Final Report

SONEX-Hydrogen Peroxide, Methylhydroperoxide and Formaldehyde Measurements

NASA NAG 2-1108
(URI Log #: 5-35840)

July 15, 1999

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Summary

We measured gas phase H_2O_2, CH_3OOH, and CH_2O on board the NASA DC-8 during the SONEX field mission, presented preliminary results at three scientific meetings, participated in two data workshops and contributed to joint publications of final results. The observations of peroxides and formaldehyde were instrumental in assessing odd-hydrogen radical chemistry, ozone chemistry, and in tracing meteorological transport paths.

Introduction

The NASA AEAP SASS SONEX field mission was directed towards understanding the impact of subsonic aircraft exhaust products on the photochemistry of the upper troposphere and lower stratosphere. A suite of *in-situ* chemical instruments, grab sample and remote sensing instrumentation was flown on board the DC-8 aircraft. Key photochemical measurements included: hydrocarbons, halogenated hydrocarbons, nitric acid vapor and aerosol nitrate, oxygenated hydrocarbons including peroxyacetylnitrate, acetone and formaldehyde, hydroxy and perhydroxyl radicals, ozone, oxides of nitrogen, hydrogen peroxide and methylhydroperoxide. Research flights focused on the North Atlantic air traffic corridor between North America and Europe with most sampling above 8km altitude. Flight plans included observations within and near the flight corridor before and after commercial traffic to determine direct impacts of aircraft. Also, survey flights to ascertain "background" chemical composition were flown. The airports of operation were Bangor, ME, Shannon Ireland, and Lajes AFB, Azores, Portugal. The campaign was conducted from mid-October to mid-November 1997.

Methods

H_2O_2, CH_3OOH, and CH_2O were measured using the method of Lee et al., (1995) and Lazrus et al., (1988), respectively. Nominal detection limits were 10, 25 and 50 pptv, respectively, for these gases. Well over 60% of the CH_2O observations were below the detection limit, and approximately 50 % of the CH_3OOH observations were below its detection limit. The temporal resolution was 2.5 minutes and 5 minutes for the peroxides and formaldehyde.

Results

A direct influence of aircraft exhaust on the measured species was not apparent in the peroxide and formaldehyde data at the analytical method levels of quantification and time resolution. Principal factors affecting the concentration of these species were geographical and meteorological. Cold temperatures, low specific humidity and high solar zenith angles (low amounts of ultra-violet light), characterized the altitude, latitude and season sampled. These conditions contributed significantly to the generally low ambient concentrations of H_2O_2, CH_3OOH and CH_2O found in SONEX. Table 1 lists data from the SONEX mission in comparison to three prior field campaigns, illustrating the relatively low concentrations found during SONEX. Higher concentrations, when observed, were associated with air transport from lower latitudes and altitudes where warmer, moister, more sunlit conditions existed. The full SONEX data set, including our data and that of the other investigators, is publicly available through the NASA DAAC system.

The peroxide ratio, H_2O_2/CH_3OOH, was a good tracer of convection. It, together with CH_3I, $CHBr_3$, C_2Cl4, and CH_2Cl_2, gave results which were in general agreement with model derived meteorological products of air mass convective influence. These results were presented at three scientific meetings (Snow et al., 1998a,b,c), and a manuscript is in preparation (Snow et al., 2000)

Our CH_2O measurements, when above the detection limit, suggest it can be a major source of odd-hydrogen radicals in the upper troposphere. However, photochemical model-measurement comparisons are equivocal (e.g., Singh et al., 1999; Jaeglé et al., 1999) and indicate a low confidence in this result.

Convective transport of H_2O_2 and CH_3OOH is shown to play only a minor role in odd-hydrogen budgets at altitudes above 8 km in SONEX (Brune et al., 1999; Jaeglé et al., 1999; Tan et al., 1999). This is in contrast to tropical observations where these species all contribute significantly.

The CH_2O and CH_3OOH measurements were combined with observations of other partially oxidized hydrocarbons, e.g., formate, acetate, acetone, methanol. It was shown that the sum of these partially oxidized hydrocarbons can be as large as the pool of non-methane hydrocarbons and thus represents a significant reactive carbon reservoir (Singh et al., 1999).

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Educational Activity

This project sponsored one graduate research assistantship and tuition for two years at the University of Rhode Island. The supported student is in their final year of schooling and should receive a Ph.D. degree within the year.

Data Workshops Attended

NASA AEAP SASS SONEX #1, Atlanta, GA., July 1998.
NASA AEAP SASS SONEX #2, Moffett Field, CA, December, 1998.

Scientific Conferences Attended

1998 Conference on the Effects of Aviation, NASA/AEAP, Virginia Beach, VA, April 27 - May 1, 1998.

Challenges in Atmospheric Chemistry, National Center for Atmospheric Research, Boulder, CO, June 8-11, 1998.

American Geophysical Union Fall 1998 Meeting, San Francisco, CA, December 6-10, 1998.

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TABLE 1: Hydroperoxide Concentrations in September – November

Hydrogen Peroxide (pptv): altitudes > 8 km; latitudes 15-30 N/S					
	Minimum	25%	median	75%	Maximum
SONEX: N. Atlantic	20	40	60	100	480
PEM-West (A): N. Pacific	50	210	290	430	2340
PEM-Tropics (A): DC-8; Pacific	lod	120	200	280	1600
Trace- A: S. Atlantic	10	150	290	560	5650
Methylhydro Peroxide (pptv): altitudes > 8 km; latitudes 15-30 N/S					
	minimum	25%	median	75%	Maximum
SONEX: N. Atlantic	lod	lod	lod	80	170
PEM-West (A): N. Pacific	lod	140	200	320	590
PEM-Tropics (A): DC-8; Pacific	lod	lod	80	170	1390
Trace- A: S. Atlantic	lod	20	70	210	1180
Hydrogen Peroxide (pptv): altitudes > 8 km; latitudes 30-45 N/S					
	minimum	25%	median	75%	Maximum
SONEX: N. Atlantic	20	40	60	100	490
PEM-West (A): N. Pacific	40	110	220	420	1700
PEM-Tropics (A): DC-8; Pacific	20	280	360	430	900
Trace- A: S. Atlantic	lod	100	140	230	900
Methylhydro Peroxide (pptv): altitudes > 8 km; latitudes 30-45 N/S					
	minimum	25%	median	75%	Maximum
SONEX: N. Atlantic	lod	lod	60	90	340
PEM-West (A): N. Pacific	lod	70	170	270	410
PEM-Tropics (A): DC-8; Pacific	lod	160	370	450	990
Trace- A: S. Atlantic	lod	lod	20	210	470
Hydrogen Peroxide (pptv): altitudes > 8 km; latitudes > 45 N/S					
	minimum	25%	median	75%	maximum
SONEX: N. Atlantic	lod	30	60	100	290
PEM-West (A): N. Pacific	100	110	220	440	620
PEM-Tropics (A): DC-8; Pacific	lod	50	140	310	870
Methylhydro Peroxide (pptv): altitudes > 8 km; latitudes > 45 N/S					
	minimum	25%	median	75%	maximum
SONEX: N. Atlantic	lod	lod	lod	60	310
PEM-West (A): N. Pacific	lod	lod	70	270	410
PEM-Tropics (A): DC-8; Pacific	lod	lod	230	510	1060