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Observation of upper tropospheric sulfur dioxide- and acetone-pollution: Potential implications for hydroxyl radical and aerosol formation

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Abstract. Aircraft-based measurements of sulfur dioxide, acetone, carbon dioxide, and condensation nuclei (CN) were made over the north-eastern Atlantic at upper tropospheric altitudes, around 9000 m. On October 14, 1993, strong SO_2- and acetone-pollution (both up to 3 ppbv) were observed, which were accompanied by a CO_2-enhancement of up to 6 ppmv, and large CN-concentrations of up to about 1500 cm^{-3} (for radii ≥ 6 nm). CN, excess CO_2, and to a lesser degree also acetone, were positively correlated with SO_2. Air mass trajectory analyses indicate, that most of the air masses encountered by our aircraft originated from the polluted planetary boundary layer of the North-Eastern U. S. approximately 4-5 days prior to our measurements, and that polluted boundary layer air experienced fast vertical transport to the upper troposphere as well as horizontal transport across the Atlantic. From our data we conclude, that in the polluted air mass around 9000 m altitude HO_x-formation, photochemical SO_2-conversion to gaseous H_2SO_4, and eventually also CN-formation by homogeneous bimolecular (H_2SO_4-H_2O) nucleation may have taken place with enhanced efficiency.

Introduction

The upper troposphere seems to be a source region for condensation nuclei (CN), which may have an important role in tropospheric and stratospheric aerosol formation. Upper tropospheric CN-formation is indicated by an observed frequent occurrence of a relative maximum in the vertical profile of the CN-number density [c.f. *Hofmann,* 1993]. After downward transport, CN of free tropospheric origin may "seed" the marine planetary boundary layer, and stimulate cloud condensation nuclei (CCN) formation [c.f. *Clarke,* 1993]. CN of upper tropospheric origin may also become transported into the stratosphere, and may "seed" the stratospheric aerosol layer. Upper tropospheric abundances for CN (with radii ≥ 0.01 µm) are typically in the range 200 - 2000 cm^{-3} [c.f. *Turco et al.,* 1982; *Clarke,* 1993; *Brock et al.,* 1995]. Probably, upper tropospheric CN-formation proceeds via homogeneous bi-molecular (H_2SO_4-H_2O) nucleation, which is promoted by low temperatures, relatively large SO_2- and H_2O-abundances, and small abundances of pre-existing aerosols. Gaseous H_2SO_4 is formed via photochemical SO_2-conversion initiated by the reaction of SO_2 with OH [c.f. *Reiner and Arnold,* 1994]. Upper tropospheric HO_x($OH + HO_2$)-sources are the reaction of $O(^1D)$ with H_2O and, as recently proposed [*Singh et al.,* 1995], also photochemical conversion of acetone (CH_3COCH_3).

Sources of acetone are thought to be mainly atmospheric oxidation of precursor hydrocarbons (propane, isobutane, and isobutene), but also biomass burning and direct emission. Typical values for upper tropospheric acetone mixing ratios are about 0.1 - 1 ppbv [c.f. *Knop and Arnold,* 1987; *Möhler et al.,* 1993; *Chatfield,* 1994]. Acetone was originally detected in the upper troposphere by the MPIK Heidelberg group (MPIK = Max-Planck-Institut für Kernphysik) [*Hauck and Arnold,* 1984; *Knop and Arnold,* 1987].

Upper tropospheric SO_2 originates mostly from vertical transport of SO_2 and photochemical SO_2 precursor gases ($(CH_3)_2S$, CS_2) from the planetary boundary layer (PBL). Markedly increased upper tropospheric SO_2-abundances may occasionally occur on regional scales, due to fast convective transport of polluted PBL-air, and possibly also due to air traffic. Both sources involve burning of sulfur-containing fossil fuels. Upper tropospheric SO_2-abundances are mostly around 0.04 - 0.2 ppbv, but occasionally abundances up to about 1.0 ppbv have been observed [c.f. *Möhler and Arnold,* 1992; *Gregory et al.,* 1993].

