ACETONITRILE IN THE STRATOSPHERE AND IMPLICATIONS FOR POSITIVE ION COMPOSITION

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Abstract. The present paper describes a probable budget for acetonitrile and discusses the release of this gas through biomass burning and human activity. The different loss processes in the middle atmosphere are mainly due to the reaction with hydroxyl radicals and atomic oxygen. It is shown that the destruction of CH_3CN by scavenging due to precipitation is probably not more efficient than the direct gas phase reactions. Losses due to ion chemistry are very difficult to estimate at present but are probably of secondary importance, except locally, where formation of multi-ion complexes is significant. A one-dimensional calculation shows that the vertical profiles of CH_3CN, deduced from ion mass spectrometry data, can be reproduced satisfactorily if an annual global emission ranging from 1.5×10^{10} g to 5×10^{11} g is adopted, depending on the values of the reaction rate constants and eddy diffusion coefficient. The global atmospheric lifetime of CH_3CN is estimated to be about 0.5 to 1.4 year. Finally the calculated acetonitrile profiles are introduced in an ion model to calculate the abundances of the major positive stratospheric ions. The results are consistent with present observations.

1. Introduction

In situ measurements of the stratospheric positive ion composition with rocketborne and balloon-borne instruments (Arnold et al., 1977; Arijs et al., 1978; Arnold et al., 1978) revealed, apart from the expected $H^+(H_2O)_n$ ions or proton hydrates (PH), the presence of the so-called nonproton hydrates (NPH) of the form $H^+X_\ell(H_2O)_m$. As a possible identification for the molecule X, Arnold et al. (1978) suggested acetonitrile. Although this hypothesis has been the subject of some controversy (Ferguson, 1978; Murad and Swider, 1979), high-resolution mass spectra (Arijs et al., 1980) as well as laboratory investigations (Böhringer and Arnold, 1981; Smith et al., 1981) have given additional support to it. Since 1978, several positive ion composition measurements between 20 and 45 km with balloon-borne instruments have enabled the derivation of the concentration of X, which in all likelihood can be identified as CH_3CN, between 20 and 45 km (for reviews, see Arnold, 1980a, 1982; Arijs, 1983; Arijs et al. 1984; for recent data, Henschen and Arnold, 1981; Arijs et al., 1983a, 1983b). The obtained mixing ratio profile (about 0.3 pptv at 45 km, increasing to approximately 4 pptv at 25 km) indicates that acetonitrile is most probably produced at the earth's surface and diffused into the atmosphere,

where it is destroyed on its way up by oxidation reactions, discussed hereafter. Although recently, Murad et al. (1984) proposed an in situ formation mechanism of acetonitrile with hydrogen cyanide as a progenitor, a new chemical analysis as well as model calculations (Brasseur et al., 1985) show that it is unlikely that HCN is an atmospheric source of CH_3CN.

The first measurement of acetonitrile near the surface (Becker and Ionescu, 1982) as well as laboratory data (Harris et al., 1981; Zetzsch, 1981a, b; Fritz et al., 1982) stimulated us to develop a model to calculate the CH_3CN profile up to 50 km altitude (Brasseur et al., 1983). In this model it was assumed that acetonitrile was produced at the earth's surface and that its destruction mainly occurred through reaction with OH, Cl, and photodissociation. The main uncertainty, however, was the loss rate due to reaction with chlorine atoms and tropospheric scavenging due to precipitation or rainout. Recent data of Snider and Dawson (1984, 1985) and Hamm et al. (1984) seem to indicate that the latter is probably small. Furthermore, additional laboratory data (Olbregts et al., 1984; Kurylo and Knable, 1984; Poulet et al., 1984) as well as new observations at the earth's surface (Snider and Dawson, 1984, 1985) became available, allowing an updating of our first model calculations. In view of the growing interest in the possible role of polyatomic molecules in the chemistry of the atmosphere we have tried to find out with a more refined model how acetonitrile can be distributed in the atmosphere, starting from ground level data. Furthermore, the implications of the obtained CH_3CN distribution on the positive ion composition of the stratosphere will be investigated.

