

Chapter 14

Chemistry of HO_x radicals in the upper troposphere

Lyatt Jaeglé, Daniel J. Jacob

Harvard University, Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, 29 Oxford St., Cambridge, MA 02138, USA
E-mail: jaegle@atmos.washington.edu

William H. Brune

Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA

Paul O. Wennberg

Division of Geological and Planetary Sciences, 1200 E. California Blvd., California Institute of Technology, Pasadena, CA 91125, USA

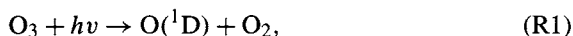
Abstract

Aircraft observations from three recent missions (STRAT, SUCCESS, SONEX) are synthesized into a theoretical analysis of the factors controlling the concentrations of HO_x radicals (HO_x = OH + peroxy) and the larger reservoir family HO_y (HO_y = HO_x + 2H₂O₂ + 2CH₃OOH + HNO₂ + HNO₄) in the upper troposphere. Photochemical model calculations capture 66% of the variance of observed HO_x concentrations. Two master variables are found to determine the variance of the 24 h average HO_x concentrations: the primary HO_x production rate, $P(\text{HO}_x)$, and the concentration of nitrogen oxide radicals (NO_x = NO + NO₂). We use these two variables as a coordinate system to diagnose the photochemistry of the upper troposphere and map the different chemical regimes. Primary HO_x production is dominated by the O(¹D) + H₂O reaction when [H₂O] > 100 ppmv, and by photolysis of acetone (and possibly other convected HO_x precursors) under drier conditions. For the principally northern midlatitude conditions sampled by the aircraft missions, the HO_x yield from acetone photolysis ranges from 2 to 3. Methane oxidation amplifies the primary HO_x source by factors of 1.1–1.9. Chemical cycling within the HO_x family has a chain length of 2.5–7, while cycling between the HO_x family and its HO_y reservoirs has a chain length of 1.6–2.2. The number of ozone molecules produced per HO_y molecule consumed ranges from 4 to 12, such that ozone production rates vary between 0.3 and 5 ppbv d^{−1} in the upper troposphere. Three chemical regimes (NO_x-limited, transition, NO_x-saturated) are identified to describe the

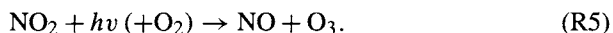
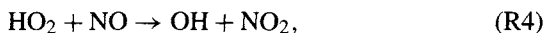
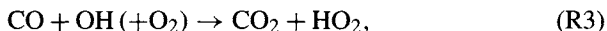
dependence of HO_x concentrations and ozone production rates on the two master variables $P(\text{HO}_x)$ and $[\text{NO}_x]$. Simplified analytical expressions are derived to express these dependences as power laws for each regime. By applying an eigen-lifetime analysis to the $\text{HO}_x\text{--NO}_x\text{--O}_3$ chemical system, we find that the decay of a perturbation to HO_y in the upper troposphere (as from deep convection) is represented by four dominant modes with the longest time scale being factors of 2–3 times longer than the steady-state lifetime of HO_y .

1. Introduction

The first measurements of HO_x radicals ($\text{HO}_x = \text{OH} + \text{peroxy}$) in the upper troposphere were obtained over the last five years in four aircraft missions: ASHOE/MAESA (Airborne Southern Hemisphere Ozone Experiment/Measurements of Atmospheric Effects of Supersonic Aircraft), STRAT (Stratospheric Tracers for Atmospheric Transport), SUCCESS (Subsonic Aircraft: Contrail and Cloud Effects Special Study), and SONEX (Subsonic Assessment: Ozone and Nitrogen Oxide Experiment) (Folkens et al., 1997; Wennberg et al., 1998; Brune et al., 1998, 1999). These measurements revealed HO_x levels frequently 2–4 times higher than expected from the commonly assumed primary source (Levy, 1971):



Such elevated concentrations of HO_x imply a more photochemically active upper troposphere than previously thought, with enhanced rates of ozone formation through reactions (R3)–(R5), and thus a potentially more important role in ozone greenhouse forcing from anthropogenic emissions of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) (Roelofs et al., 1997; Berntsen et al., 1997; Haywood et al., 1998; Mickley et al., 1999):



Another implication is faster oxidation of SO_2 by OH, producing $\text{H}_2\text{SO}_4(\text{g})$ which promotes the formation of new aerosol particles in the upper troposphere (Clarke, 1993; Raes, 1995; Arnold et al., 1997).

Convective injection to the upper troposphere of HO_x precursors other than H_2O , including acetone (Singh et al., 1995; Arnold et al., 1997), peroxides

(Chatfield and Crutzen, 1984; Prather and Jacob, 1997; Jaeglé et al., 1997; Cohan et al., 1999) and aldehydes (Müller and Brasseur, 1999), may provide the missing primary sources of HO_x in the upper troposphere. Inclusion of these sources in photochemical models improves the simulation of observed HO_x levels (McKeen et al., 1997; Folkins et al., 1997; Jaeglé et al., 1997, 2000; Wennberg et al., 1998; Brune et al., 1998).

Fig. 1 schematically illustrates the chemistry of HO_x radicals in the upper troposphere as described in current models. Because of the cycling taking place between HO_x radicals and their non-radical reservoirs, we define the larger HO_y family as $\text{HO}_y = \text{HO}_x + 2\text{H}_2\text{O}_2 + 2\text{CH}_3\text{OOH} + \text{HNO}_2 + \text{HNO}_4$. We do not include HNO₃ in the HO_y family because its lifetime (a few weeks) is much longer than that of peroxides (a few days), and under most conditions in the upper troposphere its photolysis is a small source of HO_x. Four factors control the HO_x and HO_y concentrations: the primary HO_x sources, the amplification of these primary sources through methane oxidation (Logan et al., 1981), the chemical cycling between HO_x and its reservoirs, and the sinks of HO_y. *Primary* sources in the upper troposphere are sources which are independent of local HO_x concentrations, such as (R2) and photolysis of short-lived HO_x precursors transported from the lower troposphere by convection. *Secondary* sources depend on the presence of a preexisting pool of HO_x. They include photolysis of locally produced peroxides and of CH₂O produced from methane oxidation by OH.

In this paper we synthesize the knowledge gained from the aircraft observations into a theoretical analysis of HO_x chemistry in the upper troposphere. We use the concentration of NO_x and the primary HO_x production rate, $P(\text{HO}_x)$, as master variables to map out the chemical regimes, generalizing from our previous work which showed that HO_x concentrations and ozone production in the upper troposphere can be largely described on the basis of these two variables alone (Jaeglé et al., 1998a, 1999, 2000). We show how [NO_x] and $P(\text{HO}_x)$ provide a unified framework to interpret HO_x observations not only for individual aircraft missions, but across missions spanning several seasons and locations. We examine the following questions: (1) What is the relative importance of different HO_x precursors as primary HO_x sources? (2) To what extent does methane oxidation provide an autocatalytic source of HO_x? (3) What is the role of cycling within the HO_x and HO_y families? (4) What are the chemical regimes for HO_x and ozone production? (5) What are the time scales for the relaxation of HO_y following episodic perturbations from convection?

Our analysis focuses on daytime conditions outside of clouds. The chemistry of HO_x at night and close to sunrise and sunset is still poorly understood (Brune et al., 1999; Wennberg et al., 1999; Jaeglé et al., 1999). Cirrus clouds appear to provide an efficient sink of HO_x (Faloona et al., 1998; Jaeglé et al., 2000), but their overall importance is limited because of the small volume they

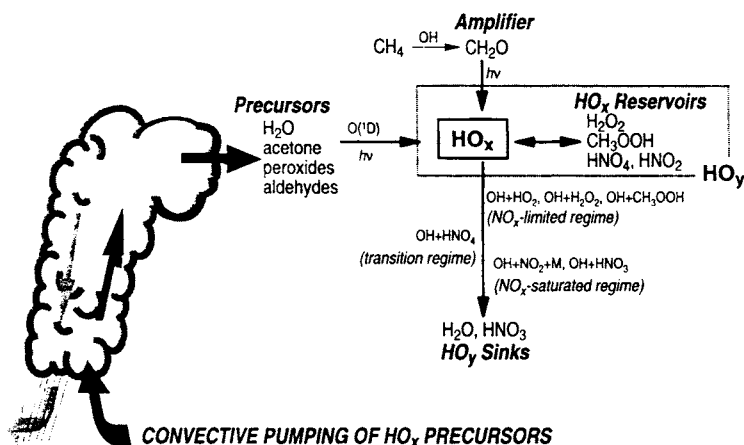


Figure 1. Schematic of the chemistry of HO_x radicals ($= \text{OH} + \text{peroxy radicals}$) and the HO_y reservoir family ($= \text{HO}_x + 2 \text{H}_2\text{O}_2 + 2 \text{CH}_3\text{OOH} + \text{HNO}_2 + \text{HNO}_4$) in the upper troposphere. The schematic illustrates the factors controlling HO_x concentrations: primary sources of HO_x , amplification of the HO_x primary source by CH_4 oxidation, cycling between HO_x and HO_y , and loss of HO_y . Depending on the levels of NO_x , three distinct chemical regimes exist for HO_y loss: the NO_x -limited regime (dominant loss pathways through $\text{OH} + \text{HO}_2$, $\text{OH} + \text{H}_2\text{O}_2$, and $\text{OH} + \text{CH}_3\text{OOH}$), a transition regime ($\text{OH} + \text{HNO}_4$) and the NO_x -saturated regime ($\text{OH} + \text{NO}_2 + \text{M}$, $\text{OH} + \text{HNO}_3$). These regimes in turn determine the dependence of HO_x concentrations and ozone production on NO_x concentrations. For a detailed discussion of the factors controlling NO_x radicals, see the review by Bradshaw et al. (2000).

occupy in the upper troposphere and the short lifetime of HO_x . It has been proposed that halogen radicals might play a role in the photochemistry of the upper troposphere (Borrmann et al., 1996; Crawford et al., 1996; Solomon et al., 1997), but there is no observational evidence for such a role.

Faloona et al. (2000) report that models systematically underestimate the concentrations of HO_x observed under very high NO_x conditions ($[\text{NO}_x] > 300$ pptv). They suggest that this could reflect flaws in our understanding of the chemistry coupling HO_x and NO_x radicals. Very high concentrations of NO_x in the observations can usually be linked to lightning or convection (Thompson et al., 1999; Liu et al., 1999). Another possible explanation for the model underestimates of HO_x under such circumstances is the presence of unmeasured HO_x precursors transported by convection or produced by lightning (Müller and Brasseur, 1999; Zuo and Deng, 1999; Jaeglé et al., 2000), combined with the increased efficiency of these precursors at producing HO_x under high NO_x conditions (Folkins and Chatfield, 2000). It remains unclear whether the results presented in Faloona et al. (2000) imply major flaws in our understanding of chemistry in the high- NO_x regime or simply an insufficient accounting

of primary HO_x sources under these unusual conditions (Brune et al., 1999). Given this remaining uncertainty, we assume the latter here and use standard tropospheric chemistry.

Section 2 begins by a presentation of the aircraft data sets providing the basis for our analysis and by an assessment of the ability of current photochemical models to simulate observed HO_x concentrations. In Section 3 we discuss the factors controlling the chemistry of HO_x and HO_y in the upper troposphere. The chemical regimes defining the dependence of HO_x concentrations and ozone production on NO_x and the primary HO_x source are analyzed in Section 4. In Section 5, the relaxation of HO_y following episodic perturbations by convection is examined with an eigenlifetime analysis (Prather, 1994, 1996). Conclusions are in Section 6.

2. Observations and models

2.1. Aircraft data sets

Extensive measurements of OH and HO₂ concentrations by laser-induced fluorescence (Stevens et al., 1994; Wennberg et al., 1995) were made in the upper troposphere (between 8 km and the local tropopause) during STRAT, SUCCESS, and SONEX. Measurements of OH and HO₂ concentrations were also obtained in the lower stratosphere during these missions, especially during STRAT where altitudes up to 21 km were sampled by the ER-2 aircraft, but few observations were made in the lower troposphere. Tropospheric HO_x measurements during ASHOE/MAESA were restricted to two profiles (Folkins et al., 1997) and we do not consider them in our analysis.

The observations extend from 15°N to 65°N latitude and cover different seasons. Median values (as well as 20th and 80th percentiles) observed between 8 km and the local tropopause are summarized in Table 1. In addition to HO_x, many other chemical species and meteorological parameters were measured. Observations at night and near the terminator (SZA > 80°), in stratospheric air ([O₃] > 100 ppbv with [CH₄] < 1760 ppbv), inside clouds, and in fresh aircraft exhaust plumes were excluded from Table 1.

STRAT took place over the North Pacific between California and Hawaii during 1995–1996 (Wennberg et al., 1998). The aircraft sampled the upper troposphere up to 17 km in tropical air, for a total of ten flights in three seasonal deployments (October–November 1995, January–February 1996, and August 1996). Frequent influence of deep marine convection transporting clean surface air to the upper troposphere can be seen in the observed 20th percentiles in Table 1 (27 ppbv O₃, 63 ppbv CO, and 24 pptv NO_x) (Jaeglé et al., 1997).

