08	0.11 ± 0.06	294.1 ± 3.2
<i>10 October</i>					
1	0.0051	85	0.54	0.27	286.7
2	0.0018	72	0.32	0.09	286.4
3	0.0036	72	0.39	0.14	285.8
4	0.0082	65	0.25	0.05	286.9
5	0.019	72	0.59	0.26	286.5
Median	0.0051	72	0.39	0.14	286.5
Avg $\pm 2\sigma$	0.0075 ± 0.014	73 ± 9	0.42 ± 0.28	0.16 ± 0.2	286.5 ± 0.8
<i>12 October</i>					
1	0.0060	41	0.67	0.17	295.0
3	0.0012 ^b	47	0.58	0.07	294.5
4	0.0012	62	0.72	0.31	295.1
6	0.0022 ^b	61	0.55	0.10	295.3
7	0.0010	64	0.68	0.23	295.3
8	0.0020 ^b	34	0.52	0.07	295.3
9	0.010	40	0.57	0.09	295.0
10	0.0006 ^b	48	0.49	0.09	294.4
12	0.0031	44	0.59	0.13	295.8
13	0.0053	58	0.57	0.21	295.1
15	0.0004 ^b	39	0.53	0.08	296.0
16	0.0062	39	0.59	0.11	296.0
17	0.0063	56	0.59	0.19	295.1
18	0.0013	59	0.61	0.14	294.7
19	0.0055	57	0.57	0.29	295.0
20	0.0009	39	0.58	0.10	295.8
Median	0.0020	47	0.58	0.11	295.1
Avg $\pm 2\sigma$	0.0033 ± 0.0056	49 ± 20	0.59 ± 0.12	0.15 ± 0.15	295.2 ± 1.0

^aUncertainty estimated at $\pm 45\%$ ($\pm 20\%$ from NO₃, N₂O₅ measurements, $\pm 25\%$ from aerosol surface area measurements, and $\pm 30\%$ from steady state approximation). Uncertainty estimate does not include covariance between NO₂ and VOC, which can skew slopes of steady state analysis plots and lead to larger uncertainty for individual determinations.

^bDetermined from plume modeling rather than steady state analysis (see text). Uncertainty in this approach estimated at $\pm 35\%$ ($\pm 15\%$ from the HNO₃ measurement, $\pm 25\%$ from the aerosol surface area measurements, and $\pm 20\%$ for plume age determinations).

uptake, with no correction for homogeneous reaction. Inclusion of homogeneous hydrolysis would further reduce the determined values, but, as section 6 argues, the observed N₂O₅ lifetimes are not consistent with the current parameterization for the homogeneous reaction. Some of the $\gamma(\text{N}_2\text{O}_5)$ in Table 2 are from plume modeling, rather than the steady state analysis, as described in section 4.

3.1. NO₃ Loss Rate Coefficients

[14] In addition to determining the N₂O₅ reactive uptake coefficients, the steady state analysis determines first-order loss rate coefficients for NO₃ from the intercepts of plots such as those shown in Figures 3 and 4. Comparison of the determined k_{NO_3} to that predicted from VOC measurements provides a consistency check on the determination of the

uptake coefficients. Figure 5 shows a plot of the time series of the k_{NO_3} from the steady state determinations and those from speciated VOC measurements from canister samples taken periodically on the 8 and 12 October flights. The k_{NO_3} from the VOC measurements are the sum of the products of the measured VOC concentrations and the rate coefficient for the corresponding NO₃-VOC reactions [Atkinson and Arey, 2003].

$$k_{\text{NO}_3}^{\text{Canister}} = \sum_i k_{\text{NO}_3+\text{VOC}_i} [\text{VOC}_i]. \quad (12)$$

The sum includes all VOCs measured from the canister samples for which NO₃ rate coefficient data are available,

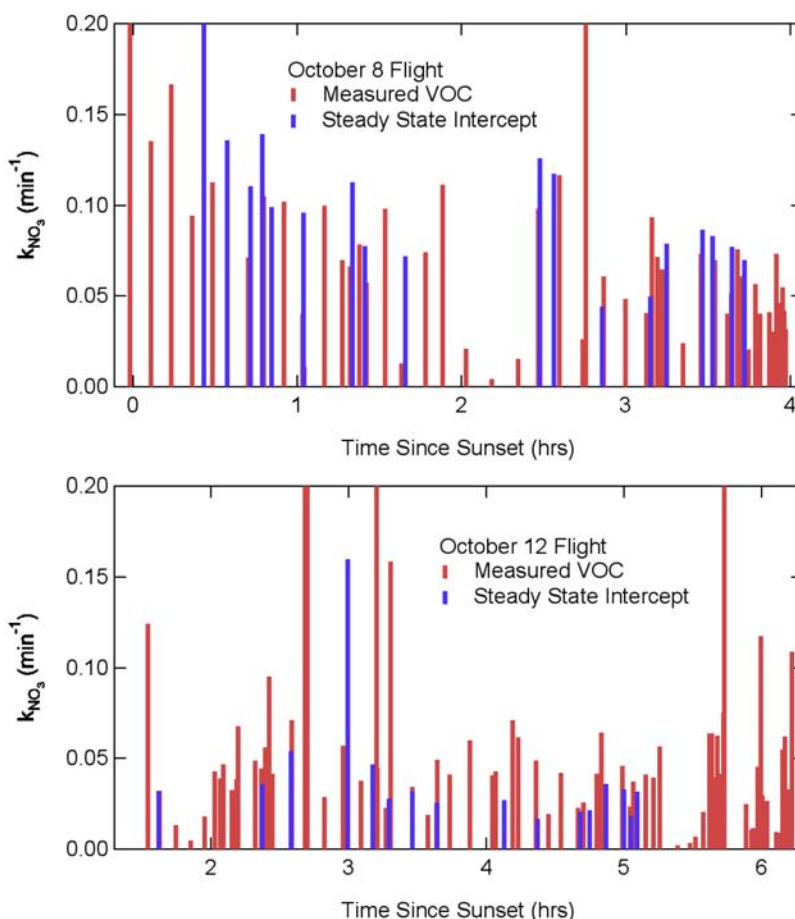


Figure 5. Loss rate coefficients for NO₃ (in inverse minutes) for the (top) 12 October and (bottom) 8 October flights. Red bars show determinations from VOC measurements according to equation (12), and blue bars show determinations from intercepts of the steady state fits in equations (9)–(11).