2. Atmospheric Chemistry of Acetonitrile

Although ion composition data only give indirect proof for the existence of acetonitrile in the stratosphere, measurements at the earth's surface definitely confirmed its presence in the troposphere. The study of the emission sources of this molecule requires an extended specialized research, and therefore this matter cannot be the subject of this section. We will, however, return to this problem in section 3.3. as part of the discussion of the model calculations. For the time being we will limit ourselves here to an enumeration of the possible atmospheric sinks of CH_3CN.

2.1. Assessment of Possible Precipitation Scavenging

Apart from the difficulty of conceiving an in situ production mechanism, one of the arguments cited to eliminate CH_3CN as the origin of NPH was that it could not reach the stratosphere because of its effective rainout in the troposphere. This
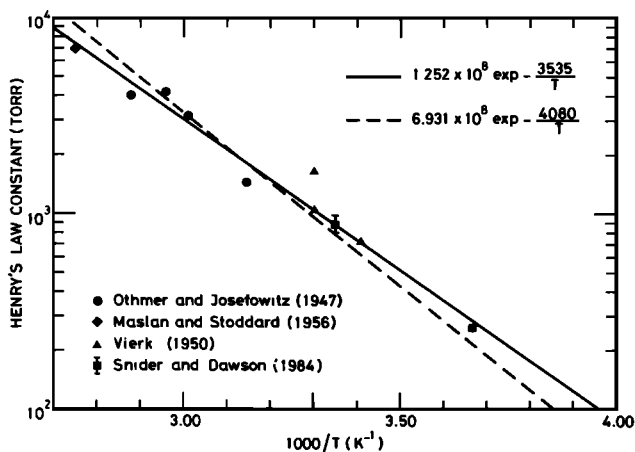
Fig. 1. Henry's Law constant for water-aceto-nitrile solution as deduced from CH_3CN vapor pressure measurements. The full line results from a regression of the data of Othmer and Josefowitz (1947), Maslan and Stoddard (1956), Vierk (1950), and Snider and Dawson (1984b). The dotted line represents the result of Hamm (1984).

belief was based on the extrapolation of information on its solubility in water as stated in some popular handbooks (Weast, 1970). To the best of our knowledge, however, no detailed computation of the rainout rate of acetonitrile has been made so far. Although Hamm et al. (1984) recently estimated the tropospheric residence time due to precipitation scavenging, their result is difficult to use for model calculations because it only gives an average over the whole tropo-sphere.

To determine the removal of atmospheric gases by rain in the troposphere, several methods have been proposed by different authors (Stedman et al., 1975; Heicklen, 1981; Crutzen and Gidel, 1983). In most of these methods a knowledge of Henry's Law constant of the component in aqueous solution is required. This constant H can be defined by

$$p_x = H M_f \qquad (1)$$

where p is the vapor pressure of CH_3CN and M_f the mole fraction of acetonitrile in the solu-tion. Both p_x and H are expressed in the same pressure units (e.g., torr). A first step in the assessment of possible washout being the deter-mination of H, we have compiled the available measurements on the acetonitrile-water liquid-vapor equilibrium as reported in the literature (Othmer and Josefowitz, 1947; Vierk, 1950; Maslan and Stoddard, 1956; Snider and Dawson, 1984, 1985). From these data, shown in Figure 1, it is concluded that Henry's Law constant as a function of temperature can be represented by

$$H = 1.25 \times 10^8 \exp\left(-\frac{3535}{T}\right) \qquad (2)$$

where H is expressed in torr. The recent result obtained by Hamm et al. (1984), also shown in Figure 1, is in reasonable agreement with the value given by formula (2). For the calculation of tropospheric rainout we have followed the

scheme as proposed by Crutzen and Gidel (1983). In order to describe the transfer of a water-soluble gas X with number density [X] in the troposphere, a downward flux due to scavenging by rain and expressed by

$$\phi_w = w_x[X] \qquad (3)$$

is superimposed on the flux due to the eddy diffusion. The downward velocity w_x is then, according to Crutzen and Gidel (1983), given by

$$w_x = K [M] \frac{\partial \mu(H_2O)}{\partial z} \frac{[X]_\ell}{[X]} \frac{1}{[H_2O]_\ell} \qquad (4)$$