SUCCESS took place over the central United States from April 15 to May 15 1996 (Toon and Miake-Lye, 1998). While OH measurements were available

Table 1. Median observations in the upper troposphere (8 km altitude to tropopause)^a

Observations	Aircraft mission			Overall medians used in standard model calculation
	STRAT	SUCCESS	SONEX	
Time period	1995–1996 ^b	15 Apr.–15 May 1996	13 Oct.–12 Nov. 1997	March 1
Number of observations ^c	560	468	1741	2769
Latitude, °N	22 (21–38)	37 (36–40)	47 (39–54)	41
Pressure, hPa	198 (163–240)	240 (209–302)	290 (242–331)	263
Temperature, K	217 (209–224)	219 (213–231)	229 (222–235)	225
Ozone column, DU	288 (257–317)	333 (329–339)	283 (251–301)	292
H ₂ O, ppmv	38 (9–72)	80 (37–204)	148 (74–294)	114
Relative humidity (ice), %	40 (17–66)	82 (48–104)	69 (35–105)	
OH, pptv	0.23 (0.11–0.39)	0.28 (0.17–0.51)	0.092 (0.051–0.15)	
HO ₂ , pptv	3.6 (2.5–5.3)	10.3 (6.3–13.4)	2.5 (1.6–3.5)	
⟨OH⟩ _{24h} ^d , pptv	0.12 (0.095–0.15)	0.13 (0.072–0.26)	0.036 (0.022–0.054)	
⟨OH⟩ _{24h} ^d , pptv	1.6 (0.93–3.7)	5.2 (4.1–6.9)	0.95 (0.63–1.5)	
H ₂ O ₂ , pptv	N/A	N/A	78 (49–147)	
CH ₃ OOH, pptv	N/A	N/A	25 (< 25–66)	
CH ₂ O, pptv	N/A	N/A	< 50 (< 50–74)	
NO, pptv	84 (20–158)	42 (19–89)	56 (20–137)	59
NO _x ^e , pptv	99 (24–179)	54 (27–118)	87 (38–202)	84
HNO ₄ ^c , pptv	21 (11–33)	31 (19–53)	56 (37–81)	
HNO ₃ , pptv	N/A	N/A	106 (59–191)	
PAN, pptv	N/A	N/A	60 (39–87)	
NO _y , pptv	217 (90–484)	317 (212–461)	307 (200–598)	
O ₃ , ppbv	48 (27–75)	64 (50–80)	53 (38–66)	54
CH ₄ , ppbv	1768 (1763–1774)	1774 (1766–1786)	1771 (1764–1780)	1772
CO, ppbv	72 (63–83)	105 (95–131)	86 (75–99)	87
Ethane, pptv	444 (384–677)	N/A	677 (590–810)	620
Propane, pptv	31 (24–95)	N/A	84 (55–144)	71
C _{4–5} alkanes, pptv	9 (5–21)	N/A	26 (12–63)	22

Table 1. (Continued)

Observations	Aircraft mission			Overall medians used in standard model calculation
	STRAT	SUCCESS	SONEX	
Acetone, pptv	N/A	N/A	515 (427–607)	
Aerosol surface area, $\mu\text{m}^2 \text{cm}^{-3}$	1.8 (0.7–2.8)	2.8 (0.56–13)	6.1 (3.6–12)	4.7
$J(\text{NO}_2)^f$, 10^{-3}s^{-1}	4.6 (4.0–5.7)	6.4 (5.8–8.0)	2.9 (2.4–3.6)	
$J(\text{O}_3 \rightarrow \text{O}(^1\text{D}))^f$, 10^{-6}s^{-1}	11 (5.9–23)	16 (14–20)	3.0 (2.1–6.1)	
$P(\text{HO}_x)^g$, pptv d ⁻¹	65 (48–103)	212 (147–328)	54 (34–105)	83
HO _x yield from acetone + $h\nu^h$	2.9 (2.1–3.0)	2.5 (1.9–2.9)	2.8 (2.4–3.0)	
HO _x yield from CH ₄ + OH ⁱ	0.52 (0.36–0.55)	0.41 (0.24–0.53)	0.47 (0.37–0.51)	
Amplification factor $A_{\text{CH}_4}^j$	1.4 (1.3–1.9)	1.2 (1.1–1.5)	1.4 (1.2–1.7)	
HO _x chain length ^k	5.5 (2.8–7)	3.6 (2.5–5.2)	5.0 (3.7–6.3)	
HO _y chain length ^l	1.7 (1.6–2.2)	1.8 (1.6–2.1)	1.8 (1.7–2.1)	
HO _x lifetime, min	37 (19–50)	25 (13–33)	36 (20–51)	
HO _y lifetime, d	1.9 (1.2–3.0)	2.3 (1.1–3.4)	4.6 (2.7–8.1)	
$P(\text{O}_3)^m$, ppbv d ⁻¹	0.85 (0.6–1.1)	2.3 (0.97–5)	0.54 (0.35–0.8)	

Table 1. (Continued)

^aThe values are medians. The 20th and 80th percentiles are listed in parentheses. Observations below the limit of detection are included in the statistics. Observations in the lower stratosphere ($[O_3] > 100$ ppbv, $[CH_4] < 1760$ ppbv), in clouds, in fresh aircraft exhaust, and outside daytime ($SZA > 80^\circ$) are excluded.

^bUpper tropospheric flights during the STRAT mission took place on three deployments: October–November 1995, January–February 1996, and August 1996.

^cNumber of 1 min HO_2 observations in the upper troposphere.

^d24 h average concentrations of OH and HO_2 are obtained by scaling observed HO_x with a model derived diel factor (Appendix A).

^eModel calculated values for NO_x ($NO_x = \text{observed NO} + \text{modeled } NO_2$) and HNO_4 .

^fPhotolysis frequencies calculated from observed actinic fluxes and then averaged over 24 h using a model scaling factor.

^gThe primary HO_x production rate, $P(HO_x)$, is a 24 h average value calculated using observed H_2O and acetone concentrations. During STRAT and SUCCESS acetone was not measured, we use instead a correlation between acetone and CO derived from previous aircraft missions (McKeen et al., 1997). The HO_x yield from acetone photolysis is calculated for the observed conditions and ranges from 2 to 3 (see entry below and Section 3.1).

^hNet number of HO_x molecules produced in the complete oxidation of acetone to CO, including contributions from acetone photolysis and from CH_2O photolysis (Section 3.1).

ⁱNet number of HO_x molecules produced in the oxidation of methane to CO (Section 3.2).

^jThe amplification factor for methane oxidation A_{CH_4} is defined as the relative increase in the primary source of HO_x due to oxidation of CH_4 by OH (Eq. (4)).

^kRatio of HO_2 to HO_x loss rates, measuring the efficacy of cycling within the HO_x family (Eq. (5) in Section 3.3).

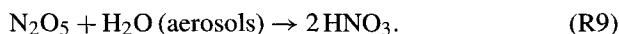
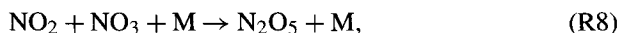
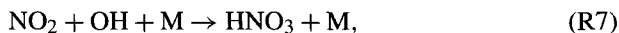
^lRatio of HO_x to HO_y loss rates, measuring the efficacy of cycling between HO_x and its HO_y reservoirs (Eq. (6) in Section 3.3).

^mThe ozone production rate, $P(O_3)$, is calculated using observed NO and HO_2 concentrations and averaged over 24 h using a model-derived diel factor (Appendix A).

throughout the mission, HO₂ was only measured for the flights in May. The composition of the upper troposphere was strongly impacted by convective injection of continental air from the United States as indicated by measurements of high concentrations of CO and NO_y (Table 1) (Jaeglé et al., 1998b), and of aerosols rich in crustal material (Talbot et al., 1998) and sulfate (Dibb et al., 1998).

SONEX focused on the North Atlantic region between 13 October and 12 November 1997 (Singh et al., 1999). It included measurements of acetone, peroxides, and CH₂O, which were missing in STRAT and SUCCESS. The atmosphere sampled by SONEX was influenced by an ensemble of NO_x sources: lightning, convection and aircraft emissions (Liu et al., 1999; Thompson et al., 1999; Koike et al., 2000). Photochemistry was less active than in STRAT or SUCCESS because of higher latitudes and the fall season.

The composition of the upper troposphere has several features that distinguish it from the rest of the troposphere. Levels of H₂O are low (10–300 ppmv) because of the cold temperatures (210–235 K), and result in a primary source of HO_x radicals from O(¹D) + H₂O which is 1–2 orders of magnitude smaller than in the lower troposphere. Other primary sources of HO_x such as convective injection of acetone, peroxides and aldehydes from the lower troposphere can play an important role in the upper troposphere. Concentrations of NO_x are relatively high in the upper troposphere (typically 50–100 pptv, Table 1), due to high-altitude sources (lightning, convective transport of surface pollution, transport from the stratosphere, aircraft emissions) combined with a long lifetime against oxidation to HNO₃. The lifetime of NO_x is proportional to the NO_x/NO₂ ratio as NO₂ is the reactant species for the conversion to HNO₃:



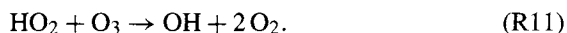
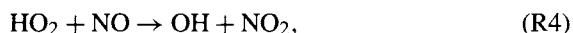
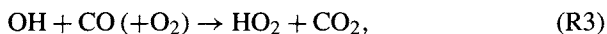
The partitioning of NO_x in the daytime upper troposphere favors NO relative to NO₂ ([NO]/[NO_x] ≈ 0.6–0.9, Table 1) because of the temperature dependence of reaction (R6) and the low O₃ concentrations. The lifetime of NO_x in the upper troposphere is 5–10 d compared to ~1 d in the lower troposphere (Jacob et al., 1996; Jaeglé et al., 1998b).

The last column in Table 1 summarizes median upper tropospheric conditions across all three missions. These median conditions will be used as constraints for our standard model calculations presented in Sections 2.2, 3, 4 and 5.

2.2. Comparison between models and observations

Fig. 2 and Table 2 show summary comparisons between observations and model calculations of HO₂, OH, and the HO₂/OH ratio for STRAT, SUCCESS, and SONEX. Each point is a 1 min average. The calculations were done with the Harvard photochemical zero-dimensional (0-D) model (see Appendix A) constrained with local observations of NO, O₃, H₂O, acetone, CO, CH₄, C₂H₆, C₃H₈, C_{4–5} alkanes, aerosol surface area, pressure, temperature, and actinic flux. Concentrations of acetone in STRAT and SUCCESS are estimated on the basis of correlations with CO (McKeen et al., 1997); since acetone varies only over a narrow range this assumption is of little consequence. Peroxides and aldehydes are assumed to be in chemical steady state. We restrict the comparison to daytime, upper tropospheric observations (> 8 km altitude) in clear air and outside of aircraft exhaust plumes, following the criteria of Table 1. Comparisons for individual missions have been discussed previously (Brune et al., 1998, 1999; Faloona et al., 2000; Jaeglé et al., 1997, 1998a, 2000; McKeen et al., 1997; Wennberg et al., 1998).

As seen in Fig. 2c, the HO₂/OH concentration ratio is generally reproduced by model calculations to well within the combined uncertainties of observations (reported accuracy of ±20%) and rate coefficients (+120 to −70%, Wennberg et al. (1998)). The median model-to-observed ratio for HO₂/OH is 1.08 with a correlation coefficient $r^2 = 0.76$ (Table 2). The cycling between OH and HO₂ in the model takes place on a time scale of a few seconds and is mainly controlled by



In the upper troposphere, loss of OH through reaction with CO (R3) largely dominates over its reactions with O₃ (R10), methane, and non-methane hydrocarbons. Assuming pseudo-steady state for OH and HO₂, and neglecting (R10), we have the concentration ratio:

$$\frac{[\text{HO}_2]}{[\text{OH}]} \approx \frac{k_3 [\text{CO}]}{k_4 [\text{NO}] + k_{11} [\text{O}_3]}, \quad (1)$$

where k_i represents the rate constant for reaction (R_i). Eq. (1) is generally accurate to within 25%. Reaction (R11) dominates over (R4) only for very low NO concentrations ([NO_x] < 10–20 pptv). Under most conditions in the upper

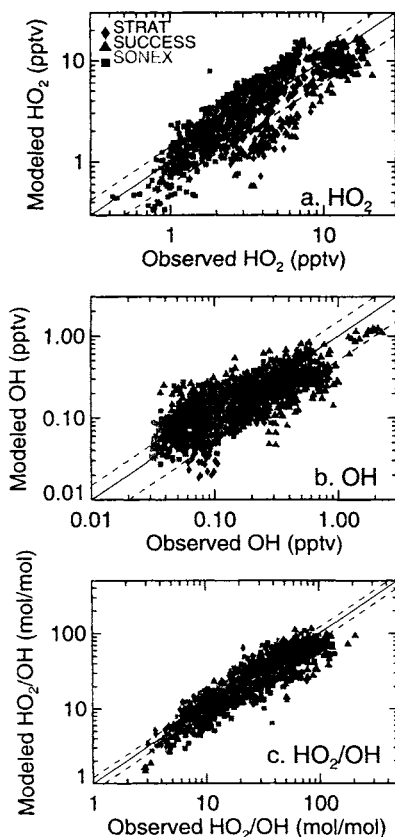


Figure 2. Comparison between observations and model calculations for (a) HO_2 concentrations, (b) OH concentrations, and (c) the HO_2/OH concentration ratio in the upper troposphere (8 km altitude to the local tropopause). One-minute averages corresponding to STRAT, SUCCESS, and SONEX are shown respectively by diamonds, triangles, and squares. Observations inside cirrus clouds, influenced by stratospheric air, in fresh aircraft exhaust, or at high solar zenith angle (SZA) ($\text{SZA} > 80^\circ$) are excluded from this figure. The calculations were obtained with a diel steady-state photochemical model constrained with local observations of HO_x precursors (see Appendix A). The 1 : 1 line is shown as solid. The dashed lines represent the instrumental accuracies ($\pm 40\%$ for OH and HO_2 , $\pm 20\%$ for HO_2/OH).

troposphere, $k_4[\text{NO}]$ is the dominant term of the denominator. The observed $[\text{HO}_2]/[\text{OH}]$ ratio varies between ~ 5 and 100 (Fig. 2); changes in $[\text{NO}]$ and $[\text{CO}]$ account respectively for 60 and 15% of this variability. As shown in Table 1, $[\text{NO}]$ varies over almost one order of magnitude in the upper troposphere while $[\text{CO}]$ varies by only a factor of 2. When the sources or sinks of HO_x com-

Table 2. Comparison between observed and model-calculated HO_x concentrations in the upper troposphere (> 8 km altitude) during STRAT, SUCCESS, and SONEX^a

Variable		STRAT	SUCCESS	SONEX	All
HO ₂	<i>R</i>	0.97	0.70	1.20	1.09
	<i>r</i> ²	0.53	0.61	0.84	0.66
	<i>N</i>	330	232	1163	1725
OH	<i>R</i>	0.80	0.78	1.20	0.98
	<i>r</i> ²	0.84	0.60	0.64	0.63
	<i>N</i>	357	635	1081	2073
HO ₂ /OH	<i>R</i>	1.15	0.78	0.96	1.08
	<i>r</i> ²	0.87	0.61	0.76	0.76
	<i>N</i>	313	229	1072	1614

^a *R* is the median model-to-observed ratio, *r*² is the correlation coefficient between the model and observations, and *N* is the number of points for which the comparison is conducted.

pete with HO_x cycling reactions (for example, for [NO_x] < 10 pptv and large HO_x precursor concentrations, see Section 3.3) Eq. (1) no longer applies.

The median ratios of model-to-observed concentrations ($R_{\text{HO}_x} = [\text{HO}_x]_{\text{model}} / [\text{HO}_x]_{\text{obs}}$) are 0.98 for OH and 1.09 for HO₂ (Table 2). In addition to uncertainties in model calculations, the accuracy of observations ($\pm 40\%$) needs to be considered in evaluating R_{HO_2} and R_{OH} . We find that 75% of the HO₂ points and 60% of the OH points fall within the reported instrumental accuracies. The measurement precision is better for HO₂ than for OH because of higher mixing ratios, which likely explains the smaller scatter between model and observations. In some cases (10 and 14% of HO₂ and OH observations, respectively), the calculations underestimate the observations by factors of 1.6–4. Many of these cases have been identified as fresh convective outflows where high levels of peroxides and aldehydes might have provided additional sources of HO_x (Brune et al., 1998; Jaeglé et al., 1997, 1998a; Wennberg et al., 1998). As discussed in the Introduction, missing HO_x precursors could explain the systematic model underestimates apparent at very high NO_x. For the remaining observations (15% for HO₂, and 26% for OH), the model overestimates the concentrations of HO_x by factors of 1.4–2. Such model overestimates were observed mostly during SONEX and could be due in part to the influence of evaporating cirrus clouds (Jaeglé et al., 2000).