with the exception of furans, which were measured in some samples but would lead to NO₃ loss rates approximately 1 order of magnitude larger than those seen here. The origin of these compounds in the can samples is not clear. In general, the steady state determinations were not coincident in time with the canister samples, so a direct plume by plume comparison is not possible. However, as the overlay of the two time series shows, the steady state determinations of k_{NO_3} were similar to those derived from speciated VOC measurements. For the 8 and 12 October flights, the steady state k_{NO_3} were on average 30% larger and 40% smaller, respectively, than those from the canisters. This level of agreement, while not necessarily quantitative owing to sampling limitations, corroborates the $\gamma(\text{N}_2\text{O}_5)$ determinations by confirming the partitioning of losses between NO₃ and N₂O₅ to within the anticipated 30% uncertainty (see below) of the steady state analysis.

3.2. Validity of Steady State Approximation

[15] One of the chief uncertainties in the determination of $\gamma(\text{N}_2\text{O}_5)$ from the steady state analysis is the validity of the steady state approximation itself, which requires balance between production in reaction (1) and losses due to reactions (3) and (4). There are three conditions under which this approximation fails. The first is small values for the sink rate coefficients, k_{NO_3} and $k_{\text{N}_2\text{O}_5}$, such that a

long induction period (approximately 5 times the inverse of the first-order loss rate coefficient [Pilling and Seakins, 1995]) prevents the system from achieving a steady state [Allan et al., 2000; Carslaw et al., 1997]. The second is the time required to achieve an exact balance between the forward and reverse reactions in (2), (i.e., no slight deviation from equilibrium between NO₂, NO₃ and N₂O₅) at large ratios of N₂O₅ to NO₃ [Brown et al., 2003]. This condition delays the approach to steady state at high NO_x or low temperatures, both of which increase the ratio of N₂O₅ to NO₃. Finally, deviations from steady state may occur if the time scale for mixing is comparable to that of the chemistry itself. This effect is known to be important in nocturnal boundary layers [Stutz et al., 2004], but likely less important within the plumes analyzed here (see below).

[16] Numerical modeling using the four-reaction scheme outlined above (and as described previously [Brown et al., 2003]) provided a check on the time required to achieve steady state for each of the $\gamma(\text{N}_2\text{O}_5)$ determinations in Table 2. Figure 6 shows two examples from the 8 and 10 October flights. The solid lines are the inverse of the quantity in the center of equations (5) and (6), i.e., the ratio of the concentration of NO₃ and N₂O₅, respectively, to the NO₃ production rate. The dashed lines are the inverse of the right-hand sides of equations (5) and (6), i.e., ($k_{\text{NO}_3} +$

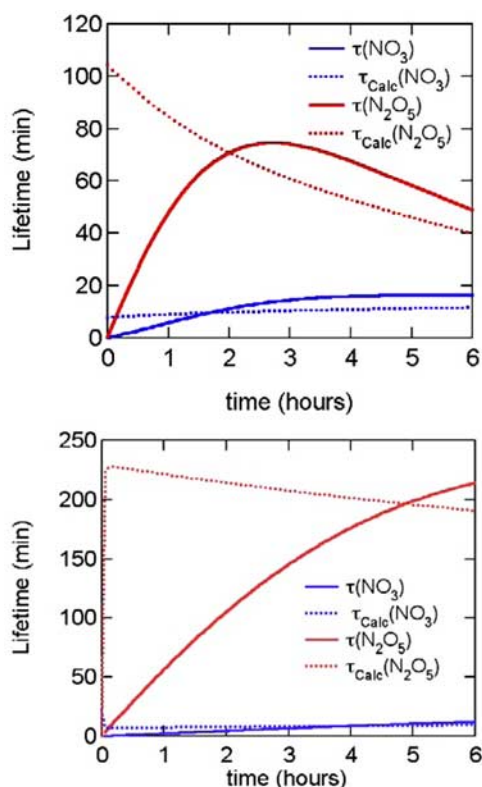


Figure 6. Calculation of approach to steady state for two of the analyzed plumes: (top) mixed urban from 8 October and (bottom) Parish power plant from 12 October. Solid lines are NO₃ and N₂O₅ lifetimes defined in equations (5)–(6), i.e., $\tau(\text{NO}_3) = [\text{NO}_3]/P(\text{NO}_3)$ and $\tau(\text{N}_2\text{O}_5) = [\text{N}_2\text{O}_5]/P(\text{NO}_3)$. Dashed lines are the sum of the first-order loss rate coefficients according to the right-hand sides of equations (5) and (6). Steady state was achieved (i.e., approximate agreement between the two curves) to within 30% after 2 h in the first example, but required at least 5 h in the second.

$K_{\text{eq}}[\text{NO}_2]k_{\text{N}_2\text{O}_5})^{-1}$ for the NO₃ plot, and $(k_{\text{N}_2\text{O}_5} + k_{\text{NO}_3}/(K_{\text{eq}}[\text{NO}_2]))^{-1}$ for the N₂O₅ plot. When the observed steady state lifetimes in the solid lines approximately match the calculated lifetimes in the dashed lines in Figure 6 (to within $\pm 30\%$), the steady state relationships in the equations are approximately valid to within the error of the measurement derived values. The error in the determined $\gamma(\text{N}_2\text{O}_5)$ due to the approximate steady states can be estimated as the difference between observed and calculated lifetimes.

