

ACETONITRILE IN THE ATMOSPHERE

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Abstract. The vertical distribution of acetonitrile between 0 and 55 km altitude is calculated assuming that CH_3CN is released at the Earth's surface and that the main loss process in the stratosphere is the reaction with hydroxyl radicals. The influence of different possible surface concentrations is investigated. The role of the destruction of CH_3CN by Cl, as well as the use of different eddy diffusion coefficients is briefly discussed. The results are compared with recent measurements of acetonitrile.

Introduction

Acetonitrile appears to play a considerable role in the formation of stratospheric ions (Arnold et al., 1977; Arijs et al., 1978, 1980, 1983a; Henschen and Arnold, 1981; Arnold and Henschen, 1982). Recent determinations of CH_3CN concentrations in the middle atmosphere (Arijs et al., 1983b) and at ground level (Becker and Ionescu, 1982) as well as new laboratory data (Harris et al., 1981; Zetsch, 1981, 1982 and Fritz et al., 1982) have stimulated us to develop a model to calculate a CH_3CN profile. The results of such model calculations are presented here and compared to CH_3CN mixing ratios deduced from ion mass spectrometric data obtained between 20 and 55 km altitude.

Acetonitrile budget

The origin of acetonitrile is not yet well understood. According to recent measurements by Becker and Ionescu (1982) however, large quantities of CH_3CN are known to be released when burning bush and grass. This indicates that appreciable amounts of this gas could be produced in the tropical regions in connection with agricultural practices and partly injected in the stratosphere through the equatorial Hadley cell. It is also well known that tobacco smoke contains high nitrile concentrations (Schmetz and Hoffman, 1977). Moreover, it is likely that industrial releases, synthetic rubber manufacturing and turbine emissions contribute significantly to the acetonitrile source (Graedel, 1978).

The recent measurements of CH_3CN by Becker and Ionescu (1982) have been carried out using a gas chromatography mass spectrometric technique and are based on a few samples collected near the ground at different locations in Europe. The reported mixing ratios vary between 2 and 7 ppbv, except for one sample taken in a rural area close

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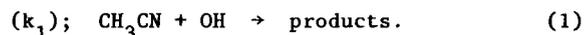
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to a bush and grass fire, where the CH_3CN mixing ratio reached 35 ppbv. If these measurements appear to be correct and to represent global average conditions, a mixing ratio of 5 ± 2 ppbv could be adopted as a background value at the Earth's surface. Local peaks in relation to man-made activity should also be considered. Comparison between observations made in the Northern and in the Southern Hemisphere should give an indication on the anthropogenic emissions versus the natural sources of CH_3CN .

According to the derivation of CH_3CN concentration from ion composition measurements (Arnold et al., 1981; Henschen and Arnold, 1981; Arijs et al., 1982, 1983a, 1983b), it appears that the mixing ratio of acetonitrile above the tropopause is less than 10 pptv, which is a factor of 500 lower than the value reported at ground level (Becker and Ionescu, 1982). If the latter are correct, a considerable sink for CH_3CN must exist in the troposphere.

In the stratosphere, an important loss process for acetonitrile is its reaction with OH:



The rate constant as measured by Harris et al. (1981) in the temperature range 298-424 K is

$$k_1 = 5.86 \times 10^{-13} \exp(-750/T) \text{ cm}^3 \text{ s}^{-1} \quad (2)$$

This constant is a factor of 2 higher than the value measured by Fritz et al. (1982) at 295 K and 7 torr and the one obtained by Zetsch (1981). Destruction by $\text{O}(^1\text{D})$ and Cl should also be considered but, since the rates of these reactions are yet unknown, these processes will not be treated in detail here. The photodissociation of CH_3CN plays an insignificant role below the stratopause (Figure 1) since the absorption cross section (Zetsch, 1982) becomes very small at wavelengths larger than 180 nm, i.e. in the spectral region of the solar radiation penetrating into the stratosphere. The photodissociation frequencies $J(\text{CH}_3\text{CN})$ which we have calculated for two extrapolations of the absorption cross section above 185 nm as given by Zetsch (1982) are shown in Figure 1.

Modelling of CH_3CN

In order to simulate the average behavior of CH_3CN in the atmosphere, the vertical distribution of this constituent has been calculated by means of a 1-D model (Brasseur et al., 1982).

