Observations of atmospheric methyl peroxy nitrate during the Deep Convective Clouds and Chemistry experiment

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A41B-0028

Summary

- The first direct observations of atmospheric methyl peroxy nitrate ($CH_3O_2NO_2$) have been made using TD-LIF.

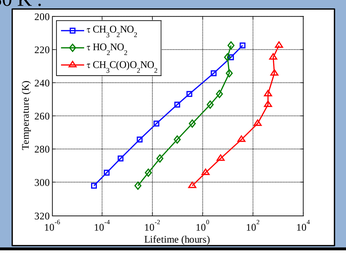
Motivation

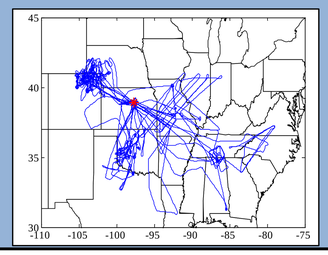
- Deep convection transports ozone precursors, RO_x ($OH + HO_2 + RO_2 + CH_3O_2$) and anthropogenic and lightning NO_x ($NO + NO_2$) to upper troposphere (UT).
- Ozone (O_3) is a greenhouse gas in the UT, but there is uncertainty in the balance of O_3 sources (transport versus chemistry) and chemistry of O_3 precursors—especially NO.
- Colder temperatures make thermally unstable peroxy nitrates, pernitric acid (HO_2NO_2) and $CH_3O_2NO_2$, important reservoirs for NO_x and RO_x in the UT, affecting O_3 chemistry.
- Deep Convective Cloud and Chemistry experiment (DC-3) provided direct measurements of RO_x, NO_x, the precursors and the reservoirs to test our understanding of this chemistry.

DC-3

During May and June, 2012, the NASA DC-8, along with two other planes, measured the chemical composition of air entraining (inflow) into deep convection, detraining (outflow) from deep convection, and aging from deep convection.

Storms were measured over Colorado, Oklahoma, Texas, and Alabama, and five flights were dedicated to the aging of the outflow from deep convection. The outflow occurred between 220 and 230 K .





Conclusions

The first ever direct observations of $CH_3O_2NO_2$ in the atmosphere were made during DC-3.

- Measurements are above the limit of detection (S/N = 2) at temperatures less than 255 K.
- There was minimal calculated interference from HO_2NO_2 (~5 %) with $CH_3O_2NO_2$ measurements.

During the aging of the outflow:

- $CH_3O_2NO_2$ reaches 100-150 pptv after 1 day
- $CH_3O_2NO_2$ makes up between 5 and 15% of the NO_y budget with a median of 10% in aged outflow.
- $CH_3O_2NO_2$ is as abundant as HO_2NO_2 during the aging process making it equally effective as a temporary sink for RO_x and NO_x in convective outflow.

Significant levels (> 500 pptv with a maximum of 880 pptv) of $CH_3O_2NO_2$ were observed on June 22, 2012, near isolated convection being influenced by a wildfire.

Measuring $CH_3O_2NO_2$ in the Deep Convective Clouds and Chemistry Experiment

$CH_3O_2NO_2$ was added to the Berkeley TD-LIF measurement suite[1,2]. for the first time during DC-3, following the analysis of ARCTAS observations by Browne et al.[3] who inferred $CH_3O_2NO_2$ is abundant in the upper troposphere where temperatures are below 240K indirectly interpreting deviations of observed "NO_2" from photostationary state with NO as $CH_3O_2NO_2$. $CH_3O_2NO_2$ rapidly dissociates at room temperature (τ = 980 ms at 25°C) making it essential to either correct NO_2 measurements for its presence or to interpret "NO_2" measurements as the sum of NO_2 and $CH_3O_2NO_2$ if the residence time within the airplane prior to detection is long compared to this lifetime. The new $CH_3O_2NO_2$ channel was set to 60°C and the residence time in the NO_2 channel was reduced to 500 ms. We use the 60°C measurements to infer an interference in that channel that was a maximum of 10% of the NO2.

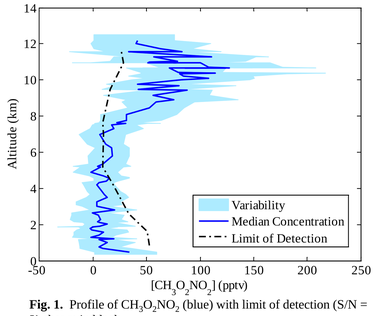


Fig. 1. Profile of $CH_3O_2NO_2$ (blue) with limit of detection (S/N = 2) shown in black.