[17] The calculations use observed ozone, NO₂ and temperature as inputs. The initial NO₂ at the start of the model is predicted from observed NO₂ according to $[\text{NO}_2]_0 = [\text{NO}_2]_{\text{obs}} \exp(k_1[\text{O}_3]\Delta t)$, where Δt is the time from either emission or sunset (depending on the plume) to the time of observation. For plumes with evidence for photochemistry, such as those with positive correlations between HNO₃ or PAN and O₃, the time is taken as that since sunset. For plumes with negative correlations between reactive nitrogen and ozone, the plume time can be estimated as the transport time from a known source, such as a power plant, or from the slope of a plot of O₃ versus NO₂, as detailed previously [Brown et al., 2006a]. The model also requires inputs for k_{NO_3} and $k_{\text{N}_2\text{O}_5}$, the quantities determined from the steady

state analysis. Values for k_{NO_3} are calculated from VOC data as described above in equation (12). Where such data are not available for a given plume, values or averages of several values from the nearest canister samples are used. Any missing NO₃ reactivity not captured by the canister measurements would make the estimated time to approach steady state an upper limit. Values for $k_{\text{N}_2\text{O}_5}$ are then taken from the steady state determination as a check on the model, i.e., if the determined value is large enough for the steady state analysis to be capable of determining it. For most determinations shown here for which steady state was valid, the k_{NO_3} were sufficient to bring the system to steady state even if $k_{\text{N}_2\text{O}_5}$ were zero.

[18] Figure 6 (top) is a simulation for the same plume shown in Figure 3 for the 8 October flight. The time to approach steady state was less than 2 h, longer than the estimated 4-h transport time for this plume, such that the determined $\gamma(\text{N}_2\text{O}_5)$ should be accurate to within $\sim 30\%$ on the basis of the differences between observed and calculated steady state lifetimes in Figure 6 (top). Figure 6 (bottom) is a model for an intercept of the Parish coal-fired power plant (identified by large SO₂ emission and an SO₂ to NO_x ratio consistent with emission inventory data [Frost et al., 2006]), located on the southwest side of Houston, on the 12 October flight. Transport time based on local wind speed and direction was 1.4 h while the time to approach steady state was approximately 5 h. Since steady state was likely invalid in this case, the determined $\gamma(\text{N}_2\text{O}_5)$ was an upper limit to the actual value. Simulations of many of the power plant plume intercepts from TexAQS II, which tended to have high NO_x and low VOC (and thus small k_{NO_3}), showed similarly long times for approach to steady state. However, as described below, determinations of $\gamma(\text{N}_2\text{O}_5)$ were still possible for these sources on the basis of the known transport time and the observed compositions within the plumes.

4. Determination of $\gamma(\text{N}_2\text{O}_5)$ From Plume Modeling

[19] The model described above can also be used to determine $\gamma(\text{N}_2\text{O}_5)$ for point emission sources such as power plants. These determinations do not rely on the steady state approximation but instead on the transport time from the source and the observed O₃, NO₂ and HNO₃ levels within the plumes. The model is the same as that described above, initialized by an injection of NO into an O₃ background at time zero. The model includes chemical conversion of NO to NO₂, which is rapid compared to further oxidation of NO₂ to NO₃. Dilution and mixing during transport were modeled from observations of the widths of plume intercepts at various times downwind from the point of emission. Uncertainty due to dilution primarily affects the evolution of the plume at short times, when the mixing and dilution appear to be more rapid than at later times on the basis of the observations of similar plume widths at multiple distances downwind from the same source. Rapid initial mixing may result from turbulence present upon emission of a relatively warm plume. This process is not represented in the model, which shows only the chemical titration of O₃ subsequent to an instantaneous injection of NO. The model assumes that HNO₃ produced

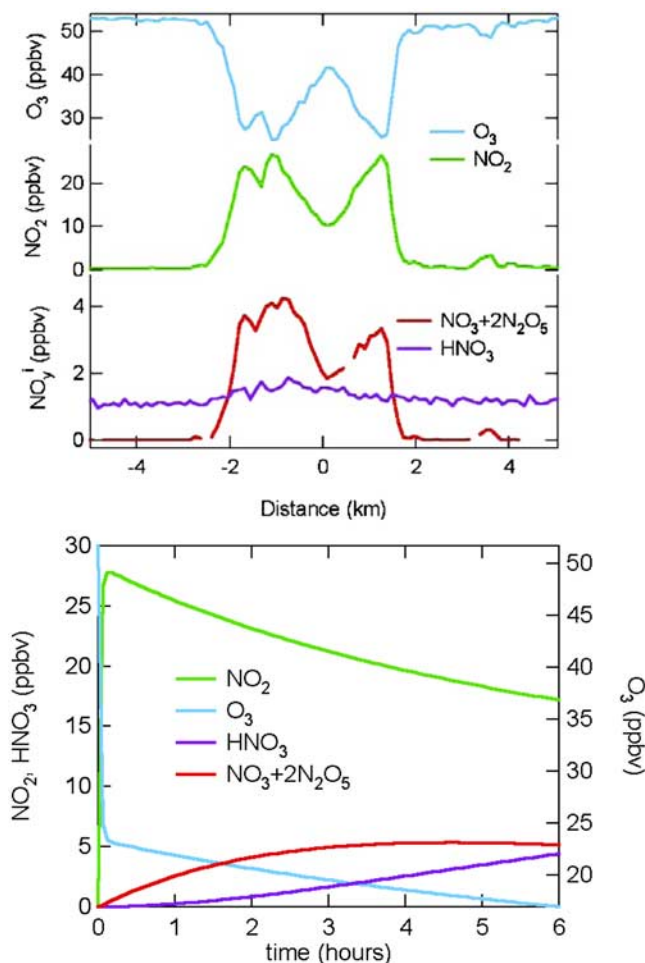


Figure 7. (top) Intercept of a plume from the Parish power plant from the 12 October 2006 flight showing mixing ratios for O₃, NO₂, HNO₃, and the nocturnal nitrogen oxide sum (NO₃ + 2N₂O₅), plotted against the distance from plume center. Buildup of HNO₃ was small relative to that of the nocturnal nitrogen oxides. (bottom) Model of the time evolution of nitrogen oxides and ozone at plume center.

