

4.29 VERTICAL DISTRIBUTION OF ACETONITRILE IN THE ATMOSPHERE

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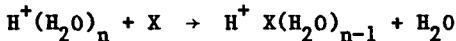
Mass spectrometric measurements of the stratospheric ion composition with rocket-borne and balloon-borne instruments showed the presence of so-called non-proton hydrates (NPH), i.e., $H^+ X_n(H_2O)$ (ARNOLD et al., 1977; ARIJS et al., 1978; ARNOLD et al., 1978). ARNOLD et al. (1978) suggested acetonitrile as a possibility for the molecule X. This hypothesis has been the subject of controversial discussions (FERGUSON, 1978; MURAD and SWIDER, 1979), but high resolution mass spectra (ARIJS et al., 1980) and laboratory investigations (BOHRINGER and ARNOLD, 1981; SMITH et al., 1981) seem to support this hypothesis.

Since 1978, positive ion composition measurements between 20 and 45 km have been performed with balloon-borne instruments (ARNOLD, 1980, 1982; HENSCHEN and ARNOLD, 1981; ARIJS, 1983; ARIJS et al., 1983a,b), to determine fractional ion abundances of proton hydrates (PH) and NPH.

As pointed out by ARNOLD et al. (1978), the number density of CH_3CN can be calculated from the observed fractional ion abundances through the continuity equation for NPH

$$k_1 [PH] [CH_3CN] = \alpha [n_-] [NPH]$$

where α is the ion-ion recombination coefficient, $[n_-]$ the total negative ion density and k_1 the rate coefficient for reactions of the type



The total fractional abundances of NPH and PH ions, $[NPH]$ and $[PH]$, can be deduced from ion mass spectra, assuming that ion count rates reflect ion abundances.

For k_1 , a value of $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ was chosen, according to laboratory measurements of SMITH et al. (1981). The $[n_-]$ was calculated with the parameterization formula of HEAPS (1978). For α a parameterization of the form

$$\alpha = 6 \times 10^{-8} \left(\frac{300}{T}\right)^{1/2} + 1.25 \times 10^{-25} [M] \left(\frac{300}{T}\right)^4 \text{ cm}^3 \text{ s}^{-1}$$

was adopted where T is the temperature in Kelvin and [M] the total neutral number density in cm^{-3} . This parameterization is a compromise for the different values of α as obtained by recent *in situ* measurements (ROSEN and HOFMAN, 1981), laboratory experiments (SMITH and ADAMS, 1982) and theoretical studies (BATES, 1982).

The volume mixing ratios of acetonitrile, obtained with our most recent mass spectra are shown in Figure 1. These results are compared with data of the MPIH group (Max Planck Institute, Heidelberg), which have been recalculated with the values of α and $[n_-]$ explained here.

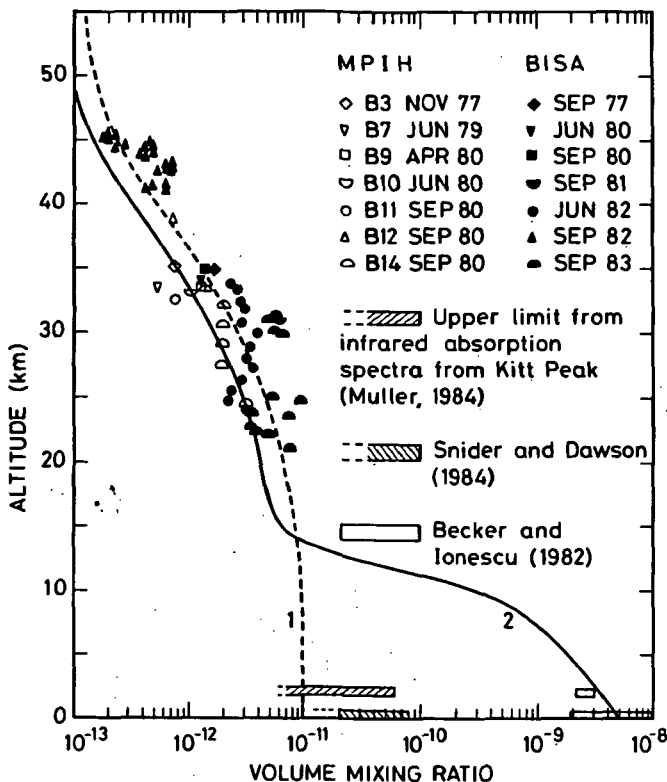
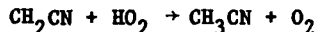
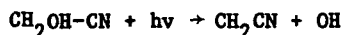
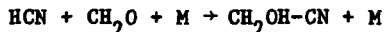
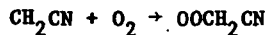


Figure 1. Vertical distribution of acetonitrile (CH_3CN) in the atmosphere.