where K is the eddy diffusion coefficient, [M] the total atmospheric number density, $\mu(H_2O)$ the mixing ratio of water, and $[X]_\ell$ and $[H_2O]_\ell$ the number density of molecules in the liquid phase of CH_3CN and H_2O, respectively. Taking into account that

$$[X]_\ell / [H_2O]_\ell = M_f = p_x/H \qquad (5)$$

formula (4) can be reduced to

$$w_x = K \frac{\partial \mu(H_2O)}{\partial z} \frac{p}{H} \qquad (6)$$

where p is the ambient pressure. Adding the flux ϕ_w to the eddy diffusion flux ϕ_E in the continu-ity equation and considering the order of mag-nitude of the different terms of $\partial\phi_w/\partial z$, the steady state continuity equation becomes

$$\frac{\partial\phi_E}{\partial z} = P - L - \mu[M] \left[\frac{\partial w_x}{\partial z} + \frac{w_x}{[M]} \frac{\partial[M]}{\partial z} \right] \qquad (7)$$

where P and L are chemical production and loss terms, and μ is the mixing ratio of X. The continuity equation thus reduces to a convent-ional form, to which has to be added a sup-plementary loss term, due to precipitation scavenging, with a loss coefficient

$$\beta_w = \frac{\partial w_x}{\partial z} + \frac{w_x}{[M]} \frac{\partial[M]}{\partial z} \simeq \frac{\partial w_x}{\partial z} - \frac{w_x}{H_s} \qquad (8)$$

where H_s is the atmospheric scale height.

We have calculated this rainout coefficient versus altitude with formulas (2), (6), and (8), using the eddy diffusion coefficient and the mixing ratio of water as obtained from a model of Brasseur et al. (1982). The result, shown in Figure 2, indicates that the rainout coefficient can be approximated by

$$\beta_w = 4.5 \times 10^{-8} \exp\left[-z^2/15.4\right] s^{-1} \qquad (9)$$

where z is the altitude expressed in kilometers. The value of this coefficient averaged over the troposphere as given by

$$\beta_m = \frac{\int \beta_w[M] \, dz}{\int [M] \, dz} = 1.67 \times 10^{-8} \, s^{-1} \qquad (10)$$

results in average lifetime versus wet precipitation of

$$\tau_m = 1/\beta_m = 6 \times 10^7 \text{ s} \qquad (11)$$

or 1.9 years. Another expression for this average lifetime as derived by Heicklen (1981) is

$$\tau_s = (1 + \kappa/f) \tau_o \qquad (12)$$

where f is the fractional volume of air occupied by liquid water, κ the dimensionless Henry's Law constant (expressed as the ratio of molecule number density in the vapor phase to molecule number density in the liquid phase), and τ_o the average lifetime with which droplet removal occurs in the troposphere. From (2) a value of κ = 9 x 10^{-5} can be derived for an average tropospheric temperature of $_6$ 245 K. Putting with Heicklen (1981), τ = 10^6 s, and taking for f = 10^{-6}, which corresponds to about 1 g m^{-3} liquid water in the air (see Crutzen and Gidel, 1983) we obtain τ_s = 9 x 10^7 s. This result and the residence^s time $_7$ for rainout, 3 ± 1.5 yrs or (9.5 ± 4.7) x 10^7 s, as obtained recently by Hamm et al. (1984), are in reasonable agreement with τ_m as calculated from (11). We therefore consider expression (9) as a valid approximation for the vertical distribution of the rainout loss coefficient and will use it in the further model study.

2.2. Loss of CH$_3$CN Through Chemical Reactions

One of the major sinks of acetonitrile in the atmosphere is its reaction with OH radicals which most likely can be written as

$$(k_{13}) \qquad CH_3CN + OH \rightarrow CH_2CN + H_2O \qquad (13)$$
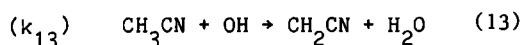
The resultant CH$_2$CN disappears rapidly by reaction with O$_2$ (Brasseur et al., 1985). Reaction (13) has been studied by different authors (Harris et al., 1981; Zetzsch, 1981a, b; Fritz et al., 1982; Kurylo and Knable, 1984; Poulet et al., 1984). The rate constant as measured by Harris et al. (1981) in the temperature range 298-420 K is

$$k_{13} = 5.86 \times 10^{-13} \exp \left(- \frac{750 \pm 125}{T} \right) \text{ cm}^3 \text{ s}^{-1}$$
$$(14)$$

whereas Kurylo and Knable (1984) report

$$k_{13} = 6.28 \times 10^{-13} \exp \left(- \frac{1030}{T}\right) \text{ cm}^3 \text{ s}^{-1} \qquad (15)$$