from reactions (1)–(4) is conserved in the gas phase during transport and not lost to dry deposition. This assumption is consistent with nighttime plumes that have a finite depth within the residual daytime boundary layer and no contact with the surface [e.g., Brown *et al.*, 2007]. Gas phase HNO₃ was large in comparison to aerosol phase NO₃[−] (10–40× for plume analyzed here) such that the latter could be neglected for this analysis. Variation of $k_{\text{N}_2\text{O}_5}$ within the model simulations to reproduce the observed HNO₃ enhancements provided a determination for $\gamma(\text{N}_2\text{O}_5)$ from equation (8) that was independent of the steady state approximation. Figure 7 shows the time series for O₃ and reactive nitrogen (here NO₂, the sum of (NO₃ + 2N₂O₅) and HNO₃ but not PAN, which was not strongly enhanced) across a plume intercept. This power plant plume is the same for which the steady state analysis was shown to be invalid in Figure 6. Figure 7 (bottom) shows a simulation of the mixing ratios at plume center (taken here as the maximum on one side or the other of the double peaked plume). The observed HNO₃ enhance-

ment of 0.5 ppbv at a transport time of 1.4 h required $k_{\text{N}_2\text{O}_5}$ of $5 \times 10^{-5} \text{ s}^{-1}$, or $\gamma(\text{N}_2\text{O}_5) = 0.002$ at the observed aerosol surface area. The simulation slightly underestimated the observed NO₃ and N₂O₅, indicating that the determined transport time based on local wind speed and distance to the source may have been too short for this particular plume (i.e., insufficient time for buildup of these compounds).

[20] Simulation of HNO₃ enhancements within plumes was also useful in corroborating the steady state approximation in cases where it was expected to be approximately correct. The plume shown in Figure 3 from the 8 October flight is one such example. Here, a value of $\gamma(\text{N}_2\text{O}_5) = 0.0016$ within the simulation reproduced the observed HNO₃ enhancement of 1.9 ppbv within the plume, shown in Figure 8, for the transport time of 3.7 h since sunset. The $\gamma(\text{N}_2\text{O}_5)$ from the steady state determination was 70% larger, at 0.0028, but both determinations gave small $\gamma(\text{N}_2\text{O}_5)$, i.e., substantially below 0.01. The simulation also produces an overall budget for nitrogen transport and/or loss within this plume, shown as the pie chart in Figure 8. At the point of sampling, just over 30% of the NO₂ that had been oxidized during nighttime transport was present as HNO₃, just under 30% as unreacted N₂O₅, and the remainder as the products of NO₃-VOC reactions. Other plumes showed smaller HNO₃ enhancements with a greater role for transport of reactive nitrogen as N₂O₅ or loss via NO₃-VOC oxidation. Where possible, the $\gamma(\text{N}_2\text{O}_5)$ values from the

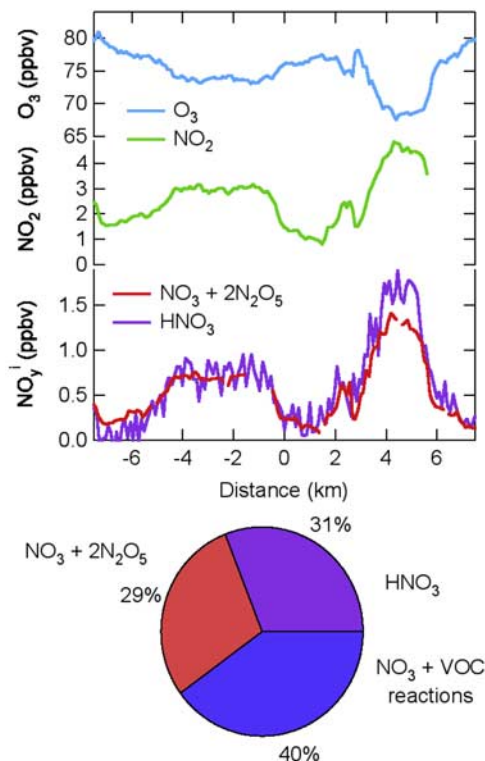


Figure 8. (top) Same as Figure 7, except for a plume intercepted on the 8 October flight. This is the same plume shown in Figure 3. The 3 ppbv background has been subtracted from the HNO₃ data. (bottom) Pie chart showing the modeled contributions of nocturnal nitrogen oxides, HNO₃, and NO₃-VOC reaction products for this plume at the time of intercept.

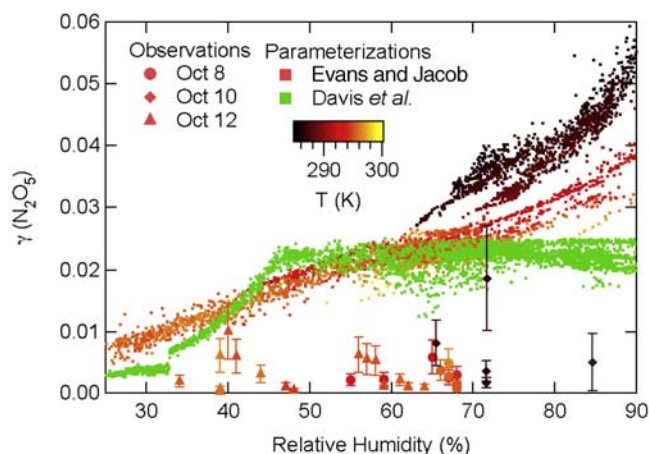


Figure 9. Determined $\gamma(\text{N}_2\text{O}_5)$ against relative humidity for three night flights, as shown in the legend. Also overlaid is the RH dependence from two recent parameterizations for all of the nighttime data from the three flights. The *Evans and Jacob* [2005] data and the observations are color coded by absolute temperature, as the legend shows.

steady state determinations were corroborated by simulations from observed HNO₃ enhancements.