The model accounts for 66% of the observed variance in HO₂ concentrations (Table 2), meaning that most of this variance can be explained on the basis of current understanding. The concentration of HO_x depends strongly on

SZA (Ehhalt and Rohrer, 2000 and references therein). Once this dependence is taken into account by examining diurnal averages, we find that the variance in the model is mostly driven by changes in [NO_x] and in the HO_x primary production rate, $P(\text{HO}_x)$. As we will demonstrate in Section 4, the dependence of [HO_x] on [NO_x] and $P(\text{HO}_x)$ is non-linear and can be approximated by power laws of the form $[\text{HO}_x] \propto [\text{NO}_x]^a P(\text{HO}_x)^b$. For each point shown in Fig. 2, we calculate 24 h averages of the observed [HO₂] and $P(\text{HO}_x)$ following the methodology discussed in the Appendix A. $P(\text{HO}_x)$ includes the contributions from (R2) and acetone photolysis (see Section 3.1). We find that a linear regression with $\ln([\text{NO}_x])$ and $\ln(P(\text{HO}_x))$ accounts for 57% of the variance of the observed $\ln([\text{HO}_2]_{24\text{h}})$ concentrations in Fig. 2. Individual regressions with $\ln([\text{NO}_x])$ and $\ln(P(\text{HO}_x))$ account for 30 and 38% of the variance, respectively.

Fig. 3 shows the ensembles of NO_x concentrations (= observed NO + modeled NO₂) and 24 h average $P(\text{HO}_x)$ for all three missions. The top panel of Fig. 3 shows the $P(\text{HO}_x)$ calculated from (R2) and acetone only, while the bottom panel also includes a hypothesized source from convection of additional HO_x precursors as needed to match the HO₂ concentrations (about 10% of observations are affected). Both [NO_x] and $P(\text{HO}_x)$ vary across two orders of magnitude. As can be seen in Table 1 and Fig. 3, $P(\text{HO}_x)$ during SUCCESS was three times higher than during STRAT or SONEX. This reflects the low amounts of UV radiation during SONEX (fall, northern midlatitudes) and the low levels of water vapor at the higher altitudes sampled in the tropical upper troposphere during STRAT. The NO_x concentrations in STRAT, SUCCESS, and SONEX varied over fairly similar ranges (Table 1 and Fig. 3).

Fig. 4 plots observed values of HO₂, OH and the HO₂/OH concentration ratio, scaled to 24 h averages, in the coordinate system {[NO_x], $P(\text{HO}_x)$ }. Values of $P(\text{HO}_x)$ include the hypothesized contribution from convected precursors (bottom panel of Fig. 3). As noted above, we use 24 h averages to remove the obvious influence of the diurnal cycle of solar radiation. Photochemical model calculations for varying [NO_x] and $P(\text{HO}_x)$, and otherwise median conditions (last column in Table 1), are shown as contour lines. In these calculations, $P(\text{HO}_x)$ is varied by specifying a generic HO_x source with a solar zenith angle dependence assumed to be the same as photolysis of CH₃OOH (see Appendix A for further details). Model [OH] increases with [NO_x] up to ~100–500 pptv NO_x due to shift in the [HO₂]/[OH] ratio towards OH (Eq. (1)), and decreases with further increases of NO_x concentrations due to HO_y loss by reactions involving NO₂, HNO₄, and HNO₃ (Fig. 1). Model [HO₂] decreases with increasing [NO_x] due to shift in the [HO₂]/[OH] ratio towards OH and thus faster HO_y loss, since HO_y is lost by reactions involving OH (Fig. 1). The [HO₂]/[OH] ratio has a strong dependence on [NO_x] and little dependence on

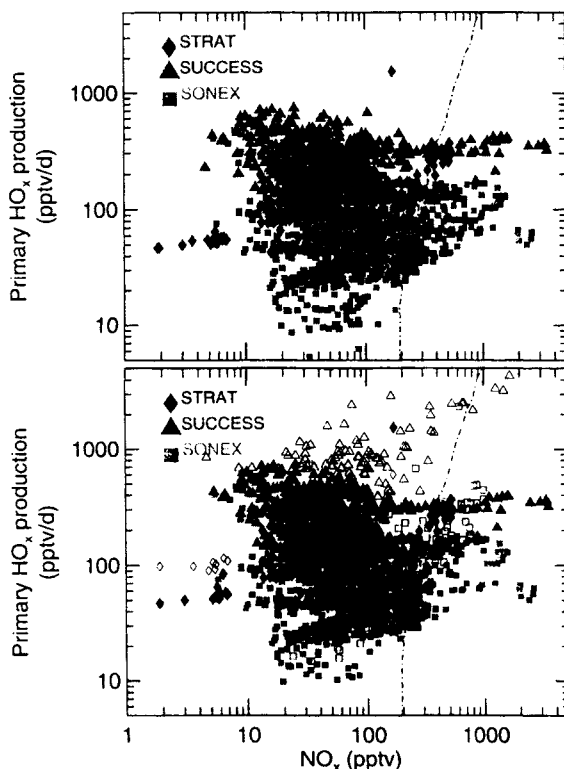


Figure 3. Ranges of $[\text{NO}_x]$ and the primary HO_x production rate $P(\text{HO}_x)$ in the upper troposphere during STRAT (diamonds), SUCCESS (triangles), and SONEX (squares). Values of $P(\text{HO}_x)$ are 24 h averages. In the top panel, $P(\text{HO}_x)$ is calculated using observed concentrations of H_2O and acetone only. In the bottom panel, an additional source from convective injection of other HO_x precursors is also added where necessary to match observed HO_2 concentrations (see Appendix A). The cases where this additional source represents more than 50% of $P(\text{HO}_x)$ are flagged by open symbols. The threshold NO_x value for the transition from the NO_x -limited regime to the NO_x -saturated regime for ozone production ($\partial P(\text{O}_3)/\partial [\text{NO}_x] = 0$) is indicated as a function of $P(\text{HO}_x)$ for otherwise median conditions in the upper troposphere (see Table 1 and Section 4).

$P(\text{HO}_x)$ as expected from Eq. (1). These model dependences are also found in the observations, as can be seen from inspection of Fig. 4.

The rate of ozone production can be expressed as

$$P(\text{O}_3) \approx k_4[\text{NO}][\text{HO}_2], \quad (2)$$

where we neglect the contributions of organic peroxy radical which account for less than 15% of $P(\text{O}_3)$ in the upper troposphere (Jacob et al., 1996; Crawford

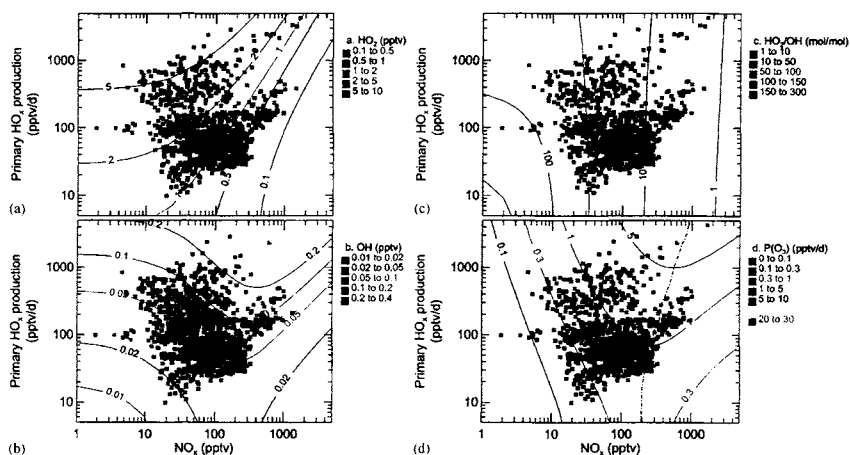


Figure 4. Dependence of (a) HO_2 concentrations, (b) OH concentrations, (c) the HO_2/OH concentration ratio, and (d) the ozone production rate $P(\text{O}_3)$ on the concentrations of NO_x and $P(\text{HO}_x)$ in the upper troposphere for STRAT, SUCCESS, and SONEX. The contour lines correspond to model calculations for median conditions in the upper troposphere (Table 1) with varying $[\text{NO}_x]$ and $P(\text{HO}_x)$. Observations are shown with color-coded squares corresponding to concentration ranges. Both model and observations for OH and HO_2 are 24 h averages (see Appendix A). Values of $P(\text{O}_3)$ are computed from observed NO and HO_2 and averaged over 24 h (see Appendix A). The dashed line in panel (d) corresponds to $\partial P(\text{O}_3)/\partial [\text{NO}_x] = 0$.

et al., 1997). Chemical loss of O_3 (reactions (R10), (R11), (R7) and (R2)) generally accounts for less than 20% of $P(\text{O}_3)$ in the upper troposphere so that Eq. (2) effectively represents the ozone tendency (Davis et al., 1996; Folkens and Chatfield, 2000). We use Eq. (2) to calculate instantaneous values of $P(\text{O}_3)$ from observed $[\text{NO}]$ and $[\text{HO}_2]$, and then average $P(\text{O}_3)$ over 24 h using a model-derived scaling factor (see Appendix A). For most observations in Fig. 4d, $P(\text{O}_3)$ increases with increasing $[\text{NO}_x]$, representing the NO_x -limited regime. However, a significant fraction of observations during SONEX lie in the transition regime where $P(\text{O}_3)$ is independent of $[\text{NO}_x]$ (Section 4.2). By sampling $P(\text{O}_3)$ at constant $P(\text{HO}_x)$ in SONEX, Jaeglé et al. (1999) observed the transition from NO_x -limited to NO_x -saturated regime in a manner consistent with model calculations. Very few observations are in the NO_x -saturated regime where $P(\text{O}_3)$ decreases with increasing $[\text{NO}_x]$.

Fig. 4 demonstrates that the two master variables $\{[\text{NO}_x], P(\text{HO}_x)\}$ can describe the overall behavior of observed HO_x and ozone production rates across different seasons and regions. In the model calculations of Fig. 4 (contour lines) we vary only $[\text{NO}_x]$ and $P(\text{HO}_x)$ while fixing all other variables to their median observed values. Where does this analysis fail in describing the observations? Some discrepancies can be noted in Fig. 4. For $P(\text{HO}_x) < 20 \text{ pptv d}^{-1}$

the model overestimates the concentrations of both OH and HO₂. These observations were obtained at high latitudes during SONEX (> 50°N), where recycling of HO_x radicals by photolysis of peroxides is much slower than for the median conditions of Table 1. They are found to be well simulated by a model constrained with the appropriate local radiative environment.

3. Chemistry of HO_x and HO_y

In this section we examine in a broader context the different chemical processes that affect HO_x and the reservoir HO_y family in the upper troposphere.

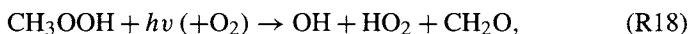
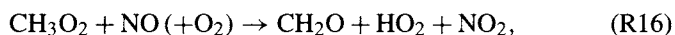
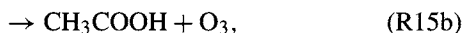
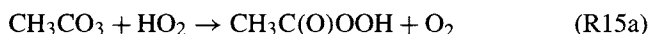
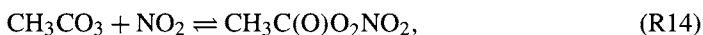
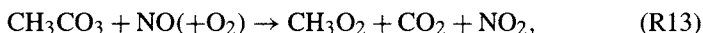
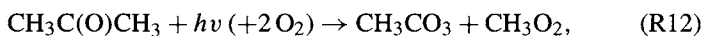
3.1. Primary sources of HO_x

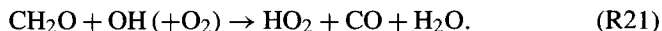
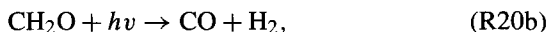
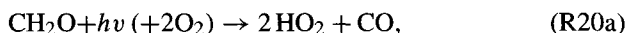
As discussed above, the primary sources of HO_x in the upper troposphere are the photooxidation of water vapor (R2), the photolysis of acetone, and the photolysis of other HO_x precursors such as peroxides and aldehydes transported to the upper troposphere by convection. The primary HO_x production rate can be expressed as:

$$P(\text{HO}_x) = 2k_2[\text{O}(^1\text{D})][\text{H}_2\text{O}] + \sum_i y_i J_i [X_i]. \quad (3)$$

The sum on the right-hand side is over all HO_x primary precursors X_i with photolysis frequency J_i and corresponding HO_x yield y_i .

An abbreviated version of the acetone oxidation chain following initial photolysis is given in (R12)–(R21). The HO_x yield from photolysis of acetone includes contributions from the initial photolysis step (R12), and the subsequent photolysis of CH₂O by (R20a):





In addition to photolysis, acetone can be lost through reaction with OH. In the upper troposphere, this pathway represents on average less than 10% of acetone loss. It becomes important at lower altitudes, as OH concentrations increase, the temperature-dependent rate constant for $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3$ increases, and the acetone photolysis quantum yield decreases (Gierczak et al., 1998).

We derive the HO_x yield from acetone photolysis (y_{acetone}) using fractional reaction rates, in a manner similar to Arnold et al. (1997) and Folkins and Chatfield (2000). The yield increases with increasing [NO_x] and decreasing $P(\text{HO}_x)$ (Folkins and Chatfield, 2000) (Fig. 5), and lies generally between 2 and 3. The theoretical maximum is 3.3. For very low [NO_x] (< 10 pptv) and high $P(\text{HO}_x)$ (> 200 pptv d⁻¹), y_{acetone} can be negative: the dominant loss pathways for CH₃CO₃ and CH₃O₂ are then (R15) and (R17) followed by (R19) which lead to net loss of HO_x. The median yields for the conditions of the aircraft missions ranged from 2.5 (SUCCESS) to 2.9 (STRAT). While concentrations of acetone are fairly uniform in the upper troposphere with a typical range from 300 to 1000 pptv (Singh et al., 1995; Wohlfrom et al., 1999), the levels of water vapor show much more variability. A linear regression of 24 h average $P(\text{HO}_x)$ with [H₂O], [CH₃C(O)CH₃], latitude, ozone column, yields r^2 correlation coefficients of 0.71, 0.03, 0.25, and 0.004, respectively. The importance of acetone relative to water vapor as a primary source of HO_x thus largely depends on the abundance of H₂O. Fig. 6 shows the relative contributions of H₂O and acetone to $P(\text{HO}_x)$ for the ensemble of observations in SONEX. Acetone becomes a significant HO_x source when H₂O drops below 200 ppmv, and becomes dominant when H₂O drops below 100 ppmv. For air masses in the lowermost stratosphere ([O₃] > 100 ppbv, and [CH₄] < 1760 ppbv), (R2) dominates again due to increasing ozone levels and decreasing acetone levels. During SONEX, acetone photolysis and H₂O + O(¹D) were on average of comparable magnitude as sources of HO_x. A more dominant role for acetone was inferred for SUCCESS and especially for STRAT due to lower H₂O concentrations (Brune et al., 1998; McKeen et al., 1997; Jaeglé et al., 1997) (Table 1).

