Vertical Profiles of Acetylene in the Troposphere and Stratosphere

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Abstract. Stratospheric measurements of acetylene up to altitudes of 30 km are presented. The air samples were collected during three different balloon flights, two of them at 44°N, one at 32°N using balloon borne, liquid neon-cooled, cryosamplers. Their acetylene concentration was measured in the laboratory by flame ionisation gaschromatography. The different profiles at 32°N and 44°N are discussed with respect to possible vertical exchange processes and compared with published model calculations.

Key words. Acetylene, stratospheric profiles, trace gas measurements, stratosphere-troposphere exchange.

1. Introduction

Light hydrocarbons are released exclusively at the Earth's surface and some are sufficiently longlived in the troposphere to mix into the stratosphere in measurable quantities. They are destroyed mostly by reaction with OH and Cl radicals, to some extent also by O^1D. Consequently the vertical stratospheric profiles of light hydrocarbons are determined by vertical transport and the stratospheric vertical profiles of these radical species. Thus stratospheric profiles of light hydrocarbons can be used to obtain information on the stratospheric exchange parameters or vertical distributions of radicals. For instance, profiles of the vertical eddy diffusion coefficient were derived from the average CH_4 profile (Wofsy and McElroy, 1973; Ehhalt *et al.*, 1974, 1975). The vertical distribution of C_2H_6 was utilized to estimate the concentration of Cl-atoms in the lower stratosphere (Rudolph *et al.*, 1981a).

In this paper we report measurements of acetylene (C_2H_2) in the stratosphere. This compound exhibits a strong latitudinal gradient in the troposphere, with mixing ratios which are by a factor of 5–10 lower in the tropics than at mid-northern latitudes, a fact which can be utilized to gain additional information about the latitude at which tropospheric air entered the stratosphere.

2. Experimental

Whole air samples were collected by balloon borne, liquid neon-cooled cryosamplers in

the stratosphere. Two samplers of similar construction were employed; both samplers followed the design described by Lueb *et al.* (1975). Tropospheric air samples were collected in evacuated all-stainless steel containers aboard an airplane. Immediately after the balloon flights, the air samples were transferred to special electropolished stainless steel containers of 0.5 or 2 dm^3 volume and transported into the laboratory for gaschromatographic analysis.

The hydrocarbons were concentrated on a precolumn at subambient temperatures (sample volume between 1 and 5 l STP), separated on a column packed with porous silica, and detected with a flame ionisation detector. The analytical procedure is very similar to that described by Rudolph *et al.* (1981b). The measurements were quantitated by comparison with a secondary air standard. This secondary standard was calibrated with mixtures of 0.1–2 ppb of C_2H_2 in synthetic air. These mixtures were prepared by two or three step static dilution. Short-time variations of the absolute calibration are less than 10%, long-time drift of the secondary standard for C_2H_2 does not exceed 15%/yr and was corrected by repeated absolute calibrations.

Both the detection limit and the analytical precision of the C_2H_2 measurements depended strongly on the sample volume which was available for the gaschromatographic determinations. The sample volume which was available for the C_2H_2 measurements from the two flights in 1979, often did not exceed 1 l of air at standard temperature and pressure. The corresponding detection limit was 0.015–0.02 ppb (2σ), precision of the analysis for mixing ratios well above the lower limit of detection was better than 10%. From the flight in 1981, much larger volumes of air were available and the volume employed for C_2H_2 analysis was 3–5 l STP. Accordingly, the detection limit was significantly lower (0.003–0.005 ppb) and the analytical precision for low mixing ratios better. The detection limits were calculated from twice the baseline noise level (2σ) and the sample volume.

3. Results

Approximately 30 stratospheric whole air samples were collected during three balloon flights. Two of these flights – on 16 and 28 June 1979 – were part of a joint project of the Max-Planck-Institut für Chemie in Mainz, the Max-Planck-Institut für Aeronomie in Lindau and the Institut für Atmosphärische Chemie in Jülich. Both of these flights were launched from Gap, Southern France, (44°N, 2°E). The sampler employed for these two balloon flights allowed for the collection of up to eight air samples per flight. During the balloon flight on 16 June, several tropospheric air samples were also collected aboard an airplane. A third flight was made in cooperation with the National Center of Atmospheric Research (NCAR), Boulder. It was launched from Palestine, Texas (32°N, 96°W) on 20 September 1981. That cryosampler was suitable for the collection of up to 16 air samples. The vertical profiles of C_2H_2 obtained from all three flights are shown in Figure 1.

