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NO_y partitioning from measurements of nitrogen and hydrogen radicals in the upper troposphere

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Abstract. Recent studies using NO, NO_y, OH and HO₂ (HO_x) observations have postulated acetone and convection of peroxides as significant sources of HO_x in the upper troposphere (UT). This work focuses on the effect these additional HO_x sources have on the modeled NO_y partitioning and comparisons of the modeled NO_x/NO_y ratio to observations. The measured NO_x/NO_y ratio is usually much higher than predicted regardless of the presence of acetone in the model. The exception occurs for air parcels having low NO_y and O₃ values. For these air parcels the measured NO_x/NO_y ratio is much lower than the calculated ratio unless acetone is included in the model. In all cases acetone increases the fraction of NO_y that is peroxy acetyl nitrate (PAN) from typical values of much less than 0.1 to values as high as 0.35. Including acetone also reduces the scatter in a comparison between modeled and observed NO_x/NO_y ratios.

Introduction

Nitric oxide (NO), nitrogen dioxide (NO₂), hydroxyl radical (OH), and the hydroperoxy radical (HO₂) are involved in the principal production and loss reactions of ozone (O₃) in the upper troposphere (UT). The NO abundance directly affects the efficiency of the HO_x-initiated, catalytic ozone production cycle involving the oxidation of carbon monoxide (CO) [Ehhalt and Rohrer, 1994]. In addition OH is the principal oxidizing species in the UT [Logan, 1981], and reactions with NO and NO₂ (NO_x) can be important sinks for HO_x. Thus, determining how the UT region responds to changes in NO_x and the processes that control the partitioning of the reactive nitrogen reservoir (NO_y) is critical for understanding the photochemistry of this region and predicting the effects of anthropogenic perturbations such as aircraft emissions [Ehhalt and Rohrer, 1994; WMO, 1994].

The reactive nitrogen and hydrogen families are coupled by the reactions of OH with NO₂ and nitric acid (HNO₃), and HNO₃ photolysis. These reactions are also the principal gas-phase reaction pathways between NO_x and the less reactive NO_y species. In this work we use a box model constrained by observed NO and long-lived tracer species to examine the

partitioning of NO_y and HO_x concentrations in the UT at midlatitudes. The importance of these quantities in relation to O₃ production over the Pacific has been reviewed elsewhere [Folkins et al., 1998].

Observations

The observations reported here were obtained with instruments on board the NASA ER-2 high-altitude aircraft during the October-November 1995 (fall), January-February 1996 (winter), and July-August 1996 (summer) phases of the Stratospheric Tracers of Atmospheric Transport (STRAT) campaign. The flights originated from Moffett Field, California (38° N, 122°W), and Barbers Point Naval Air Station, Hawaii (21° N, 158°W). The data used here are descent data obtained from both locations at altitudes between 20 km to 8 km. Previous studies have used ER-2 data taken during level flight sections only as low as 10.5 km. The ER-2 payload consists of a suite of instruments designed for *in situ* measurements of reactive and long-lived species and aerosol parameters [Fahey et al., 1995]. Radicals measured are NO, OH, and HO₂. Long-lived species measured include NO_y, O₃, H₂O, CH₄, and CO. The sampling times for most measurements are less than 5 s. Aerosol measurements include condensation nuclei number for diameters between 0.008 and 2 μm, and number, surface area and volume of particles with diameters between 0.08 and 2 μm. Measurements of the non-methane hydrocarbons ethane, propane, butane, and others, were obtained at a lower time resolution by canister sampling with post-flight analysis. Photodissociative flux and column O₃ measurements were also obtained *in situ*. HCN interference in the NO_y measurements was not important in these flights based on conversion tests made during STRAT [S. G. Donnelly, personal communication]. Interference in the HO₂ measurement from RO₂ species (R = CH₃, C₂H₅) is estimated to be less than 20% under the kinetic conditions of the measurement.