5. Comparison to Model Parameterizations

[21] The values for $\gamma(\text{N}_2\text{O}_5)$ determined from these aircraft observations fall generally below 0.01 over a range of relative humidity (RH), temperature and aerosol composition. As such, they are below the range of most laboratory determinations on pure sulfate aerosols but closer to the range determined for some organic aerosol substrates and nitrate salts. They are also generally below the range of most parameterizations that have been published to date for use in atmospheric model studies. Figures 9–12 compare the $\gamma(\text{N}_2\text{O}_5)$ determined from the three flights during this study to these recent parameterizations as a function of RH, aerosol organic fraction and nitrate to sulfate ratio.

[22] Figure 9 shows the determined $\gamma(\text{N}_2\text{O}_5)$ against RH for all three flights and two model parameterizations that explicitly consider the dependence of $\gamma(\text{N}_2\text{O}_5)$ on RH. The points from the model parameterizations are for all nighttime data at the time resolution of the aerosol composition measurements from the AMS (Table 1) and show the variation of $\gamma(\text{N}_2\text{O}_5)$ with RH for all of the conditions encountered on all three flights. The determinations from individual plumes are fewer in number and more limited in the sampled conditions. The variation in the parameterizations at any given RH is due to the dependence on aerosol composition and temperature. The *Evans and Jacob* [2005] points show a distinct T dependence, as shown in the color code, while the *Davis et al.* [2008] points are not strongly T-dependent (no color code). Data for 8 and 12 October clustered between 292 and 296 K, while the more limited data for 10 October was near 286 K, as shown by the color code. *Evans and Jacob* assumed that organic aerosol have small $\gamma(\text{N}_2\text{O}_5)$ that is linearly dependent on RH below 57% and a constant, larger value of 0.03 above on the basis of a recent laboratory study [Thornton et al.,

2003] on pure organic substrates. *Evans and Jacob* [2005] also included elemental carbon, dust and sea salt, though these aspects of their parameterization were not used in this comparison. *Davis et al.* [2008] did not explicitly consider organic aerosol, instead parameterizing the RH dependence of $\gamma(\text{N}_2\text{O}_5)$ on inorganic aerosol substrates. Their parameterization considered the RH dependence from several different laboratory studies, but ultimately recommended a dependence that did not include data from *Kane et al.* [2001], since this study showed a much stronger RH dependence than the others. *Davis et al.* [2008] also explicitly considered the dependence on aerosol acidity, i.e., between ammonium sulfate ((NH₄)₂SO₄) and bisulfate (NH₄HSO₄). For the TexAQS II data, aerosol composition measurements showed a predominance of ammonium sulfate (and in some cases ammonium nitrate; see below), so the variation in Figures 9–11 does not reflect the acidity dependence of *Davis et al.* [2008].

[23] In contrast to the two parameterizations, the determined $\gamma(\text{N}_2\text{O}_5)$ show no clear dependence on RH, and are uniformly low over the studied range of 35–85%. The majority of the data from the 8 October flight cluster in a range between 60 and 70% RH, however, while those from the 12 October flight span a range from 35 to 65%. Levels of RH were higher on the 10 October flight, although there were fewer $\gamma(\text{N}_2\text{O}_5)$ determinations. There is only a single determination above 73% RH from the entire data set, such that the majority of points do not characterize the high-RH region where *Evans and Jacob* [2005] show a steep increase in $\gamma(\text{N}_2\text{O}_5)$. The range of RH represented by the determinations is consistent with that sampled during night flights within the residual daytime boundary layer. RH values within this layer are typically lower than below the nocturnal boundary layer or within the marine boundary layer at night. This effect has been demonstrated in previous vertical profiling studies in the northeast United States [Brown et al., 2007], where observed vertical profiles in RH over small altitude ranges near the surface at night were associ-

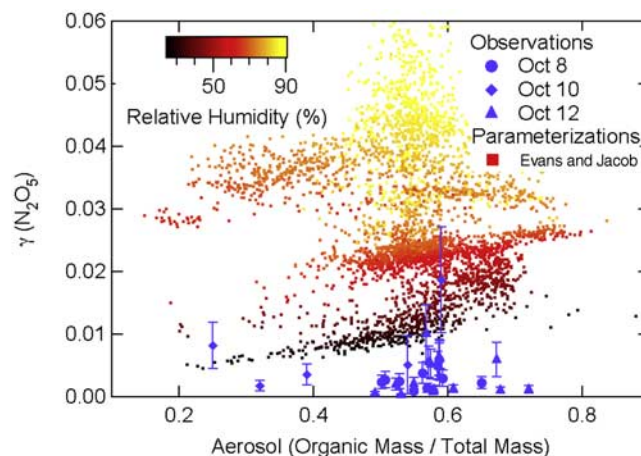


Figure 10. Determined $\gamma(\text{N}_2\text{O}_5)$ against aerosol organic fraction (from the AMS). The *Evans and Jacob* [2005] parameterization, which has an explicit dependence on organic aerosol, is overlaid and color coded by relative humidity, as shown in the legend.

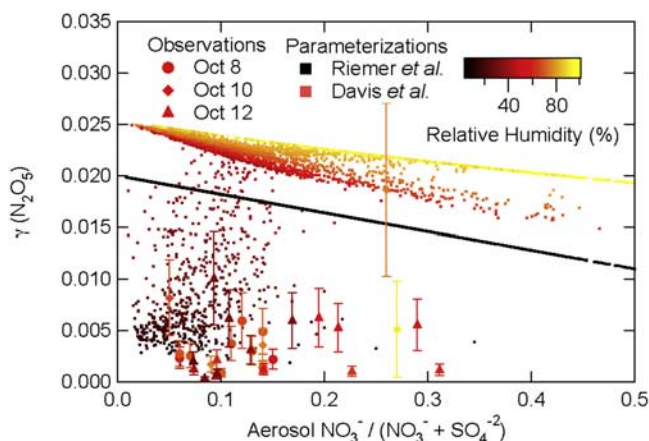


Figure 11. Determined $\gamma(\text{N}_2\text{O}_5)$ against aerosol nitrate to (nitrate + sulfate) mass ratio (from the AMS) for the three flights. Overlaid is data from the parameterizations that include a nitrate effect (see text). Points for *Davis et al.* [2008] are color coded by relative humidity.

ated with changes in particle surface area and, potentially, N₂O₅ hydrolysis rates.