The data contain one point (at 29 km altitude during the flight on 16 June) which is significantly higher than the value found for the next sample below. This points to contamination. On the other hand, this straggling point cannot be ascribed to a general
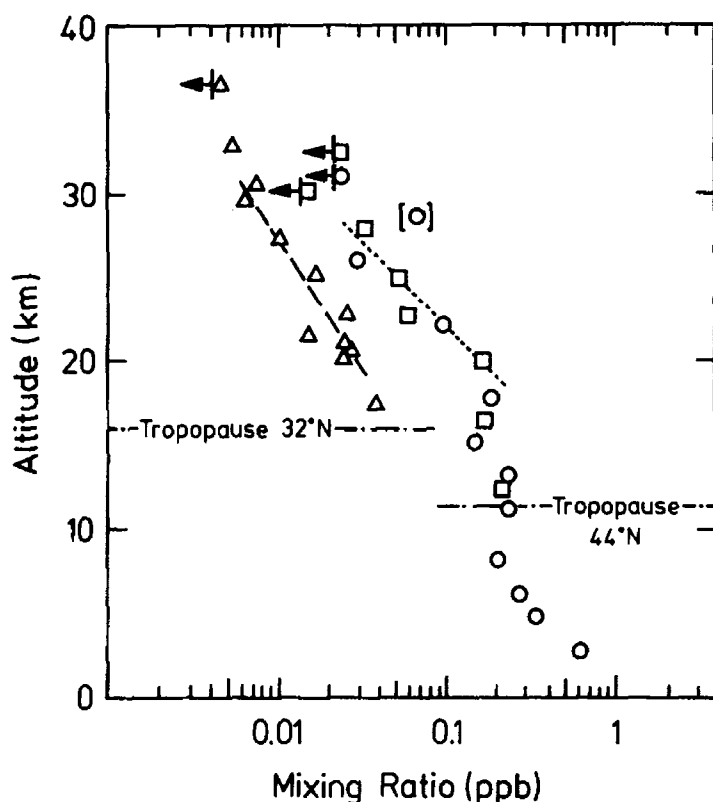
Fig. 1. Vertical profiles of acetylene mixing ratios in the troposphere and stratosphere. Circles: 16 June 1979 at 44°N/2°E Squares: 28 June 1979 at 44°N/2°E, Triangles: 20–21 September 1981 at 32°N/96°W. Dotted line: least square fit to exponential profile for data from 44°N for 20–30 km altitude, data point in brackets is possibly contaminated. Dashed line: same as dotted line, but for data from 32°N. Points with a left arrow represent the detection limit for those samples where C_2H_2 could not be detected.

contamination problem because the next higher samples from the same flight had C_2H_2 mixing ratios below the limit of detection (see Figure 1). The extent of contamination during that flight can be estimated, assuming that the lower limit of detection of 0.015— 0.02 ppb represents the actual C_2H_2-concentration in the uppermost samples and that this concentration is solely due to a systematic contamination in the sampling tubes. This allows to calculate upper limits for the contribution of contamination to the samples from lower altitudes. They amount to 10% or less for samples from below 20 km, 30% for samples from 20–25 km, and up to 50% for samples from 25–30 km. Thus, significant contamination cannot be ruled out completely above 25 km and the gradient of the experimental profiles above ≈25 km may be too small owing to contamination effects. However, for altitudes below 25 km, such contaminations should only be of marginal influence.

4. Discussion

The vertical C_2H_2 profiles from the two flights in June 1979 for 44°N agree within the

scatter of the experimental data. Since this scatter is approximately of the same magnitude as the analytical uncertainties of the individual measurements, smaller structures of the profiles or variations between the two flights cannot be distinguished from the experimental errors. Nevertheless, the general shape of the stratospheric and tropospheric C_2H_2 vertical profile is quite well defined for these two flights.