Model description

The photochemical box model used here was previously used to analyze clean air and acetone photochemistry in the UT and lower stratosphere (LS) [Liu et al., 1992; McKeen et al., 1997]. Briefly, JPL 97 recommended rates and photolysis parameters were used in the model along with the acetone UV absorption cross sections and quantum yields of Gierczak et al. [1998]. In addition, in light of recent measurements, the JPL 94 rate for the reaction between OH and NO₂ was used [A. Ravishankara, personal communication, 1998]. The heterogeneous conversion of N₂O₅ to HNO₃ on aerosol surfaces was included using the observed aerosol surface area and a reactive uptake coefficient of 0.1. Non-methane hydrocarbon concentrations were inferred from the low time resolution *in situ* data and correlations with CO. NO_x (where NO₂ is determined from the steady state assumption) is held fixed in the diurnal calculations and NO_y is the dependent variable. Model input came from 60 second averages of the relevant flight data. The model is run to a diurnal

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steady state with NO_x, CO, O₃, CH₄, acetone and light hydrocarbons held constant. The family group of nitrogen species NO + NO₂ + NO₃ + 2N₂O₅ + HO₂NO₂ + HONO, and each species within this family, undergo full diurnal integration with instantaneous normalization to insure mass balance within the family group. HO_x and other short-lived intermediates (e.g. CH₂O and the peroxides) are likewise integrated over the full diurnal cycle.

The assumption of steady state within the model calculations is not possible to justify rigorously in this study given the relatively long lifetimes of PAN (25-45 days), NO_x, and HNO₃ in the UT. Moreover, without further information regarding NO_y partitioning, it is not possible to determine the appropriateness of the steady state assumption for a particular air mass. Because time-dependent box model calculations are inherently ill-posed without knowing initial conditions and integration times, the steady-state calculations provide the only logical reference point from which box-model and observations can be compared. It is important to keep in mind that the box-model results are both dependent and limited by the steady state assumption within the comparisons presented here.

The possible impact of acetone on OH and PAN has been discussed by Singh *et al.* [1995]. The importance of incorporating acetone and other odd-hydrogen radical sources in order to match observed HO_x values in the UT is discussed in detail by Wennberg *et al.* [1998], Jaeglé *et al.* [1997], and McKeen *et al.* [1997]. Since acetone was not measured during STRAT, mixing ratios were inferred from observed correlations between acetone and CO in the UT and LS during other field campaigns over the Pacific [McKeen *et al.*, 1997; Singh *et al.*, 1997]. The model can also be used to quantify the amount of acetone (or other radical source) needed in order to match modeled HO_x with the observations.

Discussion

A comparison between modeled and observed OH values for the three measurement periods is presented in Figure 1. All figures presented here have corresponding data points for the UT (circles). For the fall and winter STRAT flights, calculated OH based only on O₃, H₂O and CH₄ oxidation sources (Figure 1a, red and green points) is consistently less than observed values. For these flights the inclusion of acetone in the model at levels inferred from the observed CO data increases the calculated OH and significantly improves the comparison (Figure 1b). For the fall data the addition of acetone brings approximately half of the model levels to values within the uncertainty of the OH measurement (25%, dotted lines), while almost all of the winter model values fall within the uncertainty limits of the measured data. This is consistent with the other HO_x studies noted above. In contrast, the calculated OH for the summer flights based only on O₃, H₂O and CH₄ oxidation sources is often comparable or even greater than the observed values (Figure 1a, purple points). No process has been identified that would lower model OH values to fit the observations. However, these data points correspond to low values of NO (<20 pptv, with measurement accuracies of ±5 pptv) and the uncertainties in the observations and subsequently model calculations for these points are somewhat higher than for the other data points.

The addition of acetone to the model has the largest effect on the OH levels that are under-predicted by the model without acetone (Figure 1). The sensitivity of each modeled OH data point to the addition of acetone depends upon the relative HO_x production from H₂O and other sources. This sensitivity could reflect a seasonality in the sources of HO_x in the UT.

A seasonality in the sources of HO_x is suggested by comparison of the amount of acetone inferred from the CO measurements to the amount required in the model to match the observed OH values. The inferred acetone levels are always

between 300 and 500 pptv. In contrast the required acetone levels for the model OH to match the observations range from over 1000 pptv during the fall to less than 300 pptv in the winter. These required values and the implied seasonal dependence are consistent with acetone values ranging from 1440 pptv at 10 km in July to less than 400 pptv in February, as reported by Arnold *et al.* [1997]. The implied change in the correlation between CO and acetone awaits confirmation from *in situ* measurements. Since acetone is only one possible source of HO_x in the UT, the seasonality could also be caused by changes in other sources such as peroxides or formaldehyde.