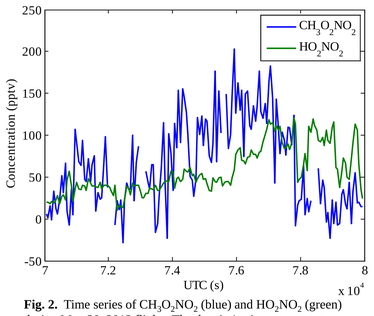


Fig. 2. Time series of $CH_3O_2NO_2$ (blue) and HO_2NO_2 (green) during May 30, 2013 flight. The data is 1 minute averages.

Other measurements made simultaneously on the DC-8 during DC-3 included NO_2, ΣPNs (PAN + PPN + $CH_3O_2NO_2$ + HO_2NO_2 + . . .), and ΣANs[2], numerous organic molecules[3,4,5], NO_y[6] , j-values[7], OH[8], and HO_2[8].

Fig. 1. shows the vertical profiles of $CH_3O_2NO_2$ for the entire DC-3 campaign. The blue line is the median profile for the entire mission, and the blue shaded area bounds the central 50%. The black line shows the limit of detection (S/N = 2) for one minute measurements, which depnds on the ambient NO_2 that is subtracted.. Measurements made above ~7 km (or ~255 K) are above the limit of detection.

Fig. 2. shows HO_2NO_2 and $CH_3O_2NO_2$ measurements. As HO_2NO_2 is also has a weak bond and short lifetime to thermal dissociation, we checked that our thermal design was capable of discriminating between the two molecules and detection only $CH_3O_2NO_2$. These observations confirm any interference is 5% of HO_2NO_2 or less.

Table 1. Methods used to measure other speciated NO_y on the NASA DC8 during DC-3.

NO_y Species	Method	Reference
NO	Chemiluminescence	Ryerson et al. (2000)[6]
HO_2NO_2	Chemical Ionization Mass Spectrometry	Kim et al. (2007)[10]
HNO_3	Chemical Ionization Mass Spectrometry	Crounse et al. (2006)[11]

Production of Thermally Unstable Peroxy Nitrates Observed In Aged Outflow

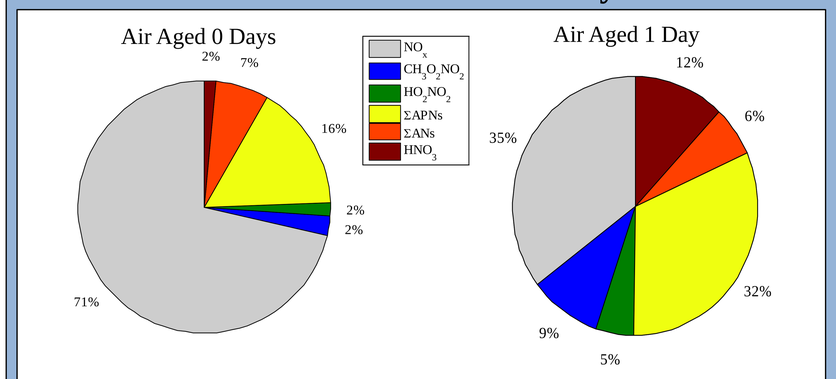


Fig. 3. Pie chart of the median initial NO_y partitioning during DC-3 (left) and median partitioning after 1 day of aging (right).

After one day of aging, $CH_3O_2NO_2$ is almost as important as a NO_x sink as HNO_3. As the air subsides on subsequent days, NO_x is released more rapidly from the thermally unstable reservoir ($CH_3O_2NO_2$) compared to the very slow release by reaction of OH with HNO_3.