A given concentration at ground level and a zero flux at 100 km are specified as boundary conditions for CH_3CN . In a first calculation (curve 1 - Figure 2) the only loss process considered is the reaction with OH, for which the rate constant of Harris et al. (1981) is adopted. It is then found that in order to reproduce the CH_3CN distribution, as observed in the strato-

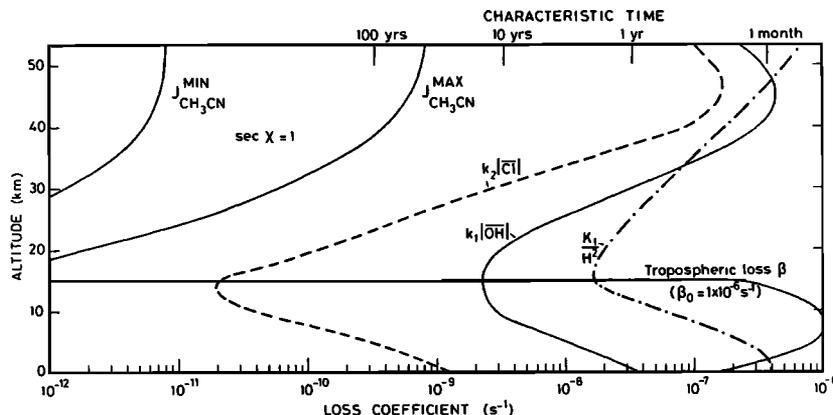


Fig. 1 Loss coefficients of CH_3CN , due to the reaction with OH, Cl and the photodissociation. The loss coefficient of CH_3CN versus Cl is based on a rate constant assumed to be identical to that of CH_3Cl versus Cl. An example of the specified tropospheric loss (β) is also shown. The inverse of the characteristic time for diffusion is indicated by the dashed dotted lines.

sphere an acetonitrile mixing ratio at the Earth's surface of 10 pptv must be specified. This number is far below the observations by Becker and Ionescu (1982) which are of the order of 5 ppbv.

To fit simultaneously these high values at ground level and the low stratospheric data (< 10 pptv) it is therefore necessary to introduce a supplementary sink in the troposphere. To consider such a possibility an arbitrary loss coefficient of the form

$$\beta = \beta_0 \left[1 - \left(\frac{z-8}{8} \right)^2 \right] s^{-1} \quad (3)$$

was introduced, where z is the altitude expressed in km. In fact the flux of acetonitrile, which is injected in the stratosphere is not affected by the detailed shape of the profile appearing in the adopted expression (3) but by the overall

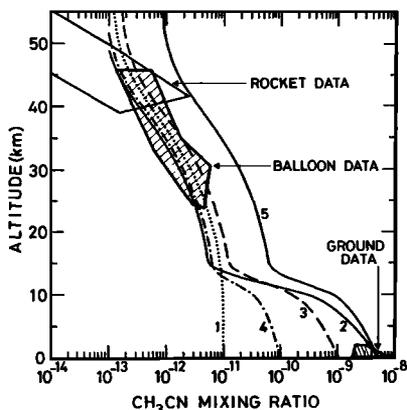


Fig. 2 Calculated distribution of acetonitrile mixing ratios for the different cases of Table 1 compared to experimental results. The area labelled "Rocket data" covers the data deduced from rocket ion mass spectrometry measurements (Arnold et al., 1978, and Henschen and Arnold 1981). The area "balloon data" summarizes the range of CH_3CN mixing ratios, from balloon ion mass spectra (Arijs et al., 1982, 1983a, 1983b; Arnold and Henschen, 1981; Henschen and Arnold, 1981). The area "ground data" represents the observations of Becker and Ionescu, 1982.

tropospheric lifetime of CH_3CN , which can be adjusted through the proper choice of β_0 .

To reproduce consistently both ground level and stratospheric data by model calculations, a tropospheric lifetime for acetonitrile of about 11 days must be adopted as illustrated by curve 2 in Figure 2. From the model calculations (see Table 1 - case 2) it then follows that these conditions imply a world emission of CH_3CN of about 400 MT/yr., corresponding to an annual injection of nitrogen of nearly 140 MT. Such a value can hardly be accepted without investigating the impact on the global atmospheric nitrogen cycle. This emission is indeed about 14 times larger than the source strength of NO_x from ammonia as determined by Levine (1982) and 8 to 32 times larger than the estimated NO_x production by lightning (Dawson, 1980; Hill et al., 1980). It exceeds the estimated anthropogenic production of NO_x by a factor of 10 and is considerably larger than the natural release of NO from soils (Ehhalt and Drummond, 1981) and than the NO_x emission by biomass burning (Crutzen et al., 1979; Ehhalt and Drummond, 1981). It should be noted however that the injected acetonitrile will not interfere with the NO_x budget if the main tropospheric loss would be direct wash-out of CH_3CN molecules by rain. At present however it is difficult to evaluate the effectiveness of such a wash-out, since little is known about the CH_3CN vapor pressure above aqueous solutions with low acetonitrile concentrations, at low temperatures.

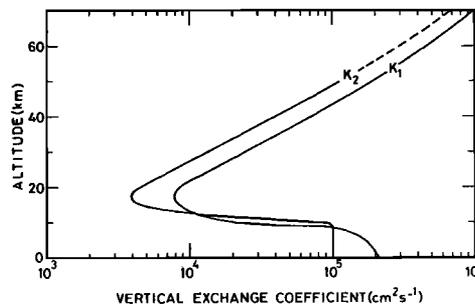


Fig. 3 Vertical distribution of the eddy diffusion coefficients used in this work.