For each of the points in Figure 1, the corresponding NO_x/NO_y value is shown in Figure 2. The observed NO_x/NO_y ratio utilizes steady-state NO₂ values since NO₂ was not measured. For all three time periods, most calculated NO_x/NO_y ratios at 38° N are less than the observed ratio with and without acetone included in the model. The disagreement is slightly greater with acetone although including acetone also reduces the scatter in a comparison between modeled and observed NO_x/NO_y ratios. In addition, no model values in the fall data set are higher than the observed values when the ± 20% observational uncertainty is included. This is consistent with previous tropospheric measurements of NO and NO_y that exhibited higher NO_x/NO_y ratios than could be modeled. Chatfield [1994] and Jacob *et al.* [1996] argue that missing HNO₃ to NO_x conversion processes must be present. Processes affecting UT air masses with time scales less than a couple of weeks, that are not considered in the steady state model, such as episodic removal of HNO₃ by clouds or lightning generated NO_x, would also explain the fall model ratios in Figure 2. In contrast, for data from 21° N during winter and summer the calculated NO_x/NO_y ratios without acetone (Figure 2a, green and purple points) are significantly higher than the observed values. With acetone, the calculated NO_x/NO_y ratios decrease to become comparable to observed values. These points span almost the entire range of NO_x/NO_y ratios observed during STRAT and are characterized by low amounts of NO_y (175 - 200 pptv vs. 350 - 850 pptv at other times) and O₃ (37 - 43 ppbv vs. 70 - 90 ppbv at other times). These low values of NO_y and O₃ are indicative of clean oceanic lower-tropospheric air [Jacob *et al.*, 1996.]. These data are also characterized by much lower NO₂/NO ratios than the other descent data (0.10 - 0.15 vs. 0.22 - 0.25). This is caused by the lower O₃ values observed during the January and July time periods.

The altitude distributions of the data in Figure 2 are shown in Figure 3. For each profile, the tropopause altitude is identified using the measured temperature profile. Included in this figure are data points (triangles) taken in the lower stratosphere (LS). In the LS the model NO_x/NO_y values are less than or equal to the observed values. This is true for all three seasons and is consistent with other modeling studies using ER-2 data [R. S. Gao, private communication, 1998]. In part because the inferred values of acetone are low in the stratosphere, the addition of acetone to the model does not significantly affect the comparison. In the UT for the descents at 38° N, the model NO_x/NO_y values are lower by up to a factor of three than the observed values at all altitudes. The model NO_x/NO_y values at 21° N in winter and summer are significantly higher than the observed values in the region between 2 and 4 km below the tropopause when acetone is not included in the model. As shown in Figure 2, these differences occur at all NO_x/NO_y values and hence are not a function of the absolute value of the NO_x/NO_y ratio. The differences more likely reflect an additional NO_x sink that results from extra OH (the model usually underestimates OH without acetone) or formation of PAN. PAN formation occurs when NO₂ reacts with the peroxy acetyl radical formed from acetone photolysis. Depending upon the relative concentrations of NO and NO₂, PAN formation can be a significant sink of NO_x.

The altitude distribution of the modeled PAN/NO_y ratio is shown in Figure 4. In the LS the ratio is much less than 0.1 with

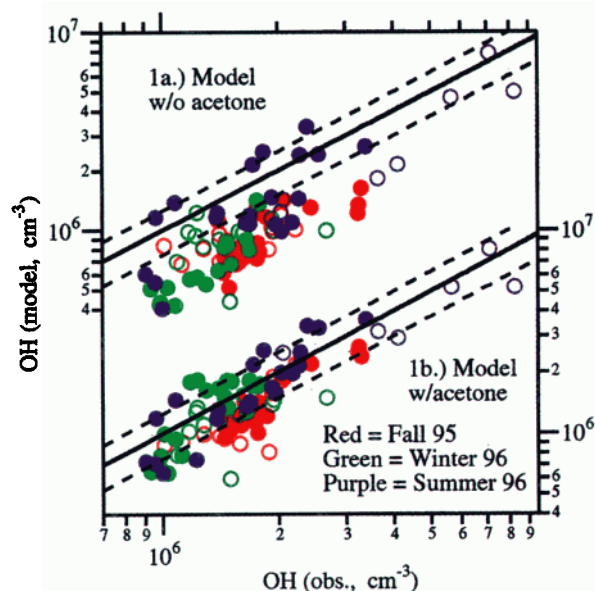


Figure 1. Modeled vs. observed tropospheric OH values. The solid line is the 1:1 line and the dashed lines denote $\pm 25\%$ from this line. Solid(open) symbols are from descents at 21°N(38°N). Model results are shown without (a) and with (b) acetone included. In both cases, the N₂O₅ heterogeneous reaction is included.