It is worthwhile to note that the result of Kurylo and Knable is in better agreement with the room temperature measurement of Fritz et al. (1982), Zetzsch (1981a, b) and Poulet et al. (1984). In the model calculations to be discussed hereafter we use both expressions (14) and (15) in the different case studies.

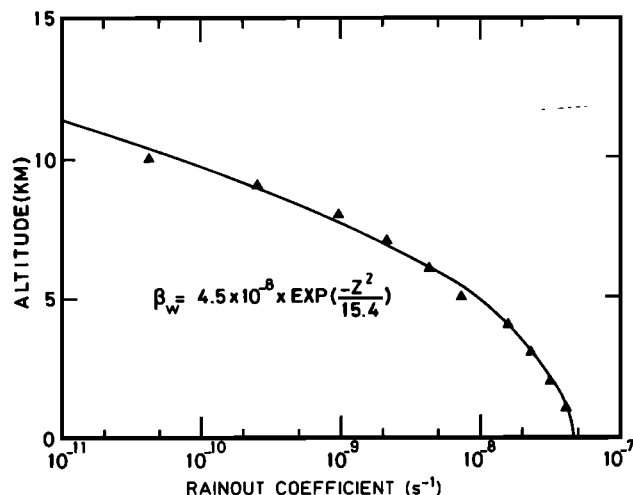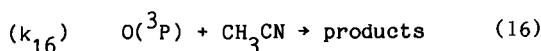Another atmospheric loss reaction for acetonitrile studied by Bonanno et al. (1977) is

$$(k_{16}) \qquad O(^3P) + CH_3CN \rightarrow products \qquad (16)$$

Fig. 2. Loss coefficient of scavenging due to precipitation for CH$_3$CN as a function of altitude deduced with the method of Crutzen and Gidel (1983).

The corresponding rate constant found by the previous authors is

$$k_{16} = (7.27 \pm 1.75) \times 10^{-13} \qquad (17)$$
$$\exp \left(- \frac{2385 \pm 100}{T} \right) \text{ cm}^3 \text{ s}^{-1}$$

Reaction (16), however, only becomes important at altitudes above 50 km, as will be seen in the model treatment hereafter.

Destruction of acetonitrile by atomic chlorine, which has been suggested before (Brasseur et al., 1983) as being possibly important, has also been investigated in the laboratory. The rate constant obtained by Olbregts et al. (1984), 8 x 10^{-11} exp(- 3000/T) cm^3 s^{-1}, as well as the upper limit reported by Kurylo and Knable (1984), 2 x 10^{-15} cm^3 s^{-1} at 298 K, and the recent data of Poulet et al. (1984), 3.46 x 10^{-11} exp (- 2785/T), show that the reaction of CH$_3$CN + Cl is of minor importance for stratospheric studies.

Finally, the loss due to CH$_3$CN + O(^{1}D) should also be considered. Unfortunately, no measurement of this reaction rate is available, and therefore a working value of 10^{-10} cm^3 s^{-1}, in analogy with the rate constant adopted for HCN + O(^{1}D) by Cicerone and Zellner (1983), is used in the model.

2.3. Photodissociation of Acetonitrile

Absorption spectra of CH$_3$CN have been studied by Herzberg and Scheibe (1930) in the wavelength region 154 nm to 180 nm and by Cutler (1948) from 100 to 180 nm. Unfortunately, no absolute values of the absorption cross section can be derived from these early measurements. More recent photodissociation studies of CH$_3$CN by McElcheran et al. (1958) and by Okabe and Dibeler (1973) led to the determinations of the bond dissociation energies D(CH$_3$-CN) = 5.32 eV and D(H - CH CN) = 3.12 eV. We are not aware of any published data on the absolute values of the absorption coefficient in the wavelength region of interest for

the stratosphere, but unpublished results of C. Zetzsch (private communication, 1983) have allowed us to calculate the vertical distribution of the photodissociation frequency of aceto-nitrile. These results have been reported before (Brasseur et al., 1983) and will be used un-modified hereafter.