TABLE 1. Characteristics and results of different model runs.

Case	Mixing ratio at ground level	Wash-out coefficient σ (s^{-1})	Global lifetime	Required flux at ground level ($cm^{-2}s^{-1}$)	Required World emission of CH_3CN (MT/yr) ³
1	1×10^{-11}	0	3 yrs	2.0×10^6	0.023
2	5×10^{-9}	2×10^{-6}	11 days	3.6×10^{10}	400
3	1×10^{-9}	1×10^{-6}	20 days	5.1×10^9	55
4	1×10^{-10}	0.5×10^{-6}	36 days	3.4×10^8	3.6
5	5×10^{-9}	1×10^{-6}	20 days	2.5×10^{10}	280

Keeping in mind that the ground level concentrations reported by Becker and Ionescu (1982) may be more representative for polluted areas and could be far removed from global average conditions, we have also investigated cases with lower surface boundary conditions in our model calculations. Table 1 shows the different model cases considered together with the prescribed tropospheric lifetime of CH_3CN and the global emission which is required to balance the total atmospheric sink. The results of the calculations are also shown in Figure 2.

Any further progress in our understanding of the acetonitrile budget requires new independent observations of CH_3CN in the troposphere, studies of individual source strengths and sinks of this molecule and investigations of a possible wash-out.

All calculations presented up to now have been performed with a rather large eddy diffusion coefficient K_1 (Brasseur et al., 1982) assuming strong vertical mixing (see Figure 3). A computation with conditions similar to that of case 3 was made with the K_2 profile suggested by Massie and Hunten (1981). The latter, also represented in Figure 3, leads to an increase by 40 percent of the characteristic diffusion time in the stratosphere. Although below 30 km the stratospheric acetonitrile distribution obtained with the K_2 profile of Massie and Hunten (Figure 4) is

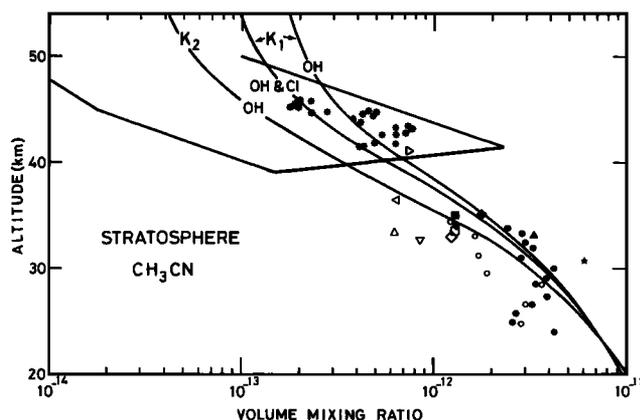


Fig. 4 Vertical distribution of acetonitrile calculated for different eddy diffusion coefficients (see Figure 3) assuming destruction by OH only and both OH and Cl. The measurements are again shown for comparison. Open symbols are data from Henschen and Arnold (1981) and full symbols those of Arijs et al. (1983a, 1983b).

almost identical to these distributions derived using the K_1 profile, deviations appear above 30 km, leading to a factor of 4 difference at the stratopause. The distributions based on the K_2 profile seem to fit quite well the observations obtained from rocket flights (Arnold et al., 1977; Henschen and Arnold, 1981) at high altitude.

Finally, the possibility of a supplementary destruction of CH_3CN by chlorine atoms has been considered. To our knowledge, the rate of this reaction has never been measured but an order of magnitude can be inferred from similar reactions. We have adopted a rate constant k_2 equal to that of $CH_3Cl + Cl$, i.e. $3.4 \times 10^{-11} \exp(-1260/T) cm^3 s^{-1}$ as recommended by WMO (1982). The corresponding distribution of acetonitrile computed with this loss coefficient and the original large eddy diffusion coefficient K_1 is shown in Figure 4. The effect of chlorine could be significant, particularly in the upper stratosphere and could even be the dominant loss if the reaction rate was similar to that of $CH_3OH + Cl$. Laboratory work dealing with this question is urgently required.

Conclusion

Model calculations show that the available observations of acetonitrile can be consistently reproduced by making different assumptions about the processes affecting this molecule. A more detailed understanding of the CH_3CN budget in the atmosphere requires a better knowledge of the strengths of all plausible sources and of the exact loss rate in the troposphere and in the stratosphere. Supplementary observations of acetonitrile at ground level and in the whole troposphere (particularly in the vicinity of the tropopause) would give useful information about the various source strengths of CH_3CN , its tropospheric lifetime and its injection rate in the stratosphere. Moreover, measurements at different locations on the Earth's surface are required to confirm the recent observations reported by Becker and Ionescu (1982).

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