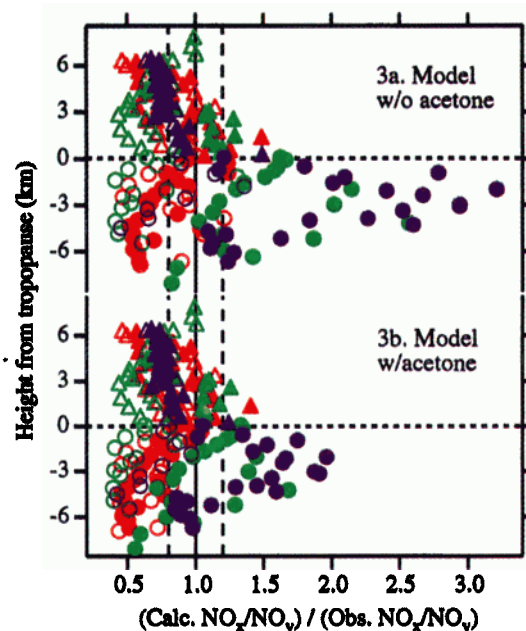


Figure 3. Ratio of the calculated to observed NO_x/NO_y ratio as a function of height relative to the tropopause. Other details same as Figure 1 except dashed lines denote $\pm 20\%$.

or without acetone included in the model. In the UT the ratio without acetone is less than 0.1 except for a few points from descents at 38° N (Figure 4a). When acetone is included, the PAN/NO_y fraction increases dramatically (Figure 4b). The largest changes occur in the summer data at 21° N and at altitudes between 2 and 6 km below the tropopause. The addition of acetone can increase both PAN and HNO₃, but PAN formation is found to predominate whenever daytime NO is less than 60 pptv or the NO₂/NO ratio is greater than 0.25. This is because the peroxy acetyl radical from acetone photolysis requires high enough NO levels in order to serve as an effective HO_x source with a subsequent increase in HNO₃. With low NO_y and NO levels for the summer and winter UT data, the effect of the NO₂

reaction with the peroxy acetyl radical to form PAN exceeds the effect of increased HO_x on HNO₃. Although many of the high PAN/NO_y values shown in figure 4 are higher than the 0.15 average value reported by Kondo et al. [1997] for UT maritime conditions at ~ 9.5 km, the associated PAN mixing ratios are still quite low (10-50 pptv between 9 and 17 km) for those points due to correspondingly low NO and NO_y. The median values of NO, O₃, and model PAN for the winter STRAT flights out of Barbours Point from 8 to 12.7 km are 36 pptv, 33 ppbv, and 28 pptv, respectively. While the NO and O₃ values are quite similar to medians reported by Kondo et al. for winter, maritime samples over the same altitude region (NO, 43 pptv; O₃, 37 ppbv) our

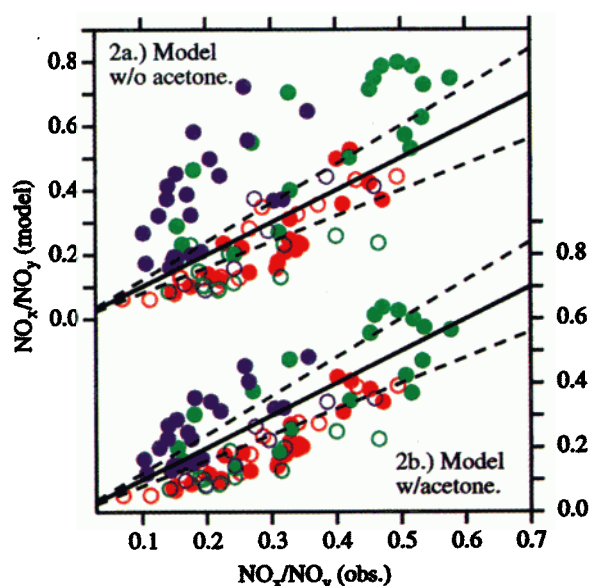


Figure 2. Modeled vs. observed tropospheric values of NO_x/NO_y. Other details same as Figure 1 except dashed lines denote $\pm 20\%$.