2.4. Acetonitrile Loss Through Ion Chemistry

An additional sink for CH_3CN recently sug-gested by Murad et al. (1984) is the reaction with proton hydrates (PH)

$$(k_{18}) \quad CH_3CN + H^+(H_2O)_n \rightarrow$$
$$H^+CH_3CN(H_2O)_{n-1} + H_2O \quad (18)$$
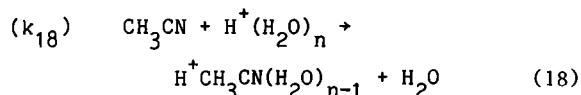
This is a well-established ion-molecule reaction with a very fast rate of about 3×10^{-9} cm^3 s^{-1} (Smith et al., 1981) which, in spite of the low number density of PH, may lead to an effective loss rate for acetonitrile. It should be noted, however, that the subsequent recombination with negative ions Y^-,

$$H^+CH_3CN (H_2O)_n + Y^- \rightarrow products \quad (19)$$
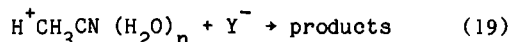
is not well understood and that the products of reaction (19) are not established. Conventionally it is assumed that recombination of negative and positive ions leads to the net production of neutrals, such as, for instance,

$$H^+CH_3CN(H_2O)_n + NO_3^- (HNO_3)_m \rightarrow$$
$$(m + 1) HNO_3 + n(H_2O) + CH_3CN \quad (20)$$
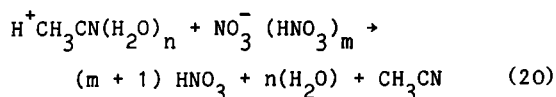
In this case it is reasonable to accept that CH_3CN consumed by reaction (18) will reappear again after recombination, and ion molecule reactions cannot be a significant sink for aceto-nitrile. However, under certain conditions, when the recombination process is endothermic, stable solvated ion pairs (Ferguson, 1979), also called multi-ion complexes (Arnold, 1980b), may be formed, and CH_3CN may be effectively lost. The criterion to be fulfilled for the formation of stable ion pairs is according to Arnold (1980b)
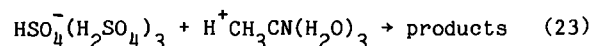
$$E_A + S^- + S^+ > E_c + IP \quad (21)$$

where S^+ and S^- are the total solvation energies of the positive and negative cluster ions, respectively (S^+ including the proton affinity), and E_A the electron affinity of the neutral precursor of the negative ion core. IP is the ionization potential of the neutral precursor of the positive ion core (which for the PH an NPH observed in the stratosphere is the hydrogen atom and thus IP = 13.6 eV). E_c is the energy released on formation of a chemical bond such as, e.g., H-NO$_3$ in reaction (20). With the appropriate values of E_c and IP as estimated by Arnold (1980b), inequality (21) reduces to
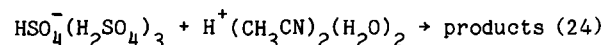
$$E_A + S^- + S^+ > 417 kcal/mol \quad (22)$$

This condition can be investigated by inserting in (22) the electron affinity E_A and the thermo-chemical data (S^+ and S^-) for positive and

negative ion clusters measured in the laboratory (Lau et al., 1982; Meot-Ner, 1978, 1984, and private communication, 1985; Walder and Franklin, 1980; Davidson et al., 1977; Wlodek et al., 1980; Viggiano et al., 1980) or derived from in situ ion composition data (Arnold et al., 1981; Arijs et al., 1982). It is found that most of the recombinations given by equation (19) can be neglected for the formation of stable ion pairs for the ions observed in the stratosphere, apart from