[24] One potential reason for the lack of agreement between the RH dependences in the determinations and parameterizations is the presence of organic aerosol, which as noted above, is neglected in some parameterizations. Figure 10 shows the variation in determined $\gamma(\text{N}_2\text{O}_5)$ with aerosol organic fraction (defined here as the organic mass to total aerosol mass ratio from the AMS) along with that for the *Evans and Jacob* [2005] parameterization. The comparison suggests that if the smaller $\gamma(\text{N}_2\text{O}_5)$ determined from the field data are the result of organic aerosol, then the parameterization does not fully characterize the magnitude of the reduction. A variety of laboratory studies have suggested reductions in $\gamma(\text{N}_2\text{O}_5)$ due to organic aerosol similar to those seen in the field determinations [*Badger et al.*, 2006; *Cosman and Bertram*, 2008; *Cosman et al.*, 2008; *Folkers et al.*, 2003; *McNeill et al.*, 2006; *Park et al.*, 2007]. The formalism of *Anttila et al.* [2006] treats organic aerosol by regarding the organic fraction as a coating. Since it requires detailed knowledge of the aerosol mixing state, it is not compared to field data here, although the reader is referred to a recent model study (N. Riemer et al., The relative importance of organic coatings for the heterogeneous hydrolysis of N₂O₅, submitted to *Journal of Geophysical Research*, 2009). We note, however, that the AMS data for the night flights on which $\gamma(\text{N}_2\text{O}_5)$ were determined showed SOA-like aerosol (oxygenated organic fraction > 60%, with an average of approximately 80%) with size distributions consistent with internally mixed organic and inorganic aerosol, similar to the aerosol composition during daytime flights (R. Bahreini et al., Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, submitted to *Journal of Geophysical Research*, 2009).

[25] A second potential reason for the smaller observed $\gamma(\text{N}_2\text{O}_5)$ is the nitrate effect. Laboratory studies show that $\gamma(\text{N}_2\text{O}_5)$ is significantly smaller on pure nitrate salts (e.g., NaNO₃) than on other inorganic aerosol such as sulfate

[*Hallquist et al.*, 2003; *Mentel et al.*, 1999; *Wahner et al.*, 1998b] at certain RH. Mechanistically, this effect is thought to arise from the solution phase reaction of NO₃⁻ with H₂O·NO₂⁺, the reverse of the ionization of N₂O₅ that leads to its solvation. Parameterizations of this effect generally assume a linear dependence on the NO₃⁻ content of the bulk aerosol. Figure 11 shows the determined and parameterized $\gamma(\text{N}_2\text{O}_5)$ as a function of aerosol nitrate to nitrate + sulfate mass from the AMS. As in the previous comparisons, the determined values show no clear dependence on aerosol nitrate fraction in the inorganic phase. The *Davis et al.* [2008] parameterization has an upper limit that depends on this ratio, with additional variation due to the relative humidity dependence seen in Figure 9. The *Riemer et al.* [2003] parameterization was specifically intended to test the importance of the nitrate effect on formation of ozone and nitrate aerosol for conditions in Europe and incorporates only the linear dependence on nitrate fraction, with no RH or organic aerosol dependence. Although the determined $\gamma(\text{N}_2\text{O}_5)$ show no clear dependence on aerosol nitrate fraction, the nitrate effect may still be partly responsible for the observed smaller $\gamma(\text{N}_2\text{O}_5)$ if its dependence is nonlinear in NO₃⁻. As previously noted by *Davis et al.* [2008], laboratory studies on mixed nitrate and sulfate aerosol are required to supplement the existing database on pure nitrate salts in order to characterize this effect more fully.

[26] Figure 12 summarizes the data in Figures 9–11 as a direct comparison of the parameterized to the determined $\gamma(\text{N}_2\text{O}_5)$. There is no clear relationship between the two, other than that the determined values are uniformly lower than the parameterizations. The low values are consistent, and appear to be applicable to the relative humidity range (25–72%) and aerosol composition (inorganic aerosol present as fully neutralized ammonium sulfate with measurable nitrate content, and organic content between 0.2 and 0.8 of total mass) encountered on night flights during TexAQS II. Similarly small values for $\gamma(\text{N}_2\text{O}_5)$ were determined on similar aerosol types in a previous aircraft campaign in the

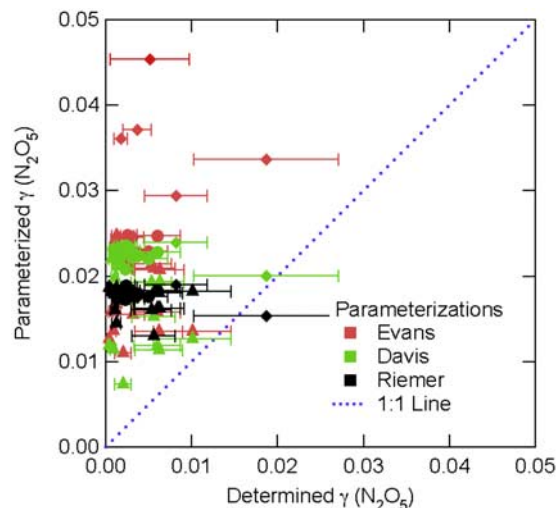


Figure 12. Direct comparison of parameterized to determined $\gamma(\text{N}_2\text{O}_5)$ to different parameterizations. The dashed line is 1:1.