The present paper reports on aircraft-based observations of an extremely SO_2- and acetone-rich air mass in the upper troposphere over the north-eastern Atlantic, which was also rich in CO_2 and CN. The observed pollution event was probably due to fast vertical transport from the polluted PBL of the north-eastern U.S., followed by long-range horizontal transport across the Atlantic.

Measurements

The aircraft-based measurements to be reported here were made on October 14, 1993 around 9000 m altitude over the north-eastern Atlantic, north-west of Ireland. They were part of an aircraft campaign (POLINAT = Pollution in the North Atlantic Flight Corridor), which aimed for an investigation of the potential impact of air traffic on the atmosphere.

Sulfur dioxide and acetone were measured by MPIK using a cryogenically pumped ion-molecule-reaction mass spectrometer (IMR-MS). The detection limit for both acetone and SO_2 was about 20 pptv, and the time resolution was 13 s, corresponding to a horizontal resolution of about 2600 m. For both SO_2 and acetone, the uncertainty and precision are ± 30% and ± 20%, respectively. More detailed descriptions of the MPIK-Heidelberg IMR-MS instrument can be found in *Arnold et al.* [1992], *Möhler and Arnold* [1992], and *Möhler et al.* [1993]. CN-measurements were made by the University of Missouri-Rolla (UMR), using an optical CN-counter, which had a detection limit, in terms of CN-radius, of 6 nm, and a time response of 3 s

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(for details see *Hagen et al.* [1992], [1994]). Carbon dioxide was measured by DLR-IPA (Deutsche Forschungsanstalt für Luft- und Raumfahrt, Institut für Physik der Atmosphäre), using differential infrared absorption. [c.f. *Schulte and Schlager,* 1994]. Uncertainty and precision for the CO_2-measurement are ± 1 ppmv and ± 0.3 ppmv, respectively. The IMR-MS, the CO_2-detector, and the CN-counter were part of a scientific payload, flown on the research jet aircraft "Falcon", which was operated and coordinated by DLR-IPA. Besides the above instruments, the payload also contained a hygrometer and an NO-detector (DLR-IPA).

On October 14, in the region where the measurements took place, meteorological conditions were characterized by north-westerly winds ($\approx$ 50 ms^{-1} around 9000 m). Temperatures were around 242 K at FL 290 (flight level 29000 feet, corresponding to 8830 m) and 238 K at FL 310 (9450 m). The local tropopause altitude was around 11000 m. Hence the measurements, which covered altitudes up to about 10000 m, took place below the local tropopause.

Results and Discussion

Figure 1 depicts abundances for SO_2, aerosol particles (with radii ≥ 6 nm), CO_2, acetone, and H_2O measured on October 14, 1993, at flight levels 290 (8830 m, until 15:23) and 310 (9450 m, after 15:25). The largest relative variations are found for SO_2, which ranges between about 0.03 and 3.0 ppbv. The minimum value is similar to "background" values (0.03 - 0.1 ppbv), observed by IMR-MS on other flights made in the aircraft campaign of October 1993. Such low SO_2-abundances were also previously observed by MPIK-Heidelberg in the upper troposphere [c.f. *Möhler and Arnold,* 1993]. Extensive upper tropospheric SO_2-measurements made by IMR-MS during project POLINAT (17 flights) mostly ranged between 0.03 and 0.3 ppbv and rarely reached 1 ppbv.