The contribution to $P(\text{HO}_x)$ from convective transport of peroxides and aldehydes from the boundary layer was examined by Müller and Brasseur (1999) using a 3-D global model. They find a contribution of more than 60%

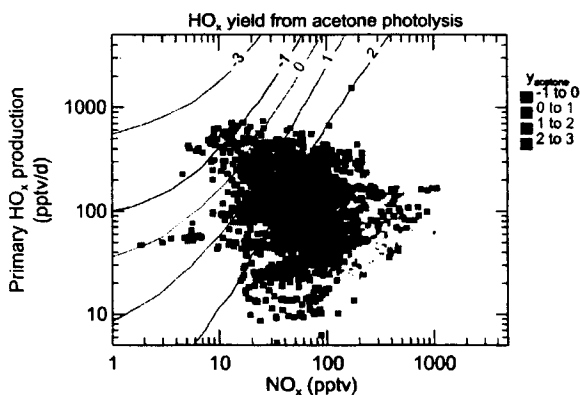


Figure 5. 24 h average HO_x yields from acetone photolysis in the upper troposphere. Contour lines show results for the median conditions in Table 1 with varying $[\text{NO}_x]$ and $P(\text{HO}_x)$. The colored symbols represent the values calculated for individual points during STRAT, SUCCESS, and SONEX.

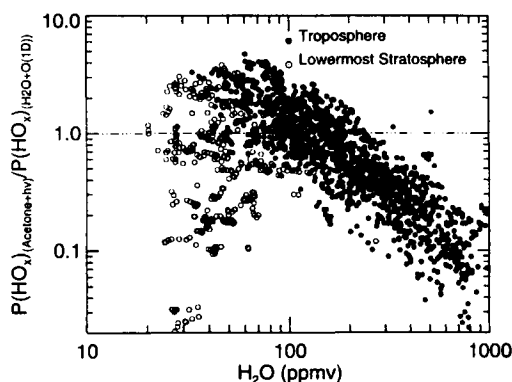


Figure 6. Ratio of the contributions from acetone and water vapor to 24 h average $P(\text{HO}_x)$, as a function of H_2O concentrations for the SONEX mission between 8 and 12 km altitude. Observations in the lowermost stratosphere ($[\text{O}_3] > 100$ ppbv and $[\text{CH}_4] < 1760$ ppbv) are shown by open circles. The HO_x yield from acetone photolysis varies mainly between 2 and 3 (Section 3.1). The HO_x yield from H_2O photooxidation is 2.

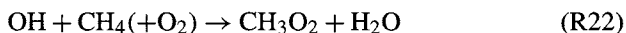
in the tropics at 10–14 km altitude, in agreement with the study of Prather and Jacob (1997), with peroxides dominating over oceans and aldehydes over continents. In their model, this source increases HO_x concentrations in the upper troposphere by 10–20% on average.

Enhancements of HO_x concentrations by factors of 2–5 were observed in convective outflows during STRAT and SUCCESS (Brune et al., 1998; Jaeglé

et al., 1997, 1998a). The additional source of HO_x necessary to account for these observations is 2–10 times higher than the local sources from H₂O and acetone. During SONEX, less than 15% of upper tropospheric observations appeared to have been recently affected by convection (Jaeglé et al., 2000). The lower altitudes and warmer temperatures during SONEX (10 K warmer compared to STRAT and SONEX, see Table 1) resulted in larger amounts of water vapor in convective outflows. A 10 K increase in temperature from 220 to 230 K results in ice saturation water vapor concentrations increasing from 90 to 300 ppmv. The high levels of H₂O in convective outflows reduced the influence of other transported HO_x precursors during SONEX.

3.2. Autocatalytic production through methane oxidation

The atmospheric lifetime of CH₄ is about 10 yr, with oxidation by OH providing the main sink. Because of its long lifetime, CH₄ has a uniform concentration of 1.7–1.8 ppmv in the upper troposphere (Table 1). The mechanism for oxidation of CH₄ to CO is initiated by



followed by reactions (R16)–(R21). Methane oxidation by OH may either be a source of HO_x (through (R20a)) or a sink of HO_x (through (R15) and (R19)) (Logan et al., 1981). We view the source of HO_x from CH₄ as secondary rather than primary because it depends on the local supply of OH. Because of its autocatalytic character, it represents an amplifying factor for the primary HO_x sources. Similar to the case of acetone photolysis, the overall HO_x yield (y_{CH_4}) from oxidation of methane increases with increasing [NO_x] and decreasing $P(\text{HO}_x)$ (Fig. 7a). The theoretical maximum of y_{CH_4} (0.62) is determined by the pressure- and temperature-dependent quantum yield of (R20a). Under most conditions observed in the upper troposphere, y_{CH_4} varies between 0.3 and 0.5.

Formaldehyde is the key intermediate species for HO_x production from methane oxidation. Model concentrations of CH₂O, from methane oxidation only, are shown by contour lines in Fig. 7b as a function of [NO_x] and $P(\text{HO}_x)$ for the median upper tropospheric conditions of Table 1. The model dependence of CH₂O on both parameters is similar to that of OH (Fig. 4b) as the source of CH₂O is proportional to OH (through (R22)). Reaction of CH₂O with OH (R21) represents typically 30–50% of the CH₂O sink, buffering the dependence of CH₂O on OH. The calculated concentration of CH₂O varies between 10 and 100 pptv. Observations of CH₂O, available from SONEX, are reported as the square symbols in Fig. 7b. A large fraction of the observations (55%) are below the limit of detection (LOD) of the instrument (50 pptv), consistent with model results. However, the remaining 45% of observations reach

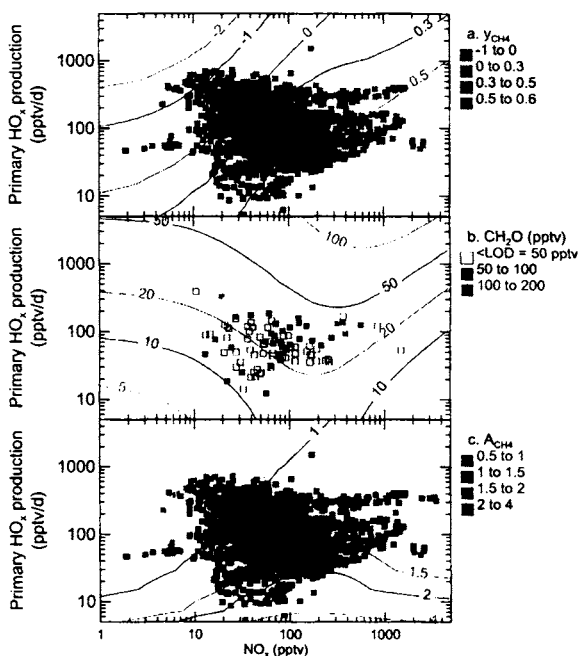


Figure 7. Same as Fig. 5, but the contour lines are for model calculated (a) HO_x yield from methane oxidation; (b) concentrations of CH_2O due to methane oxidation only; (c) amplification factor associated with methane oxidation (see text for definition). Observations of CH_2O obtained during SONEX are shown by the square symbols in panel b. Open symbols correspond to observations below the 50 pptv LOD of the instrument.

up to 300 pptv and do not exhibit any clear dependence on $[\text{NO}_x]$ or $P(\text{HO}_x)$. Sources of CH_2O from organic species other than CH_4 (including in particular acetone and methanol) are calculated to be only 30% of the source from CH_4 oxidation during SONEX and cannot resolve the discrepancy between model and observations in Fig. 7b. Convective transport from the lower troposphere is not a satisfactory explanation either, as high CH_2O is not correlated with tracers of convection. The only correlation of high CH_2O in the observations is with methanol (Jaeglé et al., 2000), suggesting a possible source from reaction of methanol on aerosols (Singh et al., 2000). In the case of SONEX, using the observed CH_2O concentrations instead of steady-state model values leads to an increase in the calculated HO_x by 30% (Jaeglé et al., 2000).

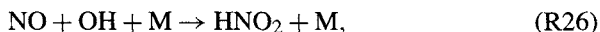
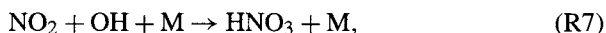
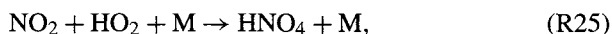
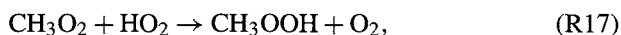
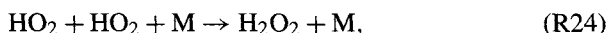
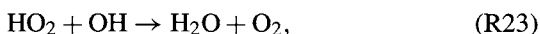
We define the amplification factor of $P(\text{HO}_x)$ associated with methane oxidation as

$$A_{\text{CH}_4} = \frac{P(\text{HO}_x) + y_{\text{CH}_4} k_{22} [\text{OH}] [\text{CH}_4]}{P(\text{HO}_x)}. \quad (4)$$

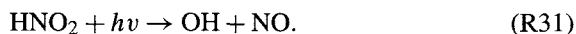
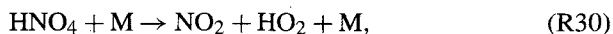
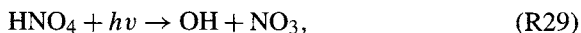
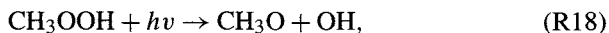
Values of A_{CH_4} smaller than unity ($y_{\text{CH}_4} < 0$) correspond to quenching of $P(\text{HO}_x)$, while values of A_{CH_4} larger than unity ($y_{\text{CH}_4} > 0$) correspond to amplification of $P(\text{HO}_x)$. A_{CH_4} is shown in Fig. 7c as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$. The amplification is largest when $P(\text{HO}_x)$ is low. The dependence of A_{CH_4} on $P(\text{HO}_x)$ acts as a weak buffer for HO_x concentrations (Crawford et al., 1999): as $P(\text{HO}_x)$ decreases, A_{CH_4} increases. For median SONEX conditions a doubling of $P(\text{HO}_x)$ at constant $[\text{NO}_x]$ increases the actual HO_x source $A_{\text{CH}_4} P(\text{HO}_x)$ by $\sim 70\%$. Similarly, for constant $P(\text{HO}_x)$ and increasing $[\text{NO}_x]$ up to 500 pptv, the increase in A_{CH_4} weakly offsets the effect of increasing HO_x loss.

3.3. Loss of HO_x and recycling from HO_y reservoirs

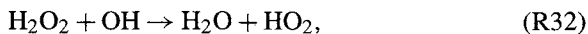
Loss of HO_x occurs through self-reactions and reactions with NO_y species:

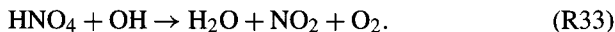
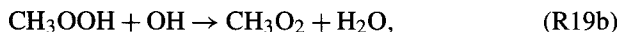
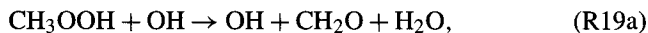


The resulting lifetime of HO_x in the upper troposphere is typically 30 min (Table 1). The HO_x reservoirs H₂O₂, CH₃OOH, HNO₂ and HNO₄ regenerate HO_x through photolysis and (in the case of HNO₄) thermal decomposition:



However, reaction of these reservoir species with OH represents a permanent sink of HO_x:





Typical upper tropospheric lifetimes of H_2O_2 , CH_3OOH , HNO_4 and HNO_2 are 2–5 d, 1–4 d, 1–4 d, and 10–30 min, respectively. The lifetime of HNO_2 with respect to photolysis is short and it is thus not an important player in HO_x chemistry except as a nighttime reservoir, and for very high NO_x concentrations. In addition, nighttime heterogeneous production of HNO_2 on aerosols might be an important source of HO_x at sunrise (Jaeglé et al., 2000).

The cycling within HO_x and between HO_x and its HO_y reservoirs play critical roles in controlling the concentration of HO_x . To illustrate their effect, we define two chain lengths. The HO_x chain length, $n(\text{HO}_x)$, is the average number of times that a HO_2 radical cycles within the HO_x family before being lost, while the HO_y chain length, $n(\text{HO}_y)$, is the average number of times that a HO_x radical cycles within the HO_y reservoirs before being lost through one of the HO_y sinks:

$$n(\text{HO}_x) = \frac{\text{Loss}(\text{HO}_2)}{\text{Loss}(\text{HO}_x)} \quad (5)$$

$$n(\text{HO}_y) = \frac{\text{Loss}(\text{HO}_x)}{\text{Loss}(\text{HO}_y)} \quad (6)$$

where $\text{Loss}(\text{HO}_2)$, $\text{Loss}(\text{HO}_x)$, and $\text{Loss}(\text{HO}_y)$ represent the ensemble of reaction rates leading to the loss of HO_2 (these reactions include (R4), (R11), (R17), (R24) and (R25)), HO_x ((R7), (R17), (R23) and (R27)) and HO_y ((R23), (R27), (R32), (R19) and (R33)), respectively. Fig. 8 shows the model-calculated dependences of HO_x and HO_y chain lengths on $[\text{NO}_x]$ and $P(\text{HO}_x)$. For $[\text{NO}_x] < 100$ pptv, $n(\text{HO}_x)$ increases with increasing $[\text{NO}_x]$ due to cycling of HO_x via $\text{HO}_2 + \text{NO}$ (R4), while at higher NO_x concentrations $n(\text{HO}_x)$ decreases because of loss of HO_x to HNO_3 and HNO_4 ((R7), (R25) and (R27)). At low $[\text{NO}_x]$, $n(\text{HO}_x)$ decreases with increasing $P(\text{HO}_x)$ because the HO_x sinks are quadratic in $[\text{HO}_x]$. The highest values of $n(\text{HO}_x)$, exceeding 6, are for low $P(\text{HO}_x)$ and intermediate NO_x (50–200 pptv). For the conditions of the aircraft missions, $n(\text{HO}_x)$ ranges from 2.5 to 7 (Table 1).