There is already a significant decrease of the C_2H_2 mixing ratios in the lower and middle troposphere. These samples were collected over continental Europe and the C_2H_2 mixing ratios in the lower troposphere are likely to be influenced by local or regional sources. Between 5 and 13 km altitude the C_2H_2 mixing ratios remain nearly constant at about 0.2 ppb. Moreover, the C_2H_2 gradient in the lower stratosphere is very weak, with a scale height of 26 ± 14 km so that the region of nearly constant mixing ratio extends to about 20 km altitude. Above 20 km altitude, there is a quite steep gradient for C_2H_2: the scale height — omitting the straggling point at 29 km — is 4.5 km ± 0.8 km. The C_2H_2 mixing ratios around 27 km are about 0.03 ppb, and less than 0.02 ppb above 30 km.

A quite different picture is presented by the vertical distribution of C_2H_2 at 32°N. Essentially, from the tropopause upwards, the C_2H_2 mixing ratios decrease considerably: from 0.04 ppb at 17 km to ≈ 0.005 ppb at 32 km altitude with a fairly constant scale height. With 6.8 ± 1.2 km between 20—30 km altitude, the scale height is slightly larger than at 44°N for the same altitude range. Especially interesting is the observation that the stratospheric C_2H_2 mixing ratios at 32°N are lower than those at 44°N by a factor of about 4.

There are no other measurements of vertical C_2H_2 profiles in the stratosphere we know of. But a few data are available on the C_2H_2 mixing ratio in the upper troposphere and lower stratosphere which can be compared to our measurements. Robinson (1978) reported measurements of C_2H_2 made by Rasmussen and Robinson in the Northern and Southern Hemisphere over the Pacific both in the troposphere and in the lower stratosphere. Northern Hemispheric values (25—75°N) are 0.2 ppb (average from 9 samples) for the troposphere and 0.05 ppb (8 samples) for the stratosphere just above the tropopause. The corresponding Southern Hemispheric data (25°S—65°S) are 0.08 ppb (17 samples) and 0.03 ppb (3 samples) respectively. Cronn and Robinson (1979) report C_2H_2 mixing ratios for the upper troposphere of 0.23 ± 0.06 ppb at 37°N/123°W and 0.08 ± 0.08 ppb at 9°N/80°W. For the lower stratosphere (between 0.5 and 3 km above the tropopause) their data for 36—38°N range from ≈ 0.2 ppb to below their detection limit of about 0.04 ppb. Both the measurements of Cronn and Robinson and of Rasmussen and Robinson were made by collection of pressurized whole air samples aboard an airplaine and subsequent gaschromatographic analysis.

Like the present measurements, the older data indicate a significant gradient with latitude. Also in absolute values these measurements compare favorably with our findings of ≈ 0.2 ppb C_2H_2 in the upper troposphere at 44°N and of ≈ 0.04 ppb in the lower stratosphere at 32°N. Our measurements in the lower stratosphere at 44°N are ≈ 0.2 ppb, significantly higher than the average value of 0.05 ppb reported by Rasmussen and Robinson for 25—75°N.

There is one measurement of the C_2H_2 mixing ratio in the upper troposphere by an entirely different technique. Goldman et al. (1981) derived an acetylene mixing ratio of 0.025 ppb ± 40% for ≈ 9 km altitude from solar spectra obtained during a balloon flight. The flight was made on 21 March 1981 from Holloman Air Force Base in New Mexico (35°N). This value is considerably lower than all the other published tropospheric C_2H_2 mixing ratios for this latitude. To a large extent, the latitudinal gradient observed in the upper troposphere and lower stratosphere is merely a reflection of the latitudinal gradient found at the surface which, in turn, reflects the distribution of the sources. Measurements in surface air over the Atlantic showed C_2H_2 mixing ratios of 0.3 to 0.4 ppb at mid-northern latitudes and a decrease from 0.3 down to 0.1–0.05 ppb between 30°N and the equator (Rudolph and Ehhalt, 1981; Rudolph et al., 1982). A similar behaviour was reported for C_2H_2 in surface air over the Eastern Pacific with mixing ratios of 0.4 ppb in the latitude range of 40°N–10°N and 0.1 ppb in equatorial regions (Singh and Salas, 1982).