Carbon dioxide is closely correlated with SO_2, although this correlation is stronger in the first part of the measurements (FL 290). Here, the linear correlation function at the 99% confidence limit yields a correlation coefficient r^2 of 0.75, while on the next flight level (FL 310) the correlation coefficient r^2 is only 0.39. The ratio $R = \Delta SO_2/\Delta CO_2$ is about 0.0005. In comparison, expected upper limits to R for different types of fossil fuels are about 0.0001 (kerosene), 0.001 (light oil), and 0.01 (hard coal, heavy oil). Here typical emission indices [c.f. *Cullis and Hirschler,* 1980] were considered. In reality R may be smaller for ground level combustion sources due to removal of SO_2 by filters or wet-removal in the atmosphere. Hence the above comparison clearly excludes air traffic as a source of the observed SO_2-enhancement. Remaining sources are ground-level combustion sources for SO_2 and CO_2 and perhaps also metal smelting for SO_2.

The measured acetone is also positively correlated with SO_2 (correlation coefficient $r^2 \approx 0.5$ for both flight levels) and reaches maximum abundances around 3 ppbv. The latter markedly exceeds typical "background" values for upper tropospheric acetone (around 0.5 ppbv, see above). Hence it seems that the SO_2-rich air masses were also polluted with respect to acetone. When SO_2 is low acetone indeed falls below 1 ppbv which is typical for "background" situation. The observed excess acetone may have originated from direct emissions and/or secondary photochemical conversion of hydrocarbons like propane, whose concentrations are elevated in the polluted boundary layer

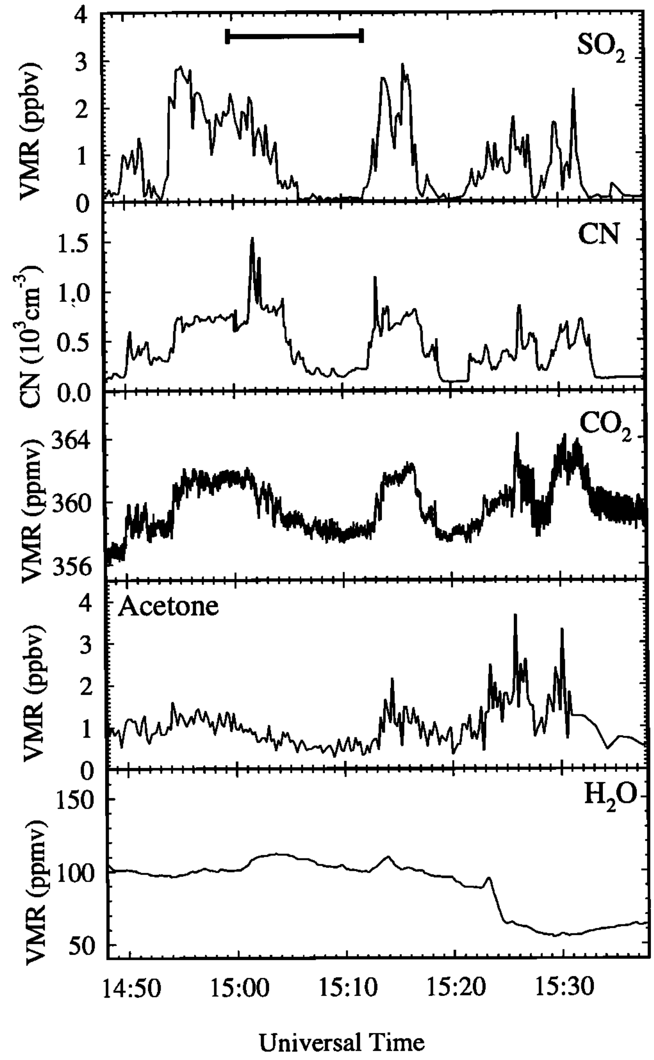

Figure 1. Abundances of SO_2, CN, CO_2, acetone and H_2O, measured on October 14, 1993 at the altitudes 8830 m (before 15:23) and 9450 m (after 15:25). SO_2 and acetone were measured by MPIK, CN by UMR, CO_2 and H_2O by DLR. The bar marks end points of trajectories which according to the analysis did not originate in North America. The decrease of H_2O at 12.24 UT marks the change from flight level 290 to flight level 310

The measured water vapor mixing ratio is about 100 ppmv and 60 ppmv for flight levels 290 and 310, respectively. This corresponds to relative humidities of about 10% (FL 290) and 8% (FL 310).