The dependence of $n(\text{HO}_y)$ on $[\text{NO}_x]$ is opposite to that of $n(\text{HO}_x)$: $n(\text{HO}_y)$ decreases with increasing $[\text{NO}_x]$ for $[\text{NO}_x] < 100$ pptv, and then it increases with further increases in $[\text{NO}_x]$. At low NO_x concentrations, HO_x cycling with its HO_y reservoirs occurs mostly through $\text{HO}_2 + \text{HO}_2$, while HO_y loss is through $\text{HO}_2 + \text{OH}$. As a result, and following Eq. (1), $n(\text{HO}_y)$ is inversely

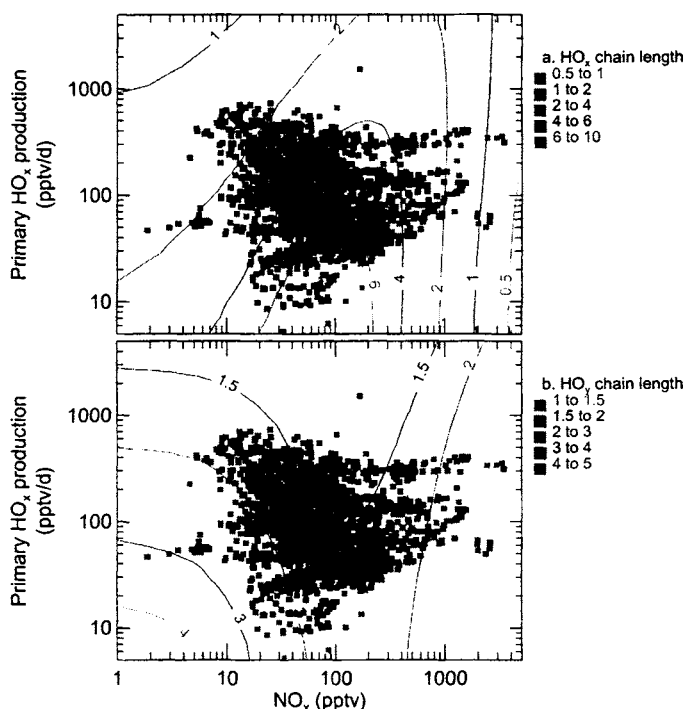


Figure 8. Model-calculated chain lengths $n(\text{HO}_x)$ and $n(\text{HO}_y)$ for HO_x and HO_y cycling (Eqs. (5) and (6)) as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$. The contour lines show results for the median conditions described in Table 1. The colored symbols show values calculated over the ensemble of conditions during STRAT, SUCCESS, and SONEX.

proportional to NO. For the range of conditions encountered in the upper troposphere, $n(\text{HO}_y)$ varies between 1.6 and 2.2 (Table 1).

The product $n(\text{HO}_x) \times n(\text{HO}_y)$ represents approximately the ozone production efficiency per unit of primary HO_x produced, as for $[\text{NO}_x] > 10$ pptv the cycling between HO₂ and OH is mostly through reaction with NO (R4). For most conditions sampled during the three missions, $n(\text{HO}_x) \times n(\text{HO}_y)$ ranges between 4 and 12.

Model-calculated steady-state concentrations of the peroxide reservoirs are shown in Fig. 9 as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$ (contour lines) for the median upper tropospheric conditions in Table 1. The dependences of H₂O₂ and CH₃OOH on $[\text{NO}_x]$ and $P(\text{HO}_x)$ follow that of HO₂ (Fig. 4a). The concentration of HNO₄ increases with increasing NO_x to reach a maximum at 100 pptv NO_x, beyond which it decreases. This decrease is due to depletion of HO₂ by increasing NO_x (Fig. 4a). For the median upper tropospheric conditions in Ta-

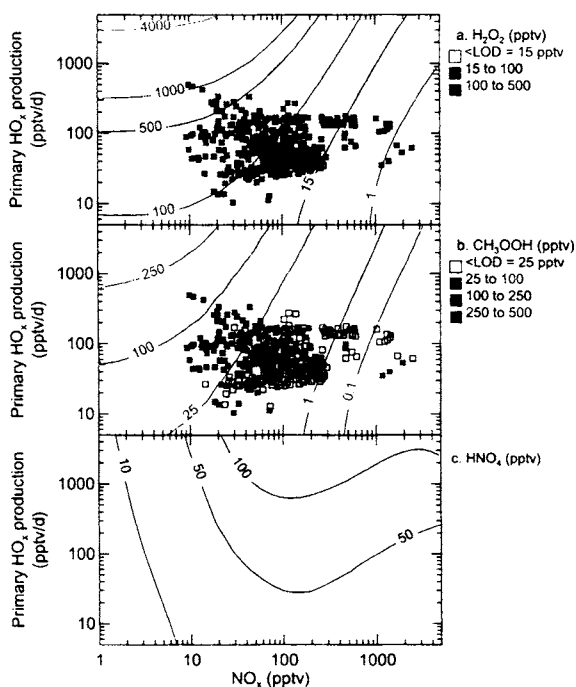


Figure 9. Steady-state concentrations of peroxides as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$ in the upper troposphere: (a) H_2O_2 , (b) CH_3OOH , and (c) HNO_4 . The contour lines show model results for the median conditions of Table 1. Observations of H_2O_2 and CH_3OOH obtained during SONEX are shown as square symbols on panels a and b. Open symbols correspond to observations below the LOD of the instrument (15 pptv for H_2O_2 and 25 pptv for CH_3OOH).

ble 1, HNO_4 loss is 10% by thermolysis (R30), 30% by photolysis (R29) and 60% by reaction with OH (R33). At the warmer temperatures and low $P(\text{HO}_x)$ of SONEX, HNO_4 loss is equally divided between (R29), (R30) and (R33).

Observed H_2O_2 and CH_3OOH concentrations in SONEX (Snow et al., 2000) are shown in Figs. 9a and b. The concentrations of H_2O_2 decrease with increasing NO_x as expected from the model calculations. The observations of H_2O_2 are reproduced by model calculations to within 50% if one allows for heterogeneous reaction of HO_2 in aerosols producing H_2O_2 (Jaeglé et al., 2000). A large fraction (47%) of the reported CH_3OOH values were below the 25 pptv LOD of the instrument. These observations generally fall below the 25 pptv contour line of the model (Fig. 9b). However, the remaining observations exhibit much higher values (up to 340 pptv) than calculated. The model underestimate of CH_3OOH by factors of 2–3 is systematic throughout SONEX and does not appear to be associated with recent convection (Jaeglé

et al., 2000). It could reflect uncertainties in the rate constant for (R17) at low temperatures (Jacob et al., 1996; Schultz et al., 1999). Despite this lack of agreement on the absolute value of CH_3OOH , the observations do show the expected trend of increase with decreasing $[\text{NO}_x]$.

The MarkIV balloon-borne instrument measured HNO_4 concentrations in the lowermost stratosphere which are a factor of 2 higher than expected. Inclusion of a speculated HNO_4 photodissociative transition in the near IR reconciles models and observations for HNO_4 and provides a missing source of HO_x at high SZA (Wennberg et al., 2000).

3.4. HO_y sinks

As we saw in the previous section, the sinks of HO_y are through reactions of HO_y and NO_x species with OH ((R7), (R19), (R23), (R27), (R32) and (R33)). The lifetime of HO_y varies between 1 and 6 days (Table 1). The relative importance of the different HO_y sinks depends mostly on the levels of NO_x , as shown by the model calculations in Fig. 10. There is usually not one single dominant pathway. For STRAT and SUCCESS, the observed ranges in $[\text{NO}_x]$ and $P(\text{HO}_x)$ (Table 1 and Fig. 3) place the upper troposphere predominantly in a regime where $\text{OH} + \text{HO}_2$ is the most important HO_y loss pathway, accounting for 30–50% of total HO_y loss (Wennberg et al., 1998; Jaeglé et al., 1998a). In contrast, for ASHOE/MAESA and SONEX, the low $P(\text{HO}_x)$ and relatively high $[\text{NO}_x]$ led to the sampling of a second regime where $\text{OH} + \text{HNO}_4$ is the most important HO_y loss pathway accounting for $\sim 35\%$ of total HO_y loss (Folkins et al., 1997; Jaeglé et al., 2000). At very high $[\text{NO}_x]$ (> 300 pptv), HO_y is expected to be mostly lost through $\text{OH} + \text{NO}_2 + \text{M}$ and $\text{OH} + \text{HNO}_3$. Only very few observations have been obtained under those conditions. Consideration of the relative importance of the different HO_y loss pathways lays the foundation for our analysis of chemical regimes in the next section.

4. Chemical regimes for HO_x and ozone production

Based on the dominant HO_y loss pathways (Fig. 10), three main chemical regimes can be defined: (1) a low NO_x regime where the dominant sinks of HO_y are reactions of OH with HO_2 , H_2O_2 , and CH_3OOH ((R23), (R32) and (R19)); (2) an intermediate NO_x regime where reaction of OH with HNO_4 becomes important (R33); and (3) a high- NO_x regime where reactions of OH with NO_2 and HNO_3 dominate ((R7) and (R27)). We refer to these three regimes as the NO_x -limited regime, the transition regime, and the NO_x -saturated regime, respectively. The NO_x -saturated regime is commonly known

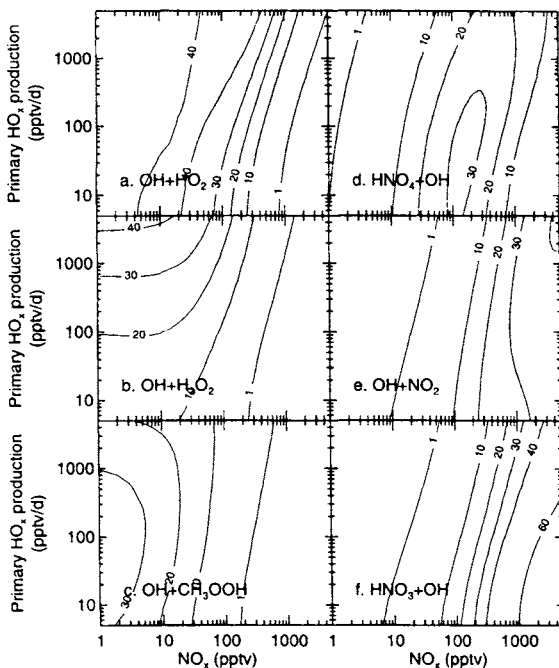


Figure 10. Percentage contributions (%) of individual reactions to the HO_y loss rate as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$. Values are model results for the median upper tropospheric conditions of Table 1.

as the hydrocarbon-limited regime in the lower troposphere, however “ NO_x -saturated” is a better terminology in the upper troposphere where non-methane hydrocarbons do not have the capacity to influence HO_x chemistry. We define the relative sensitivity of variable Y to variable X as

$$S(Y, X) = \frac{\partial \ln(Y)}{\partial \ln(X)} = \frac{X}{Y} \frac{\partial Y}{\partial X}. \quad (7)$$

$S(Y, X)$ represents the exponent in the local power law relating Y to X , i.e., $Y = X^{S(Y, X)}$. Sensitivities of $P(\text{O}_3)$ and $[\text{HO}_x]$ relative to $[\text{NO}_x]$ and $P(\text{HO}_x)$ are shown in Fig. 11 as a function of $[\text{NO}_x]$ for the otherwise median conditions of Table 1. The values represent the partial derivatives for the data shown as contour lines in Fig. 4. In the NO_x -limited regime $S(P(\text{O}_3), [\text{NO}_x])$ is positive; at very low $[\text{NO}_x]$ it has a value close to 1 and then decreases with increasing $[\text{NO}_x]$. In the NO_x -saturated regime $S(P(\text{O}_3), [\text{NO}_x])$ becomes negative and it reaches a value close to -0.5 for very high $[\text{NO}_x]$. We define the transition regime as the region where $P(\text{O}_3)$ is the least sensitive to changes in

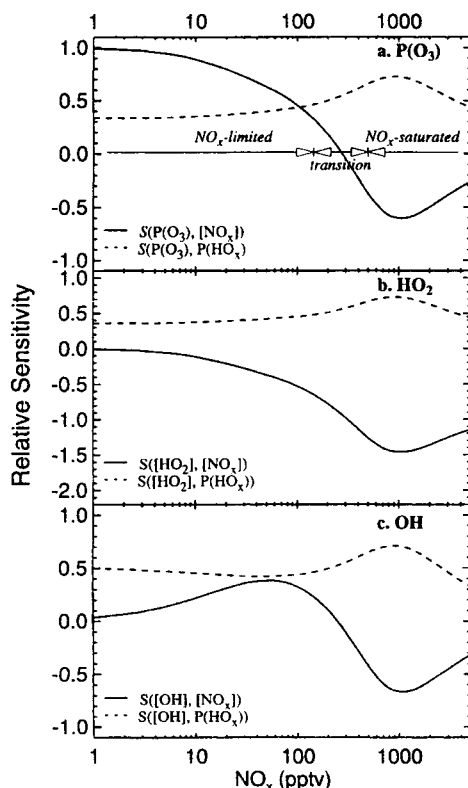


Figure 11. Relative sensitivities $S(Y, X)$ of $\text{P}(\text{O}_3)$, $[\text{HO}_2]$ and $[\text{OH}]$ to $[\text{NO}_x]$ and $\text{P}(\text{HO}_x)$, as a function of $[\text{NO}_x]$ (Eq. (7)). Values are model results for the median upper tropospheric conditions of Table 1. The relative sensitivities were obtained by perturbing the standard model simulations by 10% increases in either $[\text{NO}_x]$ or $\text{P}(\text{HO}_x)$.

NO_x : $|S(\text{P}(\text{O}_3), [\text{NO}_x])| < 0.25$. The relative sensitivity of $\text{P}(\text{O}_3)$ to $\text{P}(\text{HO}_x)$, $S(\text{P}(\text{O}_3), \text{P}(\text{HO}_x))$, is always positive and varies between about 0.3 and 1. In the NO_x -limited regime $\text{P}(\text{O}_3)$ is sensitive to changes in $[\text{NO}_x]$, while in the NO_x -saturated regime $\text{P}(\text{O}_3)$ becomes more sensitive to changes in $\text{P}(\text{HO}_x)$: $|S(\text{P}(\text{O}_3), \text{P}(\text{HO}_x))| > |S(\text{P}(\text{O}_3), [\text{NO}_x])|$ (Fig. 11). As expected from equation (2) and shown on Fig. 11, the relative sensitivities of $[\text{HO}_2]$ and $\text{P}(\text{O}_3)$ are such that $S([\text{HO}_2], [\text{NO}_x]) = S(\text{P}(\text{O}_3), [\text{NO}_x]) - 1$.

In the following, we derive simple analytical expressions approximately describing these sensitivities in each regime. Namely, we derive expressions describing the variables $[\text{OH}]$, $[\text{HO}_2]$, and $\text{P}(\text{O}_3)$ as power laws of the form $[\text{NO}_x]^a \text{P}(\text{HO}_x)^b$ where the exponents a and b are regime-dependent and correspond to the relative sensitivities defined in Eq. (7). We begin by assuming

that the HO_y family is in chemical steady state:

$$P(\text{HO}_x) + y_{\text{CH}_4} k_{22}[\text{CH}_4][\text{OH}] = [\text{OH}](2k_{23}[\text{HO}_2] + 2k_{32}[\text{H}_2\text{O}_2] + 2k_{19}[\text{CH}_3\text{OOH}] + 2k_{33}[\text{HNO}_4] + k_7[\text{NO}_2][\text{M}] + k_{27}[\text{HNO}_3]). \quad (8)$$

The assumption of chemical steady state is not applicable in convective outflows, where HO_y species can be enhanced or depleted relative to steady state. We will treat separately the effect of convection as a perturbation to the solution of Eq. (8) in Section 5.