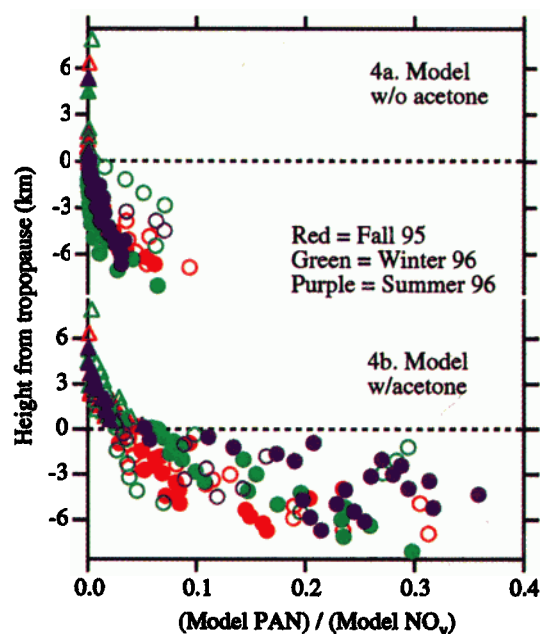


Figure 4. Calculated PAN/NO_y ratios as a function of height relative to the tropopause. Other details same as Figure 1.

median model PAN values are about half of their 58 pptv observed PAN median value.

Interpretation of the model PAN results are subject to two caveats. First, the temperature dependence of the photolysis cross-section of PAN has only been measured down to 250 K. Therefore, depending upon how the cross section varies with decreasing temperature the modeled PAN could be too high or too low. Second, the lifetime of PAN in the UT is approximately a month, which limits the applicability of the steady-state calculation. In this case the error in the modeled PAN depends upon the source location and rate of transport.

To test the sensitivity of NO_y partitioning to the heterogeneous hydrolysis of N₂O₅, model runs were performed with and without this reaction. The resulting differences in NO_y partitioning are much smaller than those that result from the addition of acetone for all of the flight data used in this study. However the model results without the N₂O₅ reaction did show an increase in the calculated NO_x/NO_y ratio with approximately half of the fall values falling within the experimental uncertainty of the observations. As pointed out by McKeen *et al.*, [1997], the model would be consistent with the observations if the reactive uptake coefficient for the N₂O₅ reaction is much less than 0.1 in the UT. For the summer and winter flights with low NO_y, O₃ and accompanying aerosol, model results are insensitive to assumptions of N₂O₅ conversion.

Summary

Simultaneous *in situ* observations of HO_x, NO, and NO_y were combined with a box model to characterize the coupling between HO_x and NO_y and the NO_y partitioning in the UT/LS region of the atmosphere. In agreement with earlier studies of HO_x concentrations observed in the UT during STRAT, a source in addition to O¹D + H₂O is usually required for the modeled HO_x to match the observations. However for the summer flights at 21° N modeled HO_x is sometimes higher than the observed values even without an additional source.

The inclusion of acetone in the model as an additional HO_x source significantly increases the fraction of NO_y that is PAN in the UT, with PAN/NO_y ratios as high as 0.35 predicted for all three seasons but at different altitudes relative to the tropopause. This served to decrease the modeled NO_x/NO_y ratio to varying degrees for all of the data studied. The much higher PAN/NO_y ratios calculated when acetone is included in the model suggest that simultaneous *in situ* measurements of HO_x, acetone, NO, NO_y, PAN and/or HNO₃ would be a valid test of the importance of acetone in UT chemistry, and also indicate the validity of the steady state assumption for modeling NO_y speciation.

For most of the flights the modeled NO_x/NO_y ratio in the UT was much lower than the observed ratio even without the addition of acetone to the model. However, for flights characterized by low NO_y and O₃ values, all at 21° N in winter and summer, the modeled NO_x/NO_y was significantly higher than the observations unless acetone was included in the model. This is in contrast to previous studies that consistently underpredicted the NO_x/NO_y ratio.

Because HO_x concentrations and NO_y partitioning are not simultaneously reproduced for all observations, these model comparisons suggest that there is additional chemistry not accounted for in the model, and/or that the dynamics are affecting the NO_y and HO_x reservoirs in a way that cannot be simulated with a steady-state model.

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