Figure 2 shows the flight-path of the "Falcon" along with SO_2-volume mixing ratios. It seems that the "Falcon" penetrated an SO_2-rich air mass which had a relatively large spatial extension. Trajectory analyses made at the Royal Netherlands Meteorological Institute for the air masses encountered by the "Falcon" on October 14 north-west of Ireland, indicate that, about five days before the encounter (October 9), most air masses indeed originated from the PBL of the heavily polluted north-eastern U. S. A. where SO_2-VMRs reach up to 10-20 ppbv [c.f. *Mueller and Hidy,* 1980]. Subsequently the air masses experienced fast vertical transport as well as horizontal transport across the Atlantic. Figure 3 shows an example of a trajectory

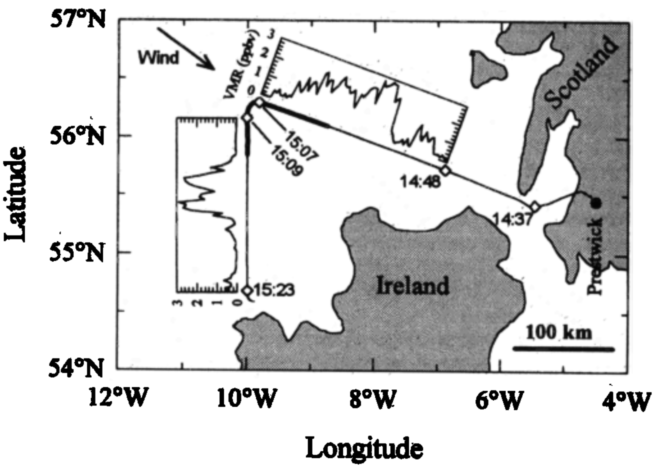

Figure 2. Flightpath for the flight of October 14, 1993 with SO_2-abundances plotted orthogonal. (Linear SO_2-scale in ppbv is indicated). Universal time is given for characteristic points. The trajectory analysis indicate that the air masses encountered between 15:00 and 15:12 (marked) did not originate from the United States.

for a specific air mass encountered by the "Falcon" on October 14, around 9000 m altitude. Around 84 hours prior to the measurements, this air mass had ascended to altitudes around 9000 m, west of Greenland (around 65°N). Until 24 hours prior to the measurements, the air mass traveled mostly north of 65°N, north-west of Iceland. During 12 hours prior to the measurements, it moved straight in from north-west towards Ireland. Hence, photochemical activity in the air mass of interest was probably not very high, due to relatively low solar elevations. By contrast 3 out of a total of 8 trajectories analyzed originated from the region between Greenland and Scandinavia. These air masses did not experience much change in altitude. The times when the "Falcon" encountered the end points of these trajectories are marked in figure 1. The observed SO_2-variation along the flight path (figure 2) may be due to the mixed air mass origin and/or different SO_2-uptake in the North-American PBL. The CN-concentrations measured at 9000 m in the SO_2-rich air mass (< 1500 cm^{-3}) are much lower than in the polluted boundary layer (up to about 10^5 to 10^6 cm^{-3}). Hence it seems that also CN experienced efficient wet-removal and coagulation during upward transport. Acetone originated probably either from direct emission at the ground and/or secondary photochemical sources including photooxidation of propane, higher alkanes, and alkenes.

The very sharp horizontal boundaries of the SO_2-rich air masses suggest, that these air masses did not travel for a long period of time around 9000 m altitude since otherwise such boundaries should be smeared out by horizontal dispersion. Typical observed horizontal scales for a 50% change of the SO_2-abundance are about 10 km. According to horizontal dispersion data, compiled by *Bauer* [1974], this corresponds to a horizontal dispersion time scale of about two days, which is roughly consistent with the trajectory analysis.