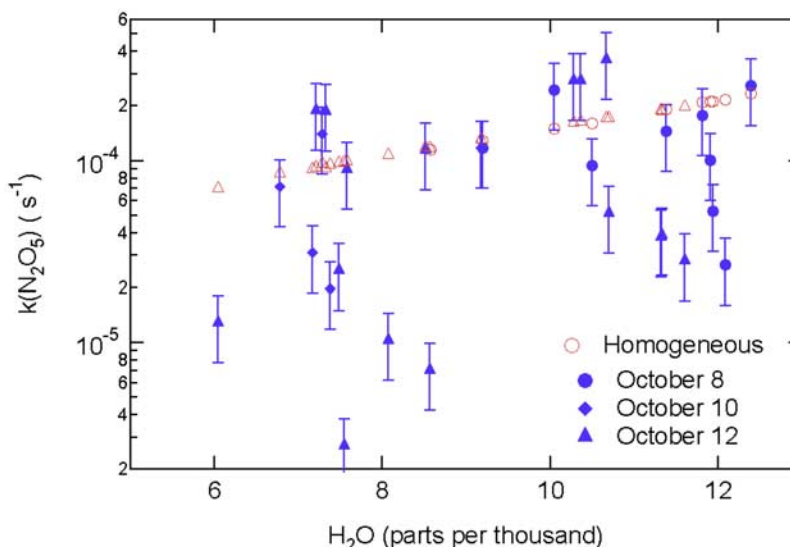


Figure 13. Plot of determined N₂O₅ first-order loss rate coefficients from fits of plume analyses to equations (5)–(7) or from plume model determinations where steady state was not applicable (see Table 2), against water vapor mixing ratio for three night flights. Also shown are predicted homogeneous hydrolysis first-order N₂O₅ rate coefficients (equation (13)) for the same time periods. Even without subtraction of heterogeneous hydrolysis, determinations are frequently smaller, and in some cases much smaller, than the homogeneous rate coefficient.

northeast United States [Brown *et al.*, 2006b]. The lack of dependence on RH or aerosol composition in the determined values may reflect the overall uncertainty in the determinations themselves, which may be too large to elucidate such effects if they occur over a range of small $\gamma(\text{N}_2\text{O}_5)$. Our previous study identified large $\gamma(\text{N}_2\text{O}_5)$ on acidic sulfate aerosol at somewhat higher RH (65–85%) [Brown *et al.*, 2006b]. This aerosol type was not prevalent on TexAQS II night flights.

6. Homogeneous N₂O₅ Hydrolysis

[27] The direct, gas phase reaction of N₂O₅ with water vapor provides an alternative route to hydrolysis that does not require uptake to aerosol. Mentel, Wahner and coworkers [Mentel *et al.*, 1996; Wahner *et al.*, 1998b] measured the first-order homogeneous hydrolysis rate coefficient in a series of chamber experiments and proposed a mechanism that was the sum of a bimolecular and a termolecular reaction with water vapor.

$$\begin{aligned} k_{\text{Homo}} &= k_{\text{I}}[\text{H}_2\text{O}] + k_{\text{II}}[\text{H}_2\text{O}]^2, \\ k_{\text{I}} &= 2.5 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \\ k_{\text{II}} &= 1.8 \times 10^{-39} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}. \end{aligned} \quad (13)$$

The rate coefficients in equation (13) place a limit on the N₂O₅ lifetime ranging from 1.2–4 h for the water vapor concentrations encountered in this study. As Figure 13 shows, the determinations from this study show N₂O₅ to frequently have been longer lived than this limit. Figure 13 shows the first-order rate coefficients for N₂O₅ loss for the three TexAQS II night flights determined directly from fits to equations (5)–(7) or from plume modeling where the steady state approximation was not applicable. Figure 13

also shows the first-order rate coefficients from equation (13) for the same data. The determined $k_{\text{N}_2\text{O}_5}$ are in many cases smaller than the homogeneous hydrolysis recommendation, and in some cases they are as much as a factor of 10 smaller. The determined rate coefficients, as plotted in Figure 13, do not account for heterogeneous hydrolysis. Subtraction of the heterogeneous uptake rate coefficient, if such a subtraction were possible with certainty, would lead to even smaller limits for the homogeneous hydrolysis loss rate coefficient. In any case, the comparison suggests a much smaller rate of homogeneous hydrolysis than equation (13) for use in atmospheric models. This conclusion is consistent with previous analysis from similar aircraft and ship-based measurements [Aldener *et al.*, 2006; Brown *et al.*, 2006b; Sommariva *et al.*, 2008].

7. Nocturnal Halogen Activation

[28] The discussion of heterogeneous N₂O₅ uptake to this point has considered HNO₃ to be the principal reaction product (reaction (4)). Recent field [Osthoff *et al.*, 2008] and laboratory [Behnke *et al.*, 1997; Finlayson-Pitts *et al.*, 1989; Thornton and Abbatt, 2005; J. M. Roberts *et al.*, Production of ClNO₂ and Cl₂ from N₂O₅ uptake on model aerosol substrates, manuscript in preparation, 2009] studies have demonstrated that uptake to chloride-containing aerosol results in production of both HNO₃ (or aerosol phase NO₃[−]) and nitryl chloride, ClNO₂, as follows.



Nitryl chloride is stable at night but photolyzes readily in the morning to yield NO₂ and atomic chlorine, such that reaction (14) is a potentially large active halogen source in regionally polluted areas. The magnitude of this source

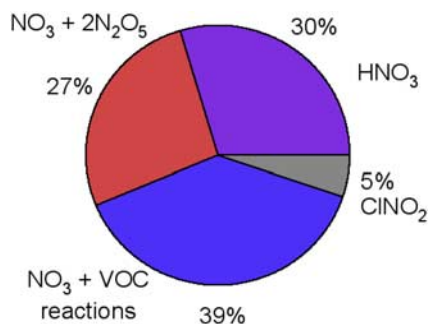


Figure 14. Pie chart showing the proportion of ClNO₂ relative to other products of nighttime NO₂ oxidation for the plume shown in Figure 8. The ClNO₂ is a calculated upper limit based on the maximum possible chloride content of the sampled aerosol.

depends upon the production rate of N₂O₅ (related to the availability of NO_x), its uptake coefficient, and the branching between reaction (14) and the conventional hydrolysis in reaction (4). Surface level measurements of ClNO₂ during TexAQS II from a ship platform (the NOAA *R/V Brown*) provided the first atmospheric detection of this compound and showed surprisingly large levels (up to 1.2 ppbv) and efficient production [Osthoff *et al.*, 2008]. Observed ClNO₂ levels required production from N₂O₅ uptake to submicron aerosol, where the median chloride concentration was [Cl⁻] = 0.05 M.