Because of its relatively short tropospheric lifetime of approximately 50 days, the mixing ratio of C_2H_2 also shows a vertical decrease in the troposphere. Combined with the latitudinal gradient, this should generate a two-dimensional concentration field where the lines of constant mixing ratio slope upward and northward. Thus, the latitudinal gradient in the upper troposphere should be shifted to northern latitudes. Such a behaviour has indeed been observed during the STRATOZ II flight of the French Caravelle research aircraft in April and May 1980 (Rudolph et al., 1984).

The present measurements can also be compared to predictions of the vertical stratospheric C_2H_2 profile from one dimensional steady state models (Chameides and Cicerone, 1978; Goldman et al., 1981). Such predictions were carried for 30°N and equinox conditions, and are thought to represent average stratospheric profiles. Examples of these calculations are shown in Figure 2 together with our measurements at 32°N. For better comparison the model profiles were scaled to a groundlevel mixing ratio of 0.3 ppb, the value found over the Atlantic at 30°N (Rudolph et al., 1982). The two model profiles exhibit large differences. Since in both models the profiles of the vertical eddy diffusion coefficient are nearly identical and since the destruction of C_2H_2 by Cl atoms is treated as a minor loss in both, the differences in the predicted profiles must be due to the way the reaction of OH with C_2H_2 is modelled. Indeed, from the many different rate constants published for this reaction (e.g., Breen and Glass, 1970; Smith and Zellner, 1973; Davis et al., 1975; Perry et al., 1977; Michael et al., 1980) Goldman et al. (1981) selected the high pressure limiting rate constant $6.8 \times 10^{-12} \exp(-646/T)$ cm^3/s^{-1} molecule^{-1} of Michael et al. (1980), whereas Chameides and Cicerone (1978) used the much slower rate constant of $5.3 \times 10^{-12} \exp(-1000/T)$ cm^3/s^{-1} molecule^{-1} given by Breen and Glass (1970). The vertical profiles of OH in the two models also differ – in shape and absolute value. The C_2H_2 profile by Goldman et al. (1982) shown in Figure 2 is their example for 'low OH'. It utilized an OH concentration profile which is between 14 and 26 km altitude about a factor of 2 lower than that used by Chameides and Cicerone (1978). Still the lower OH concentrations do not compensate for the faster rate constant used by Goldman et al. (1982) and the C_2H_2 profile predicted by their model decreases
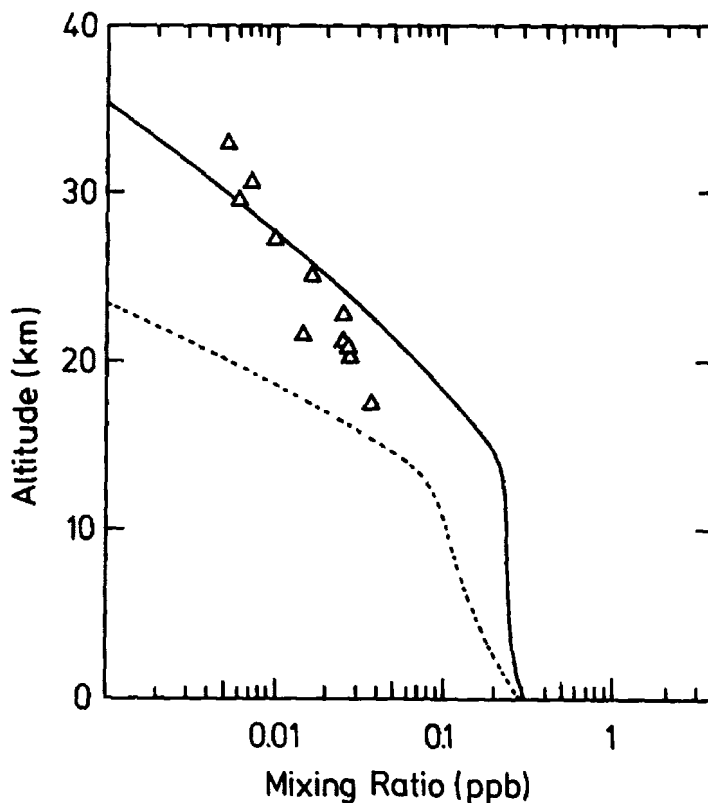
Fig. 2. Comparison of model calculations for 30°N and equinox with measurement at 32°N. Triangles: measurements. Dashed line: model predictions of Goldman *et al.* (1981) for low OH, scaled to 0.3 ppb groundlevel mixing ratio. Solid line: Model predictions of Chameides and Cicerone (1979) scaled to 0.3 ppb groundlevel mixing ratio.