$$HSO_4^-(H_2SO_4)_3 + H^+CH_3CN(H_2O)_3 \rightarrow products \quad (23)$$

and

$$HSO_4^-(H_2SO_4)_3 + H^+(CH_3CN)_2(H_2O)_2 \rightarrow products \quad (24)$$

which therefore can result in stable ion pair formation. The $HSO_4^-(H_2SO_4)_3$ cluster is only observed in a narrow altitude layer around 35 km (Arijs et al. 1981; Arnold et al., 1982), where it can, however, contribute to as much as 30% of the total negative ion content (Arijs et al., 1981). In this region, therefore, multi-ion complex formation may be significant, as was already concluded by Arnold et al. (1982), and the loss of CH_3CN through ion-molecule chemistry may become effective. An estimation of the associated loss coefficient $Fk_{18}[H^+(H_2O)_n]$, F being the fraction of recombinations giving rise to stable ion pair formation, leads to a value of about 6×10^{-7} s^{-1} in the height region around 35 km. At other altitudes, where massive HSO_4^--clusters are much less abundant, the loss through ion chemistry is probably much lower due to the considerably smaller solvation energies of $NO_3^-(HNO_3)_n$ ions, which become dominant below 30 km, and the smaller number of ligands in the ion clusters above 30 km.

It should however be emphasized that the previous conclusions are based on crude approxi-mations of solvation energies (for the HSO_4^--ions), which have not been measured in the laboratory before, and on a very simple model for MIC formation based on purely energetic con-siderations. Furthermore, the detailed mechanism of the recombination of highly complicated cluster ions as well as the resulting end products are not known at present. It cannot be excluded that MIC formation occurs with partial "boil-off" of ligands and that even CH_3CN reappears as a free molecule in endothermic recombinations. In any case the unconditioned use of reaction (19) as a sink for acetonitrile leads to results that are incompatible with observa-tions (Brasseur et al., 1985). For the time being we have therefore not taken into account ion-molecule reactions in the model calculations for CH_3CN, but the possible implications of it require further research.

3. Model Calculations for Acetonitrile

3.1. Brief Model Description

In order to understand the behavior and the budget of acetonitrile in the atmosphere, a one-dimensional model, which extends from the earth's surface to 100 km altitude, is used. In this model, already described by Brasseur et al.
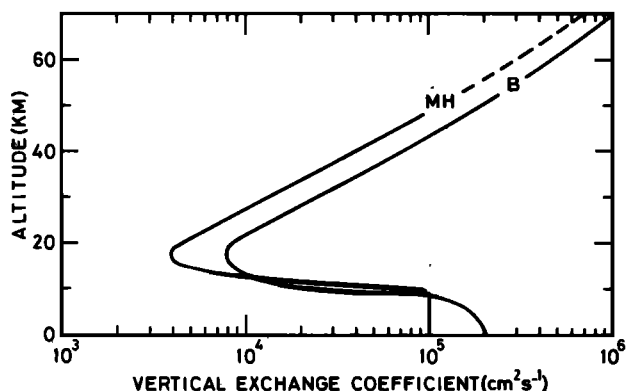
Fig. 3. Vertical distribution of the eddy diffusion coefficients used in this work. The curve M-H is taken from Massie and Hunten (1981), curve B is adopted from Brasseur et al. (1982).

(1982), fast reacting species, such as OH or $O(^1D)$, are assumed to fulfill photochemical equilibrium conditions, while the vertical distribution of long-lived constituents, such as CH_3CN, is obtained by solving a full continuity equation. In this case the vertical transport of the species is parameterized by an eddy diffusion law

$$\phi_E = - K [M] \frac{\partial\mu}{\partial z} \qquad (25)$$

Two vertical distributions of the eddy diffusion coefficients (K) are used in the present study and are displayed in Figure 3. In order to solve the steady state continuity equation, two boundary conditions have to be specified. In the case of acetonitrile a zero flux is adopted at 100 km and a given mixing ratio is specified at the earth's surface. The choice of the latter is problematic because presently published ground-level measurements (Becker and Ionescu, 1982; Snider and Dawson,

1984, 1985) are in disagreement by a factor of 100.

An inspection of very high resolution infrared spectra (Muller, 1985) obtained at Kitt Peak National Observatory (Delbouille et al., 1981) at the altitude of 2095 m on October 25, 1979 does, not show any specific CH_3CN absorption at the strongest v_1 band line (3040.5 cm^{-1}). From this study an upper limit for the acetonitrile mixing ratio of 32 pptv could be deduced, using laboratory data of Thompson and Williams (1952).