Our approach for achieving simple analytical expressions describing the asymptotic behavior shown in Fig. 11, is to drastically simplify Eq. (8) in a manner that can characterize the different chemical regimes. Specifically we assume that each regime is characterized by a single dominant HO_y loss pathway and neglect all other terms on the right-hand side of (8). This is clearly an oversimplification as there is always more than one significant pathway for HO_y loss (Fig. 10), but it allows an analysis of the key differences between the regimes. We also neglect the methane amplification term on the left-hand side of (8). As methane oxidation acts as a weak buffer to changes in NO_x and $P(\text{HO}_x)$ (see Section 3.2), this simplification will have for effect to slightly overestimate the dependence of HO_x on both variables.

In addition to [NO_x] and $P(\text{HO}_x)$, the [NO]/[NO_x] ratio is a third parameter controlling HO_x chemistry. We introduce it as a variable α , which we define by assuming NO–NO₂–O₃ photostationary steady state following (R5)–(R6):

$$\alpha = \frac{[\text{NO}]}{[\text{NO}_x]} = \frac{J_5}{J_5 + k_6[\text{O}_3]}. \quad (9)$$

Eq. (9) is accurate to within 10–30% in the upper troposphere, where the contribution of peroxy radicals to the conversion of NO to NO₂ is relatively small (Crawford et al., 1996).

4.1. NO_x-limited regime

At low NO_x concentrations (< 100 pptv), the loss of HO_y occurs mainly through (R23), (R32), and (R19) (Fig. 10). Under the median conditions corresponding to Fig. 11, (R23) is most important. Neglecting all other terms on the right-hand side of (8) and using the [HO₂]/[OH] ratio from (1), we obtain

$$[\text{OH}] = \left[\frac{k_4\alpha[\text{NO}_x] + k_{11}[\text{O}_3]}{2k_3k_{23}[\text{CO}]} P(\text{HO}_x) \right]^{1/2}, \quad (10)$$

$$[\text{HO}_2] = \left[\frac{k_3[\text{CO}]}{2k_{23}(k_4\alpha[\text{NO}_x] + k_{11}[\text{O}_3])} P(\text{HO}_x) \right]^{1/2}, \quad (11)$$

$$P(\text{O}_3) = k_4\alpha[\text{NO}_x] \left[\frac{k_3[\text{CO}]}{2k_{23}(k_4\alpha[\text{NO}_x] + k_{11}[\text{O}_3])} P(\text{HO}_x) \right]^{1/2}. \quad (12)$$

For very low NO_x concentrations (< 10 pptv), most of the cycling between OH and HO₂ takes place through (R11). As a result, both [OH] and [HO₂] are independent of [NO_x] and $P(\text{O}_3)$ is proportional to [NO_x] (Figs. 4 and 11). As [NO_x] increases above 10 pptv, (R4) dominates over (R11) and [OH] increases as [NO_x]^{*a*}, where *a* asymptotically increases towards 1/2; [HO₂] is then proportional to [NO_x]^{*a*-1} and $P(\text{O}_3)$ increases as [NO_x]^{*a*}. The dependences of [HO_x] and $P(\text{O}_3)$ on $P(\text{HO}_x)$ can be expressed by the functionality $P(\text{HO}_x)^b$ with *b* = 1/2 over the extent of the NO_x-limited regime. The full model calculation shows a smaller value for *b* (Fig. 11), reflecting the importance of other HO_y losses, (R32) and (R19), which are cubic in [HO_x].

4.2. Transition regime

To describe the transition regime we assume in (8) that (R33) is the only significant contributor to HO_y loss. As noted in Section 3.3, for the median upper tropospheric conditions in Table 1, HNO₄ loss is dominated by reaction with OH (R33). Assuming steady state for HNO₄, we have

$$[\text{OH}] = \left[\frac{k_4(J_{29} + k_{30})}{2k_3k_{25}k_{33}[\text{M}][\text{CO}]} \frac{\alpha}{1 - \alpha} P(\text{HO}_x) \right]^{1/2}, \quad (13)$$

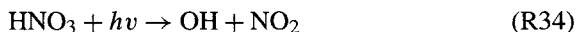
$$[\text{HO}_2] = \left[\frac{1}{[\text{NO}_x]} \frac{k_3(J_{29} + k_{30})[\text{CO}]}{2k_4k_{25}k_{33}[\text{M}]} \frac{1}{\alpha(1 - \alpha)} P(\text{HO}_x) \right]^{1/2}, \quad (14)$$

$$P(\text{O}_3) = \left[\frac{k_3(J_{29} + k_{30})[\text{CO}]}{2k_{25}k_{33}[\text{M}]} \frac{\alpha}{1 - \alpha} P(\text{HO}_x) \right]^{1/2}. \quad (15)$$

In the transition regime, [OH] is thus independent of [NO_x] while [HO₂] is proportional to [NO_x]⁻¹. One important consequence is that $P(\text{O}_3)$ is independent of [NO_x] (Jaeglé et al., 1999). Both [HO_x] and $P(\text{O}_3)$ increase as $P(\text{HO}_x)^b$ with *b* = 1/2.

4.3. NO_x-saturated regime

When the concentration of NO_x exceeds a few hundreds of pptv, loss of HO_y proceeds mainly by conversion to HNO₃ (R7) and subsequent reaction of HNO₃ with OH (R27). Photolysis of HNO₃:



becomes an important source of HO_x . In this regime, we assume that HNO_3 is in steady state and we treat it as another HO_y reservoir such that (8) is simplified as

$$P(\text{HO}_x) = 2k_{27}[\text{OH}][\text{HNO}_3], \quad (16)$$

where we neglect the role of heterogeneous production of HNO_3 on aerosols (R9) ((R9) represents 20–60% of HNO_3 production for the median conditions of Table 1). For the median conditions of Table 1, the dominant HNO_3 sink is photolysis (R34), such that

$$[\text{OH}] = \left[\frac{J_{34}}{2k_7k_{27}[\text{M}]} \frac{1}{1-\alpha} \frac{P(\text{HO}_x)}{[\text{NO}_x]} \right]^{1/2}, \quad (17)$$

$$[\text{HO}_2] = \frac{k_3[\text{CO}]}{k_4} \left[\frac{J_{34}}{2k_7k_{27}[\text{M}]} \frac{1}{\alpha^2(1-\alpha)} \frac{P(\text{HO}_x)}{[\text{NO}_x]^3} \right]^{1/2}, \quad (18)$$

$$P[\text{O}_3] = k_3[\text{CO}] \left[\frac{J_{34}}{2k_7k_{27}[\text{M}]} \frac{1}{1-\alpha} \frac{P(\text{HO}_x)}{[\text{NO}_x]} \right]^{1/2}. \quad (19)$$

As seen in Figs. 4 and 11 and the above expressions in the NO_x -saturated regime, $[\text{OH}]$ as well as $[\text{HO}_2]$ and $P(\text{O}_3)$ decrease with increasing $[\text{NO}_x]$. $[\text{OH}]$ and $P(\text{O}_3)$ decrease with the dependence $[\text{NO}_x]^a$ and $[\text{HO}_2]$ as $[\text{NO}_x]^{a-1}$ with $a = -1/2$. The concentrations of HO_x increase as $P(\text{HO}_x)^b$, with $b = 1/2$. For very high $[\text{NO}_x]$ (> 1000 pptv), reaction (R9) can no longer be neglected as it becomes a large source of HO_y , causing the upturn (downturn) of the NO_x ($P(\text{HO}_x)$) relative sensitivities shown in Fig. 11.

As noted in the Introduction, observed $[\text{HO}_x]$ appears to increase with increasing NO_x for $[\text{NO}_x] > 300$ pptv (Brune et al., 1999; Faloona et al., 2000), contrary to the expected dependence of Eqs. (17) and (18). Enhanced $P(\text{HO}_x)$ associated with high $[\text{NO}_x]$ due to convection or lightning could explain this increase, but one cannot exclude the possibility of major shortcomings in our understanding of chemistry in NO_x -saturated regime.

5. Eigenlifetimes for relaxation of a HO_y perturbation

A large fraction of the turnover of the upper troposphere may take place by deep convective injection of air from the lower troposphere, carrying with it high concentrations of HO_x precursors (Fig. 1). Prather and Jacob (1997) have suggested that with a 10 d overturning rate of the tropical upper troposphere, deep convection could cause a persistent chemical imbalance in HO_y . Such a chemical imbalance has indeed been observed a few days downwind of convective events (Cohan et al., 1999).

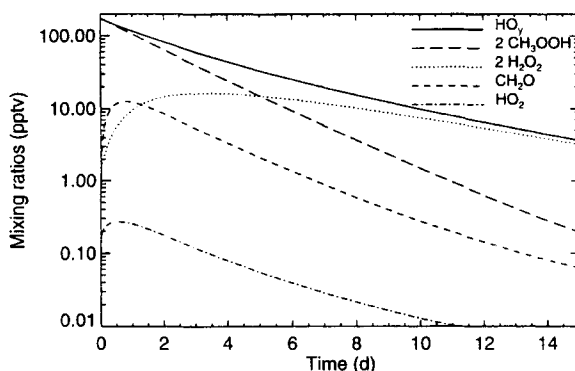


Figure 12. Temporal evolution of $\Delta\text{H}_2\text{O}_2$, $\Delta\text{CH}_3\text{OOH}$, $\Delta\text{CH}_2\text{O}$, ΔHO_2 , and ΔHO_y following a 100 pptv convective injection of CH_3OOH into the median atmosphere of Table 1. The species concentrations are initially at chemical steady state, and Δ represents the perturbations to the steady-state concentrations averaged over 24 h to remove the effect of diurnal variability.

We apply here our photochemical model to better understand the time scale for relaxation of the HO_y family to chemical steady state following an episodic perturbation such as convection. The coupling of the chemical reactions in the $\text{O}_3\text{--NO}_x\text{--HO}_x$ system makes the evaluation of the chemical cycling within the HO_y family a non-trivial problem. Let us consider for example a 100 pptv perturbation to CH_3OOH applied to the median conditions of Table 1 with HO_y initially at chemical steady state. Fig. 12 shows the decay of this perturbation. Photolysis of CH_3OOH to HO_x is followed by the formation of H_2O_2 , CH_2O , and HNO_4 . The decay of CH_3OOH after the perturbation initially proceeds with a 2.1 d e-folding decay time, which is close to the steady-state lifetime of CH_3OOH (1.9 d, defined as $[\text{CH}_3\text{OOH}]/\text{Loss}(\text{CH}_3\text{OOH})$ at steady state), but then approaches a 5.7 d decay time. After its initial production, H_2O_2 decays with a time constant of 5.7 d, longer than its steady state lifetime of 4.5 d. This 5.7 d time constant is more than twice as long as the steady-state lifetime of HO_y (2.6 d). Thus, the steady-state lifetimes of HO_y species do not describe accurately the decay time scales of a HO_y perturbation. The decay time scales are longer because of cycling within the HO_y family.

The true time scale for decay of a HO_y perturbation in the upper troposphere can be obtained with an eigenlifetime analysis (Prather, 1994, 1996) which identifies the independent modes of variability of the chemical system. For a system of n species, and corresponding concentration vector $C\{C_1, C_2, \dots, C_n\}$, let C be a steady-state solution of the set of mass balance equations,

$$\frac{dC_i}{dt} = P_i(C) - L_i(C) = 0 \quad \text{for } i = 1, n \quad (20)$$

where $P_i(C)$ and $L_i(C)$ are the production and loss rates of species i . Let J be the $n \times n$ Jacobian matrix of the functions dC_i/dt , with elements $J_{ij} = \partial(dC_i/dt)/\partial C_j$ calculated by perturbation to the steady-state solution. To first order, the decay of a perturbation ΔC about the steady-state solution C can be expressed by the first term of a Taylor series expansion (Prather, 1994):

$$\frac{d(\Delta C)}{dt} = J \Delta C. \quad (21)$$

Each of the n eigenvectors, A_k , of the Jacobian matrix J is associated with an eigenvalue, c_k . A perturbation to the concentration of a species can be expressed by a unique linear combination of these eigenvectors:

$$\Delta C(t) = \sum_{k=1}^n s_k A_k e^{c_k t} \quad (22)$$

where s_k are coefficients. The characteristic e-folding time constants with which the system responds to perturbations are thus the eigenlifetimes, $-1/c_k$.

We apply this analysis to our photochemical model for the median conditions of Table 1. We solve the steady-state Eq. (20) for $n = 30$ chemical species describing the O_3 - NO_x - HO_x system, and using 24 h average values of photolysis frequencies. We calculate the corresponding value of the Jacobian and retrieve the ensemble of eigenvectors and eigenvalues. Seventeen eigenvectors, or modes, are relevant to the HO_y system; four have eigenlifetimes longer than one hour and are listed in Table 3 as dimensionless relative perturbations in the mixing ratios (expressed in percentage). Each mode (which corresponds to a column in the table) is labeled with its eigenlifetime. The longest time constant of the HO_y system is the 5.7 d mode (mode 1), which corresponds to a H_2O_2 perturbation, with a small CH_3OOH component. Other modes include two degenerate 2.09 d CH_3OOH - HNO_4 modes (modes 2 and 3) and a 0.4 d CH_2O mode (mode 4). On shorter time scales, there is a 28-min HNO_2 mode, a 13-min OH - HO_2 - CH_3O_2 mode, and a 5 s OH mode.

