NOx Loss and Lifetime Via Its Reaction with HOx in the Upper Troposphere


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A23J-3379

Motivation

• NOx([NO + NO2]) is important in controlling O3 production and HOx ([OH + HO2]) concentrations in the troposphere.

• In the upper troposphere (UT), where O3 is an important greenhouse gas, decades of studies have indicated there is a fundamental challenge in understanding NOx chemistry due to the discrepancy between measured and modeled NOx.

• Recent laboratory and field studies1,2 have indicated that the k2b rate constant should be lower to account for the branching to produce peroxynitric acid (HOONO); however, other recent laboratory studies3 have shown that there is another potential important source of HNO3 in the upper troposphere (HO + NO → HNO3, figure to the left).

We report upper limits for k2b and k1b inferred from observations during a Lagrangian flight as well as the relationship of k2b with increasing k2a.

Table 1: Measurements used to calculate the rate constants and the accuracy for each measurement. The accuracy is 1σ unless noted otherwise.

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Figures

21 June 2012 Flight During DC-3

During this time period, both the CIMS plus AMS and IC measurements of HNO3,(p+g) measure a production of ~50 pptv (Fig. 4a) while the measured NO3 and NO decay is ~50 pptv and 250 pptv, respectively (Fig. 4b). The higher NO3 decay than HNO3 production is due to the production of other oxidized species, peroxynitrates and nitrates and alkyl and multifunctional nitrates.

Upper Limits for the Production of HNO3

We seek to follow a uniform air mass in time as the chemicals react. To do so we require winds blowing from the same direction, and an absence of clouds to prevent the uptake of HNO3. In addition it is simple to understand the chemistry if there is little variation in OH and HO2 concentrations. That is the case, the variance in the production rate of HNO3 only depends upon the change in NO or NO2. This occurred during the blue portion of the flight (Fig. 2). The range about the median values is 9.5±10 and 6.7±10 molecules/cm3 for OH and HO2, respectively (Fig. 2).

Fig. 1. The flight path (grey) of the NASA DC-8 during 21 June 2012 flight sampling the decay of a nucleate convective system. The DC-8 took off at 12:00 UTC and flew for ~6 hours. The DC-8 sampled within 10 km of the line at ~11:00 UTC and flew for ~6 hours. The DC-8 sampled within 10 km of the line at ~11:00 UTC and flew for ~6 hours.

Production of HNO3 and Loss of NO during 21 June 2012 Flight

To calculate the rate constant for either k2a or k1b, we set the other rate to zero. Then, we divide the slope by the observed dHNO3/(p+g)/dt. The value are then for k1b is 2.1±0.3×10−12 cm3/molec./s and for k2a is 2.1±0.3×10−12 cm3/molec./s. (a) Shows the calculated rate constant for k2a and k1b.

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Conclusions

• We report the observations of total HNO3 loss rate production rate at T = 2±5 K and P = 230 hPa (M = 7.3±10−4 molec/cm3/s).

• The k2b rate constant recommended by PPL and IUPAC need to decrease by at least 20% to 35% to be in agreement with these observations and the findings of Henderson et al.(2012).

• We find that the k1b rate constant needs to decrease by ~4% for each increase in β = 0.001 (increase of k2b of ~7±10−5 molec/cm3/s).

• Using the slower k2b rate constant compared to currently recommended increases HOx and O3 concentrations.

Acknowledgements

The authors would like to acknowledge Donald Blake, Jack Dibb, and Jose Fermance and their respective groups for observations used in this analysis.

The authors would like to acknowledge NASA Grant Number NNX10AR13G and NSF GRFP under Grant No. OISE 1165460.

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We calculated the upper limits for k2b and k1b (Fig. 5a and 5b). Assuming that Rb and R2a are the only source of HNO3. The calculated k2b rate constant ranges from 4.6 (4.2±10−13 to 10−12) cm3/molec/s, which is statistically similar (within 1σ) to the value recommended from Henderson et al. (2012) (Fig. 7).

The k2b rate constant is a factor of 2 higher than laboratory values.

Comparison to Other Studies

We use an instantaneous steady state model to calculate the impacts of slower k2a on OH and O3 production. O3 production is defined as

where k is the rate constant, D is the diffusion, and (p+g) is the production rate. The value are then for k1b is 2.1±0.3×10−12 cm3/molec./s and for k2a is 2.1±0.3×10−12 cm3/molec./s.

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Impacts of Slower HNO3 Production

We use an instantaneous steady state model to calculate the impacts of slower k2a on HNO3 and O3 production. O3 production is defined as

where k is the rate constant, D is the diffusion, and (p+g) is the production rate. The value are then for k1b is 2.1±0.3×10−12 cm3/molec./s and for k2a is 2.1±0.3×10−12 cm3/molec./s.

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