In view of this and the fact that Snider and Dawson (1984) state that the mixing ratio of CH_3CN at ground level is "perhaps" lower than 20^3ppt, we have adopted a working value of 10 ppt for the mixing ratio of CH_3CN at the earth's surface, in a first series ^{3}of model runs, to study the influence of chemical and transport conditions. As indicated by Brasseur et al. (1985), considerably higher values at ground level, such as those reported by Becker and Ionescu (1982), have to be rejected on the basis of model calculations unless a large loss process is present in the troposphere. We therefore believe that values for the CH_3CN mixing ratio of 2 to 7 ppbv as reported by Becker and Ionescu (1982) are overestimated or are representative of highly polluted areas.

3.2. Model Results and Discussion

The calculated distribution of acetonitrile is dependent on the chemical and transport conditions adopted. In order to test the sensitivity of the predicted concentration to these conditions, a series of model runs have been performed. The different cases are specified in Table 1. The effect of the uncertainties in the rate constants for the destruction processes of CH_3CN is assessed by considering an upper, a lower, and an average value suggested from laboratory work. The sensitivity of the vertical profile to dynamic conditions is studied by comparing the results obtained using each K profile as given in Figure 3.

TABLE 1. Conditions for Each Model Case

Case	Rate constants $CH_3CN + O(^3P)$		$CH_3CN + OH$		Eddy Diffusion Coefficient	Yearly Global Emission of $CH_3CN(x\ 10^{10}\ g)$	Lifetime, Years
2	Bonanno	min	Kurylo		B	4.55	1.36
3		mean	Kurylo		B	4.55	1.36
3'		mean	Kurylo		MH	4.73	1.28
4		min	Harris	min	B	5.68	1.08
5		mean		mean	B	7.33	0.82
5'		mean		mean	MH	7.79	0.74
6		max		max	B	9.90	0.59
6'		max		max	MH	10.54	0.52

Bonanno min, mean, and max stand for the minimum, mean, and maximum values of k_{16} obtained by using the appropriate values for the experimental uncertainties in expression (17). The same procedure applied to expression (14) gives Harris min, mean, and max. Kurylo stands for expression (15). The eddy diffusion coefficients called B and MH are given in Figure 3.
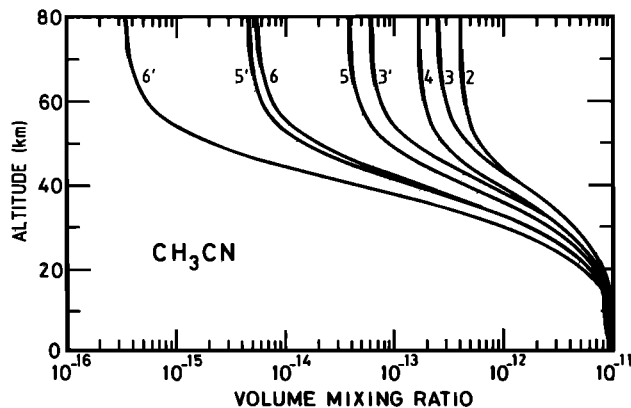
Fig. 4. Vertical distribution of CH_3CN mixing ratio predicted with a 1-D model for different cases summarizedd in Table 1.

Figure 4 shows the resulting CH_3CN distributions. Below 15-20 km, no significant difference between individual profiles is noticeable, since rapid vertical transport leads to almost complete mixing. The slight decrease in the mixing ratio however, results from both the destruction by OH and washout processes. In the stratosphere the relatively rapid decrease in the mixing ratio results from the loss by hydroxyl radicals and, in the upper levels, by atomic oxygen. The effect resulting from a change in the rate constant of the CH_3CN + O reaction can be seen when comparing curves 2 and 3. Extreme variations expected from uncertainties in the rate constants of the two major stratospheric destruction processes are given by curves 4 (minimum destruction rates), 5 (mean), and 6 (maximum). A difference in the mixing ratio of a factor 20 appears in the concentration at the tropopause. Moreover, the consequence on the calculated profiles of replacing reaction rate k_{13} as measured by Kurylo by the rate constant provided by Harris can be estimated by comparing curves 3 and 5. Finally, the adoption of the slower diffusion suggested by Massie and Hunten (1981) instead of profile B leads to a considerably lower mixing ratio of acetonitrile (profiles 3', 5', and 6' instead of 3, 5, and 6).