Implications for HO_x and Aerosols

The present observations of elevated upper tropospheric SO_2- and acetone-abundances have interesting potential implications for HO_x- and aerosol-formation in the polluted air masses:

Formation of HO_x from acetone may be quite efficient yielding about 3 HO_2-radicals per acetone molecule experiencing photolysis [*Singh et al.,* 1995]. Considering a diurnally averaged photolysis coefficient of about $1 \cdot 10^{-7}$ s^{-1} for 9 km altitude, autumn, and 55°N [c.f. *Singh et al.,* 1994], our measured maximum acetone abundance (3 ppbv, corresponding to a molecular number density of about $3 \cdot 10^{10}$ cm^{-3}) implies a diurnally averaged rate of HO_x-production of about 9000 cm^{-3}s^{-1}. In comparison the diurnally averaged rate of primary HO_x-production via $O(^1D) + H_2O \rightarrow 2\ OH$ for 9 km altitude, equinoctial conditions, 45°N, and a water vapor mixing ratio of 150 ppmv is only $\leq$ 4000 cm^{-3}s^{-1} [c.f. *Logan et al.,* 1981]. Our measured water vapor abundance was only 100 ppmv (FL 290) and 60 ppmv (FL 310) which implies an even lower HO_x-production via $O(^1D) + H_2O$. From this we conclude, that if vertical convection increases the upper tropospheric acetone mixing ratio up to 1 ppbv or more, HO_x-production via acetone represents a significant if not the most important primary source of upper tropospheric HO_x. However, other pollutants possibly contained in the polluted air masses may also contribute to increase the rate of HO_x-production.

Aerosol-growth and -formation is promoted by enhanced SO_2 and OH. The reaction of SO_2 with OH ultimately leads to gaseous sulfuric acid [c.f. *Reiner and Arnold,* 1994] which condenses and possibly may even undergo homogeneous nucleation leading to the formation of new aerosol particles. Both condensation and nucleation proceed via a bi-molecular (H_2SO_4-H_2O) mechanism. Considering our measured maximum SO_2-abundance (3 ppbv,

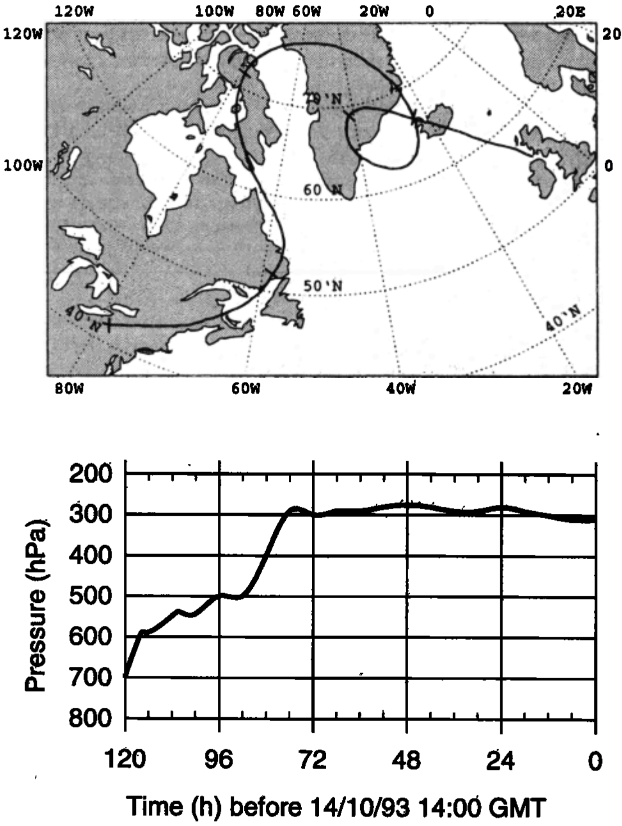

Figure 3. Three-dimensional trajectory analysis for one specific air mass encountered by the "Falcon" on October 14, 1993, at 9000 m altitude. Upper Panel: Footpoints, with 24 hour tick-marks. Lower Panel: Time evolution of the gas pressure.