Let us consider again our example of a 100 pptv perturbation to CH_3OOH from convective injection. We can use the eigenlifetime analysis to derive the exact time dependence of the response of HO_y species according to (22), as shown in Fig. 12 and expressed mathematically in Table 3 (we have neglected the modes with time scales shorter than 1 h). Modes 2 and 3 are degenerate and their terms have been combined. Each species responds as a superimposition of the same three exponential decay terms but the coefficients, $s_k A_k$, are species dependent. For CH_3OOH , of the initial 100 pptv perturbation, 0.6 pptv decay with the 5.7 d time scale, 96 pptv with the 2.09 d time scale, and 0.4 with the 0.4 d time scale. For H_2O_2 , the perturbation of 100 pptv of CH_3OOH will result

Table 3. Eigenvectors (or modes) and eigenlifetimes for the decay of a HO_y perturbation in the upper troposphere^a

	Modes (<i>A_k</i>)				Steady-state lifetime, d ^b
	1	2	3	4	
Eigenlifetime ($-1/c_k$), d	5.70	2.09	2.09	0.40	
H ₂ O ₂	100.00	0.0	-4.7	-2.0	4.55
HNO ₄	9.9	47.8	-46.5	-2.0	2.13
CH ₃ OOH	28.2	100.00	100.00	-4.2	1.93
CH ₂ O	13.7	7.2	13.1	100.00	0.34
HNO ₂	14.2	-2.1	4.3	9.9	1.86×10^{-2}
CH ₃ O ₂	15.3	1.9	8.3	9.6	3.21×10^{-3}
HO ₂	14.5	0.0	4.1	14.0	2.43×10^{-3}
OH	15.0	-2.1	4.5	10.2	6.35×10^{-5}

Decomposition of a perturbation $\Delta\text{CH}_3\text{OOH}[t=0] = 100$ pptv into modes ($\sum s_k A_k e^{c_k t}$)^c

$\Delta\text{H}_2\text{O}_2[t] = 25e^{-t/5.70} - 26.8e^{-t/2.09} + 2.4e^{-t/0.4}$

$\Delta\text{HNO}_4[t] = 2.6e^{-t/5.70} - 2.1e^{-t/2.09} + 2.5e^{-t/0.4}$

$\Delta\text{CH}_3\text{OOH}[t] = 0.61e^{-t/5.70} + 95.9e^{-t/2.09} + 0.4e^{-t/0.4}$

$\Delta\text{CH}_2\text{O}[t] = 0.74e^{-t/5.70} + 24.5e^{-t/2.09} - 26.3e^{-t/0.4}$

$\Delta\text{HNO}_2[t] = 0.005e^{-t/5.70} + 0.019e^{-t/2.09} - 0.017e^{-t/0.4}$

$\Delta\text{CH}_3\text{O}_2[t] = 0.007e^{-t/5.70} + 0.111e^{-t/2.09} - 0.022e^{-t/0.4}$

$\Delta\text{HO}_2[t] = 0.068e^{-t/5.70} + 0.423e^{-t/2.09} - 0.318e^{-t/0.4}$

$\Delta\text{OH}[t] = 0.002e^{-t/5.70} + 0.006e^{-t/2.09} - 0.006e^{-t/0.4}$

$\Delta\text{HO}_x[t] = 0.08e^{-t/5.70} + 0.54e^{-t/2.09} - 0.35e^{-t/0.4}$

$\Delta\text{HO}_y[t] = 53.9e^{-t/5.70} + 136.6e^{-t/2.09} + 7.9e^{-t/0.4}$

^aEigenlifetime analysis applied to perturbation of the O₃-NO_x-HO_x chemical system for the median upper tropospheric conditions of Table 1. The system of chemical steady-state equations is solved and the corresponding Jacobian matrix is calculated. Four principal modes with eigenlifetimes longer than 1 h are identified for the HO_y system: Mode 1 (H₂O₂ mode), mode 2 (CH₃OOH-HNO₄ mode), mode 3 (CH₃OOH-HNO₄ mode) and mode 4 (CH₂O mode). These modes are listed in the table as relative perturbations in the mixing ratios of HO_y species expressed as percentages.

^bThe steady state lifetime of a species is defined as the inverse of its 24 h average loss frequency at steady state.

^cThe time dependence of the decay of HO_y species is obtained according to Eq. (22). Modes with time constants shorter than 1 h are neglected. Modes 2 and 3 are degenerate and have been combined.

in the production of H₂O₂ with a time scale of 2.09 d, which will then decay mostly with the 5.7 d time scale. HO_y as a result will first decay with the 2.09 d time scale, with increasing contributions from the 5.7 d time scale after the first few days. For the conditions of Table 3 and Fig. 12, the decay time of HO_y following a perturbation is thus twice as long as the steady-state lifetime of HO_y (2.6 d). The 5.7 d time scale reflects the cycling between HO_x and its reservoir species H₂O₂ and CH₃OOH, effectively increasing the persistence

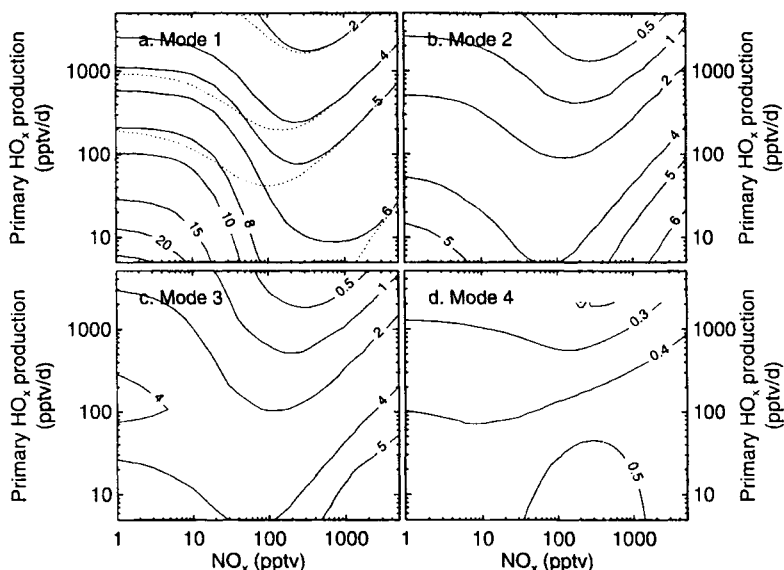


Figure 13. Eigenlifetimes, in days, for the four main HO_y modes (Table 3) as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$: (a) mode 1 (H_2O_2 mode), (b) mode 2 ($\text{CH}_3\text{OOH}-\text{HNO}_4$ mode), (c) mode 3 ($\text{CH}_3\text{OOH}-\text{HNO}_4$ mode), (d) mode 4 (CH_2O mode). These eigenlifetimes represent the e-folding decay times of a HO_y perturbation in the upper troposphere for the median conditions of Table 1. The steady-state lifetime of H_2O_2 (defined as the loss frequency of H_2O_2 under steady-state conditions) is shown by the dashed line in panel a.

of the perturbation. HO_2 in turn will respond to the perturbations in the HO_y reservoirs and decay with the same eigenlifetimes. When other perturbations are applied to the system in the form of any other HO_y species (H_2O_2 , HNO_4 , HO_2 , OH), or of CH_2O , the same long-lived modes control the decay of the perturbation.

In this discussion, we have not taken into account the role of mixing with surrounding air which will also affect the evolution of HO_y concentrations following a perturbation. Mixing can be represented with its associated eigenlifetime, and will be an additional term in the decay equations of Table 3.

The compositions of the four main HO_y modes and the associated eigenlifetimes vary with $[\text{NO}_x]$ and $P(\text{HO}_x)$. Fig. 13 shows the eigenlifetimes of these four modes as a function of $[\text{NO}_x]$ and $P(\text{HO}_x)$ for the otherwise median conditions of Table 1. The longest eigenlifetime (mode 1), which is dominantly a H_2O_2 perturbation, is always longer than the steady-state lifetime of H_2O_2 (dashed line in Fig. 13a). At high $[\text{NO}_x]$, this eigenlifetime asymptotically approaches the H_2O_2 steady-state lifetime because the cycling between H_2O_2 and the other HO_y species becomes inefficient: OH produced from photolysis

of H_2O_2 is lost by reaction with NO_2 or with HNO_3 instead of regenerating H_2O_2 .

For a given perturbation, the fraction of HO_y decaying with each eigenlifetime varies with $[\text{NO}_x]$ and $P(\text{HO}_x)$. For the median conditions of Table 1, a perturbation to HO_y will decay principally with responses from the H_2O_2 mode (mode 1) and the coupled $\text{CH}_3\text{OOH-HNO}_4$ mode (modes 2 and 3). As $[\text{NO}_x]$ increases, the role of H_2O_2 as a reservoir of HO_y diminishes and the dominant decay time is associated with the $\text{CH}_3\text{OOH-HNO}_4$ mode. For STRAT (low $[\text{NO}_x]$ and $P(\text{HO}_x)$) we find that the decay times of a HO_y perturbation are 5–10 d (mode 1) and 2–3 d (modes 2 and 3), while for the higher $P(\text{HO}_x)$ conditions of SUCCESS these decay times are 4–8 d and 1–2 d. For the tropical Pacific conditions at 8–12 km altitude examined by Cohan et al. (1999), $P(\text{HO}_x)$ is very high and the dominant decay time of a HO_y perturbation is 2–3 d, consistent with their observations in aged convective outflows. In that case the decay time is still longer than the local steady-state lifetime of HO_y (1.4 d).

6. Conclusions

We have presented a theoretical analysis of HO_x and HO_y chemistry in the upper troposphere using photochemical model calculations anchored by recent observations of HO_x from the STRAT, SUCCESS, and SONEX aircraft missions. Model calculations along the flight tracks generally agree with the observed daytime concentrations of OH and HO_2 to within the instrumental accuracy of $\pm 40\%$. Cycling between OH and HO_2 is understood to within the instrumental accuracy of the observed HO_2/OH concentration ratio ($\pm 20\%$). The model can account for 66% of the variance in the observed concentrations of OH and HO_2 . After eliminating the diurnal dependence on solar UV radiation, we find that the variance is largely determined by two master variables: the concentration of NO_x and the primary HO_x production rate, $P(\text{HO}_x)$. Consideration of these two variables allows a synthesis of the aircraft data sets taken in different regions and in different seasons. It also provides a framework for examining other aspects of the photochemistry of the upper troposphere.

The importance of acetone relative to water vapor as a primary HO_x source is determined by the abundance of H_2O , which is far more variable than the abundance of acetone. Acetone photolysis dominates over $\text{H}_2\text{O} + \text{O}(^1\text{D})$ for $[\text{H}_2\text{O}] < 100$ ppmv. The HO_x yield from acetone photolysis varies between 2 and 3 for observed conditions in the upper troposphere. Convective injection of peroxides and CH_2O from the boundary layer can also provide important primary HO_x sources under low water vapor conditions, as often observed dur-

ing STRAT and SUCCESS. Methane oxidation by OH followed by photolysis of amplifies the primary HO_x sources by a factor of 1.1–1.9.

The HO_x chain length, defined as the average number of times that HO_2 radicals cycle within the HO_x family before being lost to non-radical forms, varies between 2.5 and 7 for the conditions observed in the three aircraft missions. The HO_y chain length, defined as the average number of times that HO_x radicals cycle with their HO_y reservoirs before being lost to non- HO_y forms, varies between 1.6 and 2.2. The number of ozone molecules produced per HO_y molecule consumed (HO_y -based ozone production efficiency) varies from 4 to 12. Ozone production rates derived from observed HO_2 and NO concentrations range from 0.3 to 5 ppbv d^{-1} .

The pathways for HO_y loss determine the forms of the dependences of HO_x chemistry and the ozone production rate, $P(\text{O}_3)$, on $[\text{NO}_x]$ and $P(\text{HO}_x)$; i.e. the chemical regime. In the NO_x -limited regime ($\text{NO}_x < 100$ pptv) reactions of OH with HO_2 , H_2O_2 and CH_3OOH dominate the HO_y sink; $P(\text{O}_3)$ increases with increasing NO_x . In the transition regime ($100 < \text{NO}_x < 300$ pptv), reaction of OH with HNO_4 becomes important; $P(\text{O}_3)$ is independent of NO_x . Finally, in the NO_x -saturated regime ($\text{NO}_x > 300$ pptv), reactions of OH with NO_2 and HNO_3 are the strongest sinks of HO_y ; $P(\text{O}_3)$ decreases with increasing NO_x . Qualitative analytic expressions for each regime provide distinct power law dependences of $[\text{OH}]$, $[\text{HO}_2]$, and $P(\text{O}_3)$ on $[\text{NO}_x]$ and $P(\text{HO}_x)$ of the form $[\text{NO}_x]^a P(\text{HO}_x)^b$, where values of the exponents vary for the different regimes.

Using an eigenlifetime analysis, we find that the time scale for the relaxation of HO_y following a perturbation (such as from convection) can be factors of 2–3 longer than the steady-state lifetime of HO_y because of cycling within the HO_y family, in particular between HO_x and H_2O_2 . The time scale of decay of such a perturbation is 2–15 d depending on $[\text{NO}_x]$ and $P(\text{HO}_x)$; it is longest for low $[\text{NO}_x]$ and low $P(\text{HO}_x)$, as was observed during the STRAT mission and which explains the high sensitivity of HO_y concentrations to convection more than a week upwind during that mission (Jaeglé et al., 1997). In contrast, during the PEM-Tropics (A) mission over the tropical South Pacific, $P(\text{HO}_x)$ was high and the perturbation to HO_y from convection decayed after a few days (Cohan et al., 1999).

It appears that HO_x chemistry and ozone production in the upper troposphere can be largely described on the basis of only two master variables, the NO_x concentration and $P(\text{HO}_x)$. A complete representation of upper tropospheric chemistry thus needs to accurately describe these two variables and the factors that control them. The sources of NO_x in the upper troposphere are difficult to characterize as illustrated by the differing interpretations of observations from the SONEX mission (Thompson et al., 1999; Liu et al., 1999; Koike et al., 2000). The factors controlling water vapor in the upper troposphere are

not entirely elucidated. Our understanding of acetone sources is unsatisfactory (Singh et al., 2000). The importance of scavenging on deep convective transport of soluble HO_x precursors such as H₂O₂, CH₂O and HNO₃ needs to be better quantified (Mari et al., 2000). Further work on these issues is critical for improving our understanding of the chemistry of the upper troposphere and how it may change in the future.

Acknowledgements

This work was supported by the National Science Foundation (NSF) and by the National Aeronautics and Space Administration (NASA).

Appendix A. Photochemical model

Our calculations use the Harvard 0-D photochemical model (Jaeglé et al., 2000; Schultz et al., 1999). The photochemical mechanism is based on the recommendations of DeMore et al. (1997) and Atkinson et al. (1997), with a few updates including: temperature-dependent cross-sections and pressure-dependent quantum yields for acetone photolysis (Gierczak et al., 1998), O(¹D) quantum yields from ozone photolysis (Talukdar et al., 1998), rate constants for the OH + NO₂ reaction (Dransfield et al., 1999), and for the OH + HNO₃ reaction (Brown et al., 1999). Hydrolysis of N₂O₅ in aerosols is included with a reaction probability $\gamma_{\text{N}_2\text{O}_5} = 0.1$ (DeMore et al., 1997). We also include reaction of HO₂ in aerosols (Hanson et al., 1992; Cooper and Abbatt, 1996). Following the recommendation of Jacob (2000), we assume that the uptake of HO₂ by the aerosols can be described by first-order kinetics with $\gamma_{\text{HO}_2} = 0.2$ and the stoichiometry $\text{HO}_2 + \text{aerosol} \rightarrow \frac{1}{2}\text{H}_2\text{O}_2 + \frac{1}{2}\text{O}_2$.

The model solves the system of kinetic equations using the diel steady-state assumption (i.e. by forcing the system to reach a periodic solution with a period of 24 h). We apply the model to calculate HO_x concentrations along the flight tracks for the STRAT, SUCCESS, and SONEX missions, and compare the results to 1 min average observations (Jaeglé et al., 1997, 1998a, 2000). The model calculations are constrained by the ensemble of observations along the flight tracks for species other than HO_x, including NO, O₃, H₂O, CO, CH₄, acetone, propane, ethane, and C₄₋₅ alkanes, as well as temperature, pressure, actinic fluxes, and aerosol surface area. Peroxide and CH₂O concentrations are calculated from chemical steady state. The concentration of NO_{*t*} (= NO + NO₂ + NO₃ + 2N₂O₅ + HNO₄) is assumed constant and is calculated in the model such that the calculated NO matches the observed NO at the time of day of observations. Acetone was not observed during either STRAT

or SUCCESS, and we infer its concentration from a relationship between CO and acetone obtained during PEM-West B (McKeen et al., 1997). Observations of H_2O_2 , CH_3OOH and CH_2O are available from SONEX (Snow et al., 2000); comparisons to the steady-state model values are presented by Jaeglé et al. (2000) and are discussed in Section 3.3 of the present paper.