much more rapidly with altitude. The fact that Goldman *et al.* (1982) terminated their calculations at 26 km altitude using a flux boundary condition seems to have little influence on the C_2H_2 mixing ratios below 24 km altitude shown in Figure 2. The observed stratospheric gradient is significantly smaller than those predicted by both models, although the model profile of Chameides and Cicerone compares much better with the measurements. In view of the fact that a single measured vertical trace gas profile represents a more or less instantaneous and local picture of the stratosphere, which could differ considerably from the average conditions, it appears premature to draw far reaching conclusions from such a comparison with one-dimensional models. Nevertheless, taken together with the two C_2H_2 profiles at 44°N, the low stratospheric C_2H_2 gradient observed at 32°N provides a strong indication that the use of the high pressure limiting rate constant of Michael *et al.* (1980) causes too high destruction rates of C_2H_2 in the stratosphere and is therefore inappropriate.

Regarding the profiles measured at 44°N, the observation of nearly constant C_2H_2 mixing ratios of 0.15–0.2 ppb in the lower stratosphere up to 20 km altitude clearly demands processes which incorporate tropospheric air into the lower stratosphere in a relatively rapid way. Comparable effects have been observed in vertical profiles of methane

for the same latitude and ascribed to the tropospheric-stratospheric exchange during tropopause folding events. For acetylene, the strong latitudinal gradient in the troposphere also helps to locate the origin of the air in the lower stratosphere. With nearly 0.2 ppb of C_2H_2 that air could originate only from a latitude range between 15°N to 75°N (cf. Rudolph et al., 1982). Future measurements especially in the upper troposphere might refine that range. At present we have to keep in mind that C_2H_2, due to its average tropospheric lifetime of only 50 days (Chameides and Cicerone, 1978), may also exhibit substantial seasonal variations both in the stratosphere and troposphere.

5. Conclusions

The latitudinal variation of acetylene at groundlevel has significant influences on the stratospheric C_2H_2 distribution. Thus one-dimensional models are only of limited value for the interpretation of stratospheric C_2H_2 profiles, since in addition to vertical exchange processes horizontal transport must be considered. Owing to the large latitudinal gradient in the tropospheric C_2H_2 mixing ratios additional insight in the origin of the stratospheric air masses can be gained from the measurement of stratospheric C_2H_2 mixing ratios. Thus, it can be argued that the high C_2H_2 mixing ratios observed in the lower stratosphere at 44°N demand fast exchange with tropospheric air from latitudes with sufficiently high C_2H_2 mixing ratios – i.e., from 15–75°N latitude. It is important to remember that – due to its comparably short atmospheric lifetime – C_2H_2 will respond to changes of the stratospheric OH distribution or transport much faster than longer lived trace gases as CH_4. Thus individual C_2H_2 profiles may exhibit much more pronounced deviations from the average and inferences drawn from such individual profiles are first of all applicable to the given situation. On the other side this fact may be used to study the variability of processes in the lower stratosphere. Consequently measurements of the stratospheric C_2H_2 distribution can provide interesting information on transport and – considering its rather simple stratospheric chemical destruction – may be used as a valuable tool for the test of two-dimensional chemical models of the stratosphere.

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