corresponding to a molecular number density of $3 \cdot 10^{10}$ cm^{-3}), a "background" noon-time OH-concentration of $1 \cdot 10^6$ cm^{-3} [c.f. *Crutzen,* 1982], and an effective rate coefficient of $1 \cdot 10^{-12}$ cm^3s^{-1} for the reaction of SO_2 with OH, one obtains a noon-time rate of gaseous sulfuric acid formation $P_{GSA} \approx 3 \cdot 10^4$ $cm^{-3}s^{-1}$ or $1.1 \cdot 10^8$ $cm^{-3}h^{-1}$. In comparison the observed aerosols with a maximum number density of 1500 cm^{-3} would contain about $6 \cdot 10^8$ H_2SO_4-molecules per cm^3 if they were composed of pure H_2SO_4 and if they had a mean radius of 0.025 µm (which appears to be a reasonable value for evolution of newly formed upper tropospheric aerosol after a few days of residence time [c.f. *Clarke,* 1993]). Hence the H_2SO_4-molecules contained in these aerosols may be formed from the observed SO_2 within only about 5-6 hours. Even if the above mean radius was underestimated by a factor of 2, the formation of the mentioned number of H_2SO_4 would require about 22 hours, still well below the age of the polluted air mass.

New aerosol formation by homogeneous nucleation requires a large supersaturation and concentration of gaseous sulfuric acid (GSA) and a low total surface area density A_0 of pre-existing aerosols. The measured aerosols have an $A = 1.2 \cdot 10^{-7}$ cm^2 per cm^3 if their radius would be 0.025 µm. This would imply a GSA-lifetime τ_A with respect to collision with aerosols of about $\tau = 1500$ seconds. Considering the above $P_{GSA} = 3 \cdot 10^4$ $cm^{-3}s^{-1}$, this would lead to a steady-state GSA-concentration $(GSA)_S = P_{GSA} \cdot \tau_A = 4.5 \cdot 10^7$ cm^{-3}. This would imply a GSA-lifetime τ_D with respect to collision with another GSA-molecule of only about 200 s. (Assuming a collision-rate coefficient of $1 \cdot 10^{-10}$ cm^3s^{-1}.). Since $\tau_D \ll \tau_A$, removal of GSA is expected to occur preferably via homogeneous nucleation. If so, $(GSA)_S$ would be smaller than the above estimate.

The preceding estimations indicate that the observed excess SO_2 and acetone may induce condensational aerosol growth and also new particle formation, and it is conceivable that the observed aerosols may have been formed in the upper troposphere from the observed SO_2. However, it can not be ruled out that the observed aerosols have already been formed in the polluted PBL.

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References

Arnold, F., J. Scheid, T. Stilp, H. Schlager, and M. E. Reinhard, Measurements of jet aircraft emissions at cruise altitude I: The odd nitrogen gases NO, NO_2, HNO_2, and HNO_3, *Geophys. Res. Lett., 19,* 2421-2424, 1992.

Bauer, E., Dispersion of tracers in the atmosphere and ocean, Survey and comparison of experimental data, *J. Geophys. Res., 97,* 789-795, 1974.

Brock, C. A., P. Hamill, J. C. Wilson, H. H. Jonsson, and K. R. Chan, Particle formation in upper tropical troposphere: A source of nuclei for the stratospheric aerosol, *Science, 270,* 1650-1653, 1995.