Comparisons of simulated and observed $[\text{HO}_2]$ and $[\text{OH}]$ in Fig. 2 use instantaneous values $[\text{HO}_2]_{\text{inst}}$ and $[\text{OH}]_{\text{inst}}$ sampled in the model at the time of day of observation. Scaling of observations to 24 h averages (e.g., in Fig. 4) is done using the 24 h average concentrations from the model, for example:

$$[\text{HO}_2]_{24\text{h,obs}} = [\text{HO}_2]_{\text{inst,obs}} \frac{[\text{HO}_2]_{24\text{h,model}}}{[\text{HO}_2]_{\text{inst,model}}} \quad (\text{A.1})$$

We use a similar approach to scale instantaneous rates to 24 h averages (such as for ozone production in Fig. 4):

$$\text{Rate}_{24\text{h,obs}} = \text{Rate}_{\text{inst,obs}} \frac{\text{Rate}_{24\text{h,model}}}{\text{Rate}_{\text{inst,model}}} \quad (\text{A.2})$$

The 24 h average values of the primary HO_x production rate $P(\text{HO}_x)$ along the aircraft flight tracks (e.g., Fig. 3) are derived from the local concentrations of water vapor and acetone (Section 3.1). In cases where the model underestimates the observed levels of HO_2 , we increase $P(\text{HO}_x)$ in the model to match the observations (Fig. 3, bottom panel). This additional $P(\text{HO}_x)$ is intended to represent convective transport of other primary HO_x precursors to the upper troposphere such as peroxides and aldehydes (Fig. 1; Müller and Brasseur (1999)). It is implemented as a HO_x source with the same diel dependence as photolysis of CH_3OOH and with a stoichiometric $\text{OH} : \text{HO}_2$ ratio of unity.

The diel steady-state model is also used here to map HO_x concentrations and other parameters over the ranges of $[\text{NO}_x]$ and $P(\text{HO}_x)$ in the upper troposphere (e.g., Fig. 3). These calculations use the median conditions described in Table 1, but with NO_x and $P(\text{HO}_x)$ varying over their upper tropospheric ranges (1–5000 pptv for $[\text{NO}_x]$ and 5–5000 pptv d^{-1} for $P(\text{HO}_x)$). Similarly to above, the values of $P(\text{HO}_x)$ are specified by a generic source with the same diel dependence as photolysis of CH_3OOH and a stoichiometric $\text{OH} : \text{HO}_2$ ratio of unity.

References

- Arnold, F., Burger, V., Droste-Franke, B., Grimm, F., Krieger, A., Schneider, J., Stilp, T., 1997. Acetone in the upper troposphere and lower stratosphere: impact on trace gases and aerosols. *Geophysical Research Letters* 24, 3017–3020.

- Atkinson, R., et al., 1997. Evaluated kinetic and photochemical data for atmospheric chemistry – supplement VI. *Journal of Physical and Chemical Reference Data* 26, 1329–1499.
- Berntsen, T.K., et al., 1997. Effects of anthropogenic emissions on tropospheric ozone and its radiative forcing. *Journal of Geophysical Research* 102, 28101–28126.
- Borrmann, S., Solomon, S., Dye, J.E., Luo, B., 1996. The potential of cirrus clouds for heterogeneous chlorine activation. *Geophysical Research Letters* 23, 2133–2136.
- Bradshaw, J., Davis, D., Grodzinsky, G., Smyth, S., Newell, R., Sandholm, S., Liu, S., 2000. Observed distributions of nitrogen oxides in the remote free troposphere from the NASA global tropospheric experiment programs. *Reviews of Geophysics* 38, 61–116.
- Brown, S.S., Talukdar, R.K., Ravishankara, A.R., 1999. Reconsideration of the rate constant for the reaction of hydroxyl radicals with nitric acid. *Journal of Physical Chemistry* 103, 3031–3037.
- Brune, W.H., et al., 1998. Airborne in-situ OH and HO_2 observations in the cloud-free troposphere and lower stratosphere during SUCCESS. *Geophysical Research Letters* 25, 1701–1704.
- Brune, W.H., et al., 1999. OH and HO_2 chemistry in the North Atlantic free troposphere. *Geophysical Research Letters* 26, 3077–3080.
- Chatfield, R.B., Crutzen, P.J., 1984. Sulfur dioxide in remote oceanic air: cloud transport of reactive precursors. *Journal of Geophysical Research* 89, 7111–7132.
- Clarke, A.D., 1993. Atmospheric nuclei in the Pacific mid troposphere: their nature, concentration, and evolution. *Journal of Geophysical Research* 98, 20633–20647.
- Cohan, D.S., Schultz, M.G., Jacob, D.J., Heikes, B.G., Blake, D.R., 1999. Convective injection and photochemical decay of peroxides in the upper troposphere: methyl iodide as a tracer of marine convection. *Journal of Geophysical Research* 104, 5717–5724.
- Cooper, P.L., Abbatt, J.P.D., 1996. Heterogeneous interactions of OH and HO_2 radicals with surfaces characteristics of atmospheric particulate matter. *Journal of Physical Chemistry* 100, 2249–2254.
- Crawford, J., et al., 1996. Photostationary state analysis of the NO_2 –NO system based on airborne observations from the western and central North Pacific. *Journal of Geophysical Research* 101, 2053–2072.
- Crawford, J., et al., 1997. An assessment of ozone photochemistry in the extratropical western North Pacific: impact of continental outflow during the late winter early spring. *Journal of Geophysical Research* 102, 28469–28487.
- Crawford, J., et al., 1999. Assessment of upper tropospheric HO_x sources over the tropical Pacific based on NASA GTE/PEM data: net effect on HO_x and other photochemical parameters. *Journal of Geophysical Research* 104, 16255–16273.
- Davis, D.D., et al., 1996. Assessment of ozone photochemistry in the western North Pacific as inferred from PEM-West A observations during the fall 1991. *Journal of Geophysical Research* 101, 2111–2134.
- DeMore, W.B., et al., 1997. Chemical kinetics and photochemical data for use in stratospheric modeling. JPL Publications, 97-4.
- Dibb, J.E., Talbot, R.W., Loomis, M.B., 1998. Tropospheric sulfate distribution during SUCCESS: contributions from jet exhaust and surface sources. *Geophysical Research Letters* 25, 1375–1378.
- Dransfield, T.J., Perkins, K.K., Donahue, N.M., Anderson, J.G., Sprengnether, M.M., Demerjian, K.L., 1999. Temperature and pressure dependent kinetics of the gas-phase reaction of the hydroxyl radical with nitrogen dioxide. *Geophysical Research Letters* 26, 687–690.
- Ehhalt, D.H., Rohrer, F., 2000. Dependence of the OH concentration on solar UV. *Journal of Geophysical Research* 105, 3565–3571.
- Faloona, I., et al., 2000. Observations of HO_x and its relationship with NO_x in the upper troposphere during SONEX. *Journal of Geophysical Research* 105, 3771–3783.

- Faloona, I., Tan, D., Brune, W.H., 1998. Observations of HO_x in and around cirrus clouds. Atmospheric Effects of Aviation Program meeting, NASA SASS, Virginia Beach, VA.
- Folkens, I., et al., 1997. OH and HO₂ in two biomass burning plumes: source of HO_x and implications for ozone production. *Geophysical Research Letters* 24, 3185–3188.
- Folkens, I., Chatfield, R., 2000. Impact of acetone on ozone production and OH in the upper troposphere at high NO_x. *Journal of Geophysical Research* 105, 11585–11599.
- Gierczak, T., et al., 1998. Photochemistry of acetone under tropospheric conditions. *Chemical Physics* 231, 229–244.
- Hanson, D.R., Burkholder, J.B., Howard, C.J., Ravishankara, A.R., 1992. Measurement of OH and HO₂ radical uptake coefficients on water and sulfuric acid surfaces. *Journal of Physical Chemistry* 96, 4979–4985.
- Haywood, J.M., Schwarzkopf, M.D., Ramaswamy, V., 1998. Estimates of radiative forcing due to modeled increases in tropospheric ozone. *Journal of Geophysical Research* 103, 16999–17007.
- Jacob, D.J., et al., 1996. Origin of ozone and NO_x in the tropical troposphere: a photochemical analysis of aircraft observations over the South Atlantic Basin. *Journal of Geophysical Research* 101, 24235–24250.
- Jacob, D.J., 2000. Heterogeneous chemistry and tropospheric ozone. *Atmospheric Environment* 34, 2131–2159.
- Jaeglé, L., et al., 1997. Observations of OH and HO₂ in the upper troposphere suggest a strong source from convective injection of peroxides. *Geophysical Research Letters* 24, 3181–3184.
- Jaeglé, L., et al., 1998a. Sources of HO_x and production of ozone in the upper troposphere over the United States. *Geophysical Research Letters* 25, 1709–1712.
- Jaeglé, L., et al., 1998b. Sources and chemistry of NO_x in the upper troposphere over the United States. *Geophysical Research Letters* 25, 1705–1708.
- Jaeglé, L., et al., 1999. Ozone production in the upper troposphere and the influence of aircraft: approach of NO_x-saturated conditions. *Geophysical Research Letters* 26, 3081–3084.
- Jaeglé, L., et al., 2000. Photochemistry of HO_x in the upper troposphere at northern midlatitudes. *Journal of Geophysical Research* 105, 3877–3892.
- Koike, M., et al., 2000. Impact of aircraft emissions on reactive nitrogen over the North Atlantic Flight Corridor region. *Journal of Geophysical Research* 105, 3665–3677.
- Levy II, H., 1971. Normal atmosphere: large radical and formaldehyde concentrations predicted. *Science* 173, 141–143.
- Liu, S.C., et al., 1999. Sources of reactive nitrogen in the upper troposphere during SONEX. *Geophysical Research Letters* 26, 2441–2444.
- Logan, J.A., et al., 1981. Tropospheric chemistry: a global perspective. *Journal of Geophysical Research* 86, 7210–7254.
- Mari, C., Jacob, D.J., Bechtold, P., 2000. Transport and scavenging of soluble gases in a deep convective cloud. *Journal of Geophysical Research*, in press.
- McKeen, S.A., Gierczak, T., Burkholder, J.B., Wennberg, P.O., Hanisco, T.F., Keim, E.R., Gao, R.S., Liu, S.C., Ravishankara, A.R., Fahey, D.W., 1997. The photochemistry of acetone in the upper troposphere: a source of odd-hydrogen radicals. *Geophysical Research Letters* 24, 3177–3180.
- Mickley, L.J., Murti, P.P., Jacob, D.J., Logan, J.A., Rind, D., Koch, D., 1999. Radiative forcing from tropospheric ozone calculated with a unified chemistry-climate model. *Journal of Geophysical Research* 104, 30153–30172.
- Müller, J.-F., Brasseur, G., 1999. Sources of upper tropospheric HO_x: a three-dimensional study. *Journal of Geophysical Research* 104, 1705–1715.
- Prather, M.J., 1994. Lifetimes and eigenstates in atmospheric chemistry. *Geophysical Research Letters* 21, 801–804.

- Prather, M.J., 1996. Time scales in atmospheric chemistry: theory, GWPs for CH₄ and CO, and runaway growth. *Geophysical Research Letters* 23, 2597–2600.
- Prather, M.J., Jacob, D.J., 1997. A persistent imbalance in HO_x and NO_x photochemistry of the upper troposphere driven by deep tropical convection. *Geophysical Research Letters* 24, 3189–3192.
- Raes, F., 1995. Entrainment of free tropospheric aerosol as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer. *Journal of Geophysical Research* 100, 2893–2903.
- Roelofs, G.-J., Lelieveld, J., van Dorland, R., 1997. A three-dimensional chemistry/general circulation model simulation of anthropogenic derived ozone in the troposphere and its radiative climate forcing. *Journal of Geophysical Research* 102, 23389–23401.
- Schultz, M., et al., 1999. On the origin of tropospheric ozone and NO_x over the tropical South Pacific. *Journal of Geophysical Research* 104, 5829–5843.
- Singh, H.B., Kanakidou, M., Crutzen, P.J., Jacob, D.J., 1995. High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere. *Nature* 378, 50–54.
- Singh, H.B., Thompson, A.M., Schlager, H., 1999. SONEX airborne mission and coordinated POLINAT-2 activity: overview and accomplishments. *Geophysical Research Letters* 26, 2053–3056.
- Singh, H.B., et al., 2000. Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic. *Journal of Geophysical Research* 105, 3795–3805.
- Snow, J., et al., 2000. Peroxides during SONEX. *Journal of Geophysical Research*, in preparation.
- Solomon, S., Borrmann, S., Garcia, R.R., Portmann, R., Thomason, L., Poole, L.R., Winker, D., McCormick, M.P., 1997. Heterogeneous chlorine chemistry in the tropopause region. *Journal of Geophysical Research* 102, 21411–21429.
- Stevens, P.S., Mather, J.H., Brune, W.H., 1994. Measurement of OH and HO₂ by laser induced fluorescence at low pressure. *Journal of Geophysical Research* 99, 3543–3557.
- Talbot, R.W., Dibb, J.E., Loomis, M.B., 1998. Influence of vertical transport on free tropospheric aerosols over the central USA in springtime. *Geophysical Research Letters* 25, 1367–1370.
- Talukdar, R.K., Longfellow, C.A., Gilles, M.K., Ravishankara, A.R., 1998. Quantum yields of O(¹D) in the photolysis of ozone between 289 and 329 nm as a function of temperature. *Geophysical Research Letters* 25, 143–146.
- Thompson, A.M., Sparling, L.C., Kondo, Y., Anderson, B.E., Gregory, G.L., Sachse, G.W., 1999. Perspectives on NO, NO_y and fine aerosol sources and variability during SONEX. *Geophysical Research Letters* 26, 3073–3076.
- Toon, O.B., Miake-Lye, R.C., 1998. Subsonic aircraft: contrail and cloud effects special study (SUCCESS). *Geophysical Research Letters* 25, 1109–1112.
- Wennberg, P.O., Hanisco, T.F., Cohen, R.C., Stimpfle, R.M., Lapon, L.B., Anderson, J.B., 1995. In-situ measurements of OH and HO₂ in the upper troposphere and stratosphere. *Journal of Atmospheric Sciences* 52, 3413–3420.
- Wennberg, P.O., et al., 1998. Hydrogen radicals, nitrogen radicals and the production of ozone in the middle and upper troposphere. *Science* 279, 49–53.
- Wennberg, P.O., et al., 1999. Twilight observations suggest unknown sources of HO_x. *Geophysical Research Letters* 26, 1373–1376.
- Wohlfrom, K.-H., Hauler, T., Arnold, F., Singh, H.B., 1999. Acetone in the free troposphere and lower stratosphere: aircraft-based CIMS and GC measurements over the North Atlantic and a first comparison. *Geophysical Research Letters* 26, 2849–2852.
- Zuo, Y.G., Deng, Y.W., 1999. Evidence for the production of hydrogen peroxide in rainwater by lightning during thunderstorms. *Geochimica et Cosmochimica Acta* 63, 3451–3455.