Two different hypotheses have been advanced to explain the presence of acetonitrile in the stratosphere. MURAD et al. (1984) propose an *in situ* formation mechanism based on the following reactions:



Probably, the first reaction may be much slower than supposed by MURAD et al. (1984). However, if fast enough to explain the data of Figure 1, it should represent a major sink for HCN, and the HCN values measured by CICERONE and ZELINER (1983) should be very difficult to explain. Furthermore, the reaction



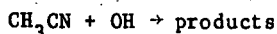
may be fast enough to destroy all CH_2CN , before any acetonitrile is formed (BRASSEUR et al., 1984).

Therefore, it appears more likely to accept the proposal suggested by BRASSEUR et al. (1983), which assumes that acetonitrile is released at the

earth's surface and that it diffuses into the atmosphere, where it is destroyed by reaction with OH radicals mainly.

Recently, measurements of CH_3CN near the earth's surface have supported this hypothesis. The two measurements reported in literature (BECKER and IONESCU, 1982); SNIDER and DAWSON, 1984) are also shown in Figure 1. As can be seen, both data sets differ by about a factor of 100.

Also given in Figure 1 are two curves obtained through model calculations by BRASSEUR et al. (1983), obtained by taking a fixed surface concentration and a zero flux at 100 km altitude as boundary conditions. The only chemical loss reaction introduced was



for which a reaction rate coefficient as measured by HARRIS et al. (1981) was adopted. Curve 1 assumes a mixing ratio at ground level of 10 pptv and no washout. Curve 2 was obtained with a surface mixing ratio of 5 ppbv and a washout coefficient of $2 \times 10^{-6} \text{ s}^{-1}$. As can be seen, both curves can reproduce the data obtained by ion mass spectrometry. However, the main problem remains a determination of the loss due to washout. If the data of BECKER and IONESCU (1982) are representative for a background atmosphere, a large loss due to rainout has to be introduced.

According to HEICKLEN (1981), the lifetime due to washout can be calculated with

$$\tau_s = \left(1 + \frac{k}{f}\right) \times \tau_0$$

where f is the fractional volume of air occupied by liquid water, τ_0 the average lifetime with which droplet removal occurs in the troposphere (about 10^6 s) and k Henry's law constant (ratio of the molecule number density in the vapour phase and the molecule number density in the liquid phase). From a compilation of available data on the acetonitrile - water liquid-vapor equilibrium, a value of $k = 9 \times 10^{-3}$ can be found for an average tropospheric temperature of 245 K (ARIJS and BRASSEUR, 1984). Taking for $f = 10^{-6}$ (about 1 g.m^{-3} liquid water in the air), a τ_s of 9×10^7 s is found. This value is in good agreement with the residence time for rain out recently found by HAMM et al. (1984).

It is therefore concluded that curve 1 is a better approximation of reality and that the measurements of SNIDER and DAWSON (1984) seem more realistic than those of BECKER and IONESCU (1982), which apparently are more representative for polluted areas.

Recent investigations of infrared spectra indicating that upper limit for CH_3CN at 2000 m altitude is about 20 pptv (Muller, private communication) seem to support this supposition.

Curve 1 corresponds to a global emission of 0.023 MT/yr. This emission can be explained easily by sources such as biomass burning, car exhaust gases and direct release of CH_3CN from industrial processes. It is expected that the actual emission calculated with a small washout loss will be somewhat larger, although we do not expect changes larger than a factor of 3.

In fact, new model calculations, taking into account loss terms such as reaction with atomic oxygen and chlorine atoms (which seem to be very low; OLBREGTS et al., 1984) and photodissociation are needed, as well as a systematic investigation of possible emission sources.

And although the vertical distribution of acetonitrile as known and presented here, is likely to be consistent with our general knowledge of its atmospheric chemistry, more *in situ* measurements (especially below 20 km) are needed to clarify the remaining problems.

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