Clarke, A. D., Atmospheric nuclei in the Pacific midtroposphere: Their Nature, concentration, and evolution. *J. Geophys. Res., 98,* 20633-20647, 1993

Chatfield, R. B., Anomalous HNO_3/NO_x ratio of remote tropospheric air: Conversion of nitric acid to formic acid and NO_x?, *Geophys. Res. Lett., 21,* 2705-2708, 1994

Cullis, C. F., and M. M. Hirschler, Atmospheric sulfur: Natural and man-made sources, *Atmos. Environm., 14,* 1263-1278, 1980

Crutzen, P. J., The global distribution of hydroxyl, in *Atmospheric Chemistry,* edited by E.D. Goldberg, pp. 313-328, Springer-Verlag, New York, 1982

Gregory, G. L., D. D. Davis, N. Beltz, A. R. Bandy, R. J. Ferek, and D. C. Thornton, An intercomparison of aircraft instrumentation for tropospheric measurements of sulfur dioxide, *J. Geophys. Res., 98,* 23325-23352, 1993

Hagen, D. E., M. B.Trueblood, and P. D. Whitefield, A field sampling of jet exhaust aerosols, *Particle Sci. & Techn., 10,* 53-63, 1992

Hagen, D. E., P. D. Whitefield, and M. B. Trueblood, Particulate characterization in the near field of commercial transport aircraft exhaust plumes using the UMR-MASS, in Schumann and Wurzel 1994, 119-124, 1994

Hauck, G. and F. Arnold, Improved positive-ion composition measurements in the upper troposphere and lower stratosphere and the detection of acetone, *Nature, 311,* 547-550, 1984

Hofmann, D. J., Twenty years of balloon-borne tropospheric aerosol measurements at Laramie, Wyoming. *J. Geophys. Res., 98,* 12753-12766, 1993

Knop. G., and F. Arnold, Stratospheric trace gas detection using a new balloon-borne ACIMS method: Acetonitrile, acetone, and nitric acid, *Geophys. Res. Lett., 14,* 1262-1265, 1987

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric Chemistry: A Global Perspective. *J. Geophys. Res., 86,* 7210-7254, 1981

Möhler, O., and F. Arnold, Gaseous sulfuric acid and sulfur dioxide measurements in the Arctic troposphere and lower stratosphere: Implications for hydroxyl radical abundances. *Geophys. Res. Lett., 19,* 1763-1766, 1992

Möhler, O., T. Reiner, and F. Arnold, A novel aircraft-based tandem mass spectrometer for atmospheric ion and trace gas measurements, *Rev. Sci. Instr., 86,* 1199-1207, 1993

Mueller, P. K., and G. M. Hidy, The sulfate regional experiment: Report of findings, Vols. 1-3, *EPRI-EA 1901,* Electric Power Research Institute, Palo Alto, CA, 1980

Reiner, T., and F Arnold, Laboratory investigations of gaseous sulfuric acid formation via $SO_3 + H_2O \rightarrow H_2SO_4 + M$: Measurement of the rate constant and product identification, *J. Chem. Phys., 101,* 7399-7407, 1994

Schulte, P., and H. Schlager, Inferred NO_x emission indices of jet engines at cruise altitudes from in situ NO and CO_2 measurements within aircraft plumes, in *Schumann and Wurzel* 1994, 113-118, 1994

Schumann, U., and D. Wurzel (Eds.), Impact of aircraft and spacecraft upon the atmosphere. *Proc. Intern. Coll.,* Cologne, April 18-20 1994, 496 pp., DLR-Mitteilung 94-06, 1994

Singh, H. B., D. O'Hara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou, and P. J. Crutzen, Acetone in the atmosphere: Distribution, sources, and sinks, *J. Geophys. Res., 99,* 1805-1819, 1994.

Singh, H. B., M. Kanakidou, P. J. Crutzen, D. J. Jacob, High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature, 378,* 50-54, 1995

Turco, R. P., R. C. Whitten, and O. B. Toon, Stratospheric Aerosols: Observation and Theory. *Rev. Geophys. Space Phys., 20,* 233-279, 1982

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