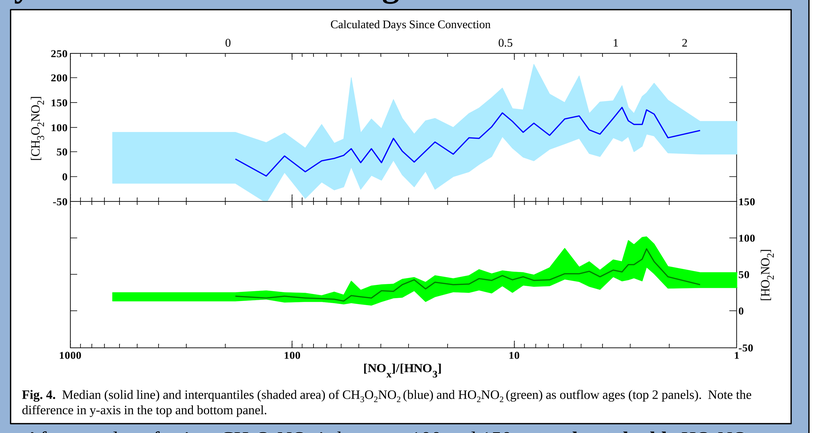


Fig. 4. Median (solid line) and interquantiles (shaded area) of $CH_3O_2NO_2$ (blue) and HO_2NO_2 (green) as outflow ages (top 2 panels). Note the difference in y-axis in the top and bottom panel.

After one day of aging, $CH_3O_2NO_2$ is between 100 and 150 pptv, **about double** HO_2NO_2. This corresponds to $CH_3O_2NO_2$ being **~10% of NO_y** whereas HO_2NO_2 is less than 10% of NO_y. The calculated time since convection (age) shown at top is derived from the rate of conversion of NO_x to HNO_3 following Bertram et al., 2007[11].

NO_y Species During Outflow Aging

Table 2. Median concentrations, in pptv, of NO_y species measured on NASA DC8, at corresponding calculated ages of the air mass.

Age (days)	NO_x	$CH_3O_2NO_2$	HO_2NO_2	ΣAPNs[d]	ΣANs	HNO_3
0[a]	1200	40	28	260	110	24
0.5[b]	790	107	50	277	160	78
1[c]	400	107	57	362	71	136

a) Median initial concentrations calculated entire DC-3 experiment.
b) Median concentrations calculated from the end of 06/21 flight.
c) Median concentrations calculated from entire DC-3 experiment.
d) ΣAPNs = ΣPNs – ($CH_3O_2NO_2$ + HO_2NO_2)

Significant Abundances Observed at Low Temperature in the UT

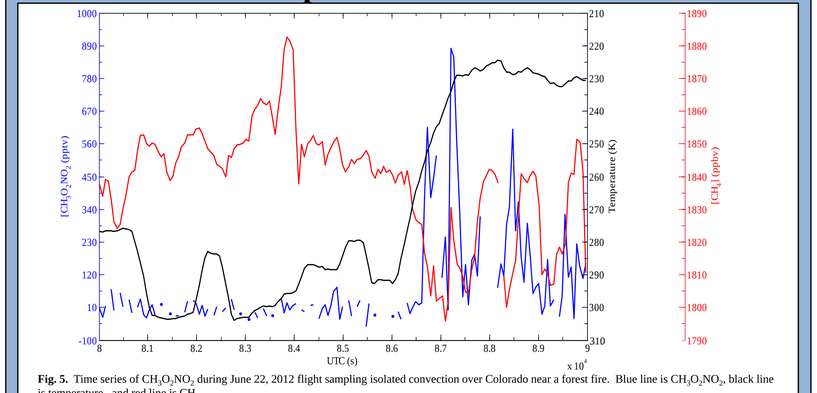


Fig. 5. Time series of $CH_3O_2NO_2$ during June 22, 2012 flight sampling isolated convection over Colorado near a forest fire. Blue line is $CH_3O_2NO_2$, black line is temperature., and red line is CH_4.

The maximum $CH_3O_2NO_2$ was observed on June 22, 2012, on a flight sampling convection over Colorado near a wildfire. **The maximum concentration was 880 pptv with sustained levels > 500 pptv**. The maximum $CH_3O_2NO_2$ occurred at low concentrations of HO_2NO_2 and NO_2 (both < 30 pptv) and low concentrations of methane (less than 1840 ppbv), indicating the air had not been recently influenced by convection and that photochemistry had aged the plume significantly since injection into the UT by a storm.

Acknowledgements

The authors would like to acknowledge NASA Grant Number NNX08AR13G and NSF GRFP under Grant No. DGE 1106400.

The authors would also like to acknowledge William Brune for the OH and HO_2 measurements, Bruce Anderson for aerosol surface area measurements, Eric Apel for OVOC measurements, and the DC-3 science team.

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