[29] Aircraft measurements of ClNO₂ were not available during TexAQS II. Aerosol chloride measurements were also limited. The AMS measured nonrefractory aerosol chloride, but there were only brief episodes during which the Cl⁻ was present above the AMS detection limit of 0.05 μg m⁻³, none coinciding with nocturnal NO_x plumes. The AMS limit for aerosol chloride mass and the measured aerosol volume provides an upper limit to aerosol chloride concentration if all chloride were nonrefractory (i.e., not present as sodium chloride). The corresponding upper limit to the ClNO₂ yield, defined as the amount of ClNO₂ produced per N₂O₅ taken up, can be calculated from available laboratory data [Behnke *et al.*, 1997; Roberts *et al.*, manuscript in preparation, 2009].

$$\Phi(\text{ClNO}_2) = \frac{\text{ClNO}_2}{\Delta\text{N}_2\text{O}_5} = \left(\frac{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}{k_{\text{Cl}}[\text{Cl}^-]} + 1 \right)^{-1}. \quad (15)$$

The rate coefficients, $k_{\text{H}_2\text{O}}$ and k_{Cl} in equation (15) are for solution phase reaction of NO₂⁺ with H₂O and Cl⁻, respectively. Behnke *et al.* [1997] and Roberts *et al.* (manuscript in preparation, 2009) give the ratio $k_{\text{Cl}}/k_{\text{H}_2\text{O}} = 836$ and 450, respectively. Upper limits for nonrefractory aerosol chloride concentration on night flights were [Cl⁻] ≤ 0.05 M – 1 M, corresponding to upper limits of $\Phi(\text{ClNO}_2) \leq 0.3$ –0.9. These limits could be larger if sodium chloride were present in the submicron aerosol. Therefore, ClNO₂ production could have been a substantial component of N₂O₅ uptake on TexAQS II night flights. The foregoing discussion has shown that although heterogeneous uptake of N₂O₅ was generally slow, it was nonzero and lead to measurable HNO₃ production, particularly for plumes with

high aerosol surface areas. The 8 October plume shown in Figure 3 can again be used as one example since nighttime HNO₃ production in this plume was among the largest observed. The limit to $\Phi(\text{ClNO}_2)$ in this plume was 0.3. Competition between reactions (4) and (14) leads to production of ClNO₂ and HNO₃ in a well-defined ratio.

$$\frac{\text{ClNO}_2}{\text{HNO}_3} = \frac{\Phi(\text{ClNO}_2)}{2 - \Phi(\text{ClNO}_2)}. \quad (16)$$

The observed HNO₃ enhancement of 1.9 ppbv in this plume corresponds to an upper limit for ClNO₂ production of ≤0.33 ppbv. Figure 14 shows the partitioning among NO₂ oxidation products for this plume for estimated limiting ClNO₂ production. If these nighttime plumes were to produce ClNO₂ levels comparable to these calculated limits, it would represent a significant halogen input from overnight heterogeneous chemistry. Further aircraft measurements that include both ClNO₂ and higher sensitivity aerosol chloride measurements will clearly be of considerable future interest.

8. Summary and Conclusions

[30] Values for heterogeneous uptake coefficients of N₂O₅ to aerosol, $\gamma(\text{N}_2\text{O}_5)$, have been determined from aircraft measurements of O₃, NO₂, NO₃, N₂O₅, and aerosol surface area. Analysis of the NO₂ scaling of the steady state lifetimes of NO₃ and N₂O₅ allowed for separation of NO₃-VOC reactions from N₂O₅ uptake to aerosol. Modeling of observed HNO₃ enhancements within plumes with well-defined nighttime transport times corroborated the steady state analysis. Determined $\gamma(\text{N}_2\text{O}_5)$ were low, generally smaller than 0.01 over a range of relative humidity and aerosol composition, with no clear dependence on either parameter. Aerosol sampled in Texas was primarily neutralized ammonium sulfate with a large organic fraction (>50% of total mass). By contrast, our previous aircraft measurements in the northeast United States showed a large regional variability in the distribution of sulfate aerosol and a larger variation in $\gamma(\text{N}_2\text{O}_5)$. The TexAQS II analysis further demonstrated that the current recommended rate coefficient for homogeneous N₂O₅ hydrolysis is likely too large, possibly by as much as an order of magnitude. Aerosol chloride was below the AMS detection limit and ClNO₂ was not measured from the aircraft during TexAQS II. Upper limits for ClNO₂ production based on maximum possible aerosol chloride content nevertheless allow for potentially significant nocturnal halogen activation.

[31] The determined $\gamma(\text{N}_2\text{O}_5)$ were significantly smaller than values calculated from several parameterizations used in atmospheric models. Further detailed laboratory work to define the uptake coefficients of N₂O₅ to mixed organic, sulfate, nitrate and chloride aerosol, and their relative humidity and temperature dependence, are needed for improvement of the parameterizations. Laboratory work to reexamine the rate coefficient for homogeneous reaction of N₂O₅ with water vapor may also be of interest for comparison with these field data. Further field measurements of N₂O₅ reactivity, including aircraft measurements of different reaction products such as HNO₃ and ClNO₂, will also be of considerable future interest.

[32] **Acknowledgments.** This work was supported by the NOAA Atmospheric Chemistry and Climate Program and the Texas Air Quality Study. The authors thank Prakash Bhavre for useful discussions regarding uptake coefficient parameterizations. The authors also thank the crew of the NOAA P-3 for their dedication and professionalism.

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