For DC-3, we utilized the measurements of CH$_3$O$_2$NO$_2$ to remove the interference in the NO$_2$ measurements. Observations of HNO$_3$ were made using chemical ionization mass spectrometry. In this technique, air is reacted with HNO$_3$, forming HF·NO$_3$. HNO$_3$ is calibrated with standard additions of gas-phase HNO$_3$ approximately hourly during flight. Observations of NO$_2$ and CH$_3$O$_2$NO$_2$ were made using Thermal Dissociation-Laser Induced Fluorescence (TD-LIF). The NO$_2$ cycle. The t below each reaction represents the approximate lifetime in seconds to HONO at temperatures between 225 and 230 K. The branching ratios for HO$_2$ and NO$_3$ to react with NO$_2$ and H$_2$O are H and R.

**DC-3 and SEAC4RS Observations of NO$_2$, CH$_3$O$_2$NO$_2$ and HNO$_3$ Observations of NO$_2$ and CH$_3$O$_2$NO$_2$ with TD-LIF**

Observations of NO$_2$ and CH$_3$O$_2$NO$_2$ were made using Thermal Dissociation-Laser Induced Fluorescence (TD-LIF). Briefly, NO$_2$ is detected via excitation of a neutral rubidium feature in the NO$_2$ spectrum at 585 nm; then, the resulting fluorescence is collected by a PMT orthogonal to the laser axis. The instrument is calibrated with an NO$_2$ standard from Praxair (4.67±0.26 ppm for DC-3 and 4.79±0.23 ppm for SEAC4RS). CH$_3$O$_2$NO$_2$ is observed by coupling thermal dissociation with NO$_2$ detection. Ambient air is heated to 60°C for CH$_3$O$_2$NO$_2$. The individual quantities are determined by subtraction (e.g., CH$_3$O$_2$NO$_2$ is defined as the difference between the respective heated channels and the unheated NO$_2$ channel).

CH$_3$O$_2$NO$_2$ was added to the Berkeley TD-LIF measurement suite for the first time during DC-3, following the analysis of ARCTAS observations by Browne et al. To have NO$_2$ measurements in the UT free of interferences, we have determined that you either need to (1) have a residence time of less than 100 ms or (2) have an NO$_2$ standard from Praxair.

**DC-3, and SEAC4RS provide measurements of NO$_2$ corrected for CH$_3$O$_2$NO$_2$ interferences to investigate HNO$_3$ production in the UT.**

**CH$_3$O$_2$NO$_2$ and HNO$_3$ Production Downwind of Convection**

During May and June, 2012 and August and September, 2013, the NASA DC-8 measured the chemical composition detraining (outflow) from deep convection and aging from deep convection. Storms were measured over Colorado, Oklahoma, Texas, and Alabama (DC-3) and over Texas and southeast United States (SEAC4RS). During DC-3, five flights were dedicated to the aging of outflow, and for both missions, air was sampled between 220 and 230 K (temperature range of maximum detrainment) to be affected by convection.

**SEAC4RS and DC-3**

**Conclusions**

- The DC-8 payload allowed for in-depth analysis of NO$_x$ chemistry in the UT after convection.
- CH$_3$O$_2$NO$_2$ and HNO$_3$ are both import as NO$_x$ sinks in the first 6 – 12 hours of photochemistry of convective outflow.
- During a Lagrangian flight in DC-3, the production rates of CH$_3$O$_2$NO$_2$ and HNO$_3$ were ~ 20 ppt/vol and 15 pptv/hr, respectively.
- The median production rate of HNO$_3$, and CH$_3$O$_2$NO$_2$ qualitatively are similar in the two campaigns.
- Without the interference from CH$_3$O$_2$NO$_2$, the production and rate constants for HNO$_3$ were investigated.

We calculated new rate constants of 7.4(±1.7)x10$^{-12}$ cm$^3$/molec/s, which is slower than laboratory determined rate constant as well as the recommendations from JPL and INPAC, but consistent with the analysis of Henderson et al.

We hypothesize that HONO is more stable at the temperatures and pressures of the UT, creating the bias in the laboratory results for HNO$_3$ production.

The new rate constant increases the NO$_x$ lifetime in the UT, impacting O$_3$ production in the UT.

**Using the Data to Constrain HNO$_3$ Production and Rate Constant for OH and NO$_2$ at T = 225 K and P = 227 hPa**

**Figure 4.** dHNO$_3$/dt versus NO$_2$ from the DC-3 06/21/2012 flight. The data used in the fits is taken at UTC 7.5 x 10$^{-19}$ s$^{-1}$, HONO at 7 x 10$^{-19}$ s$^{-1}$, which is equal to k[HO]. The data is at T = 225 K and P = 227 hPa. The thinner red line is the standard error of the slope.

A comparison of laboratory measured OH + NO$_2$ rate constants as well as the calculated rate constant from this study is shown in Figure 5. For the laboratory rate constants, an 20% reduction has been applied to account for branch into HOONO (20% branching). Subtracting the reported rate constant by the calculated rate (7.4(±1.7)x10$^{-12}$ cm$^3$/molec/s) would need to be applied to get the laboratory measurements or recommendations from JPL to match our observed rate constant.

Henderson et al. used NO$_2$ observations, after correcting for CH$_3$O$_2$NO$_2$ interference, in the UT from INTEX-NA, and they calculated a rate constant of 6.5x10$^{-12}$ cm$^3$/molec/s at the same T and P (45% higher than our calculated value).

**Median Production in Both Campaigns**

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**References**