Despite the large dispersion of the calculated distributions, it is not yet possible to determine the most probable case, since observed data also exhibit large scatter. Furthermore, all these profiles are obtained for a single value at the lower boundary, and sensitivity calculations should be done with changing mixing ratios at the earth's surface. In this case the curves would be displaced over a constant factor at all altitudes.

The importance of all chemical reactions in the destruction process of CH_3CN can be inferred from Figure 5. As indicated previously, the main loss mechanisms in the middle atmosphere are the reactions with OH and $O(^3P)$. The effect of chlorine as well as the photodissociation can be entirely neglected, while reaction with $O(^1D)$ always plays a secondary role. The characteristic time for transport is clearly smaller than all chemical lifetimes in the troposphere and in the mesosphere, where consequently the vertical gradient in the predicted mixing ratio is small.

3.3. Emission Sources for Acetonitrile

Figure 6 shows a comparison of the experimental data for CH_3CN mixing ratios with three model calculations A, B, and C. Curve A, which is obtained by multiplying the values of curves 6' in Figure 4 by a factor of 5, corresponds to a calculation with the conditions of case 6' of Table 1, but with a ground-level mixing ratio of 50 pptv and a global annual emission of about 5×10^{11} g. Similarly, curve B, resulting from a reduction of the concentration shown by curve 2 in Figure 4 by a factor of 3, corresponds to a calculation with the same rate constants as in case 1 (Table 1) and a ground-level mixing ratio of 3.3 pptv. The latter is equivalent to a global annual emission of 1.5×10^{10} g. Curve C is identical to case 3' of Figure 4 and corresponds to a global annual emission of 4.7×10^{10} g. Apparently, the experimental results can be fit with different computation results, but the use of the two extreme cases (A and B of Figure 6) lead to an upper and lower limit of the global annual emission Em, given by

$$1.5 \times 10^{10} \text{ g} < Em < 5 \times 10^{11} \text{ g} \qquad (26)$$

We will now investigate the possible emission sources of CH_3CN.

Acetonitrile being a widely used solvent, starting material or intermediate product in many processes (U.S. Environmental Protection Agency, 1978) a first possible emission source for CH_3CN is direct release from industry. The annual CH_3CN production for the United States has been estimated to be 6.1×10^{10} g, of which about 51% is released to the environment (Dorigan et al., 1976). No production rates being available for other industrialized countries, we have doubled this value to obtain a global annual emission
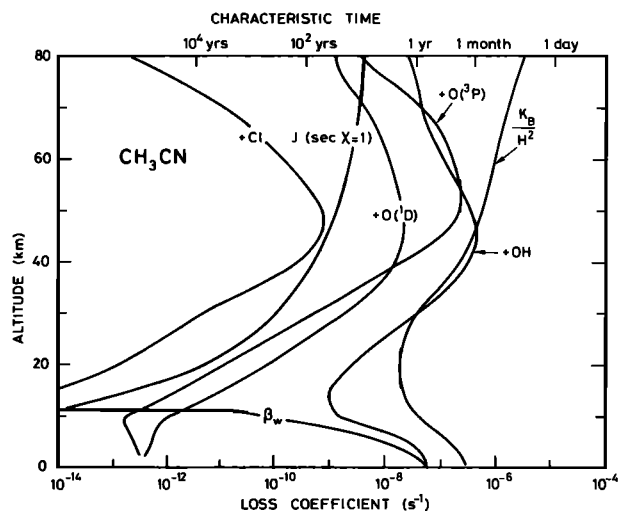

Fig. 5. Calculated loss coefficients of CH_3CN versus altitude due to reactions with OH, $O(^3P)$, $O(^1D)$, Cl. The curve labeled J (sec χ = 1) shows the photodestruction for an overhead sun calculated with the cross sections measured by Zetzsch (1983). The characteristic time constant for vertical exchanges (H^2/K_B) can be compared with the chemical lifetime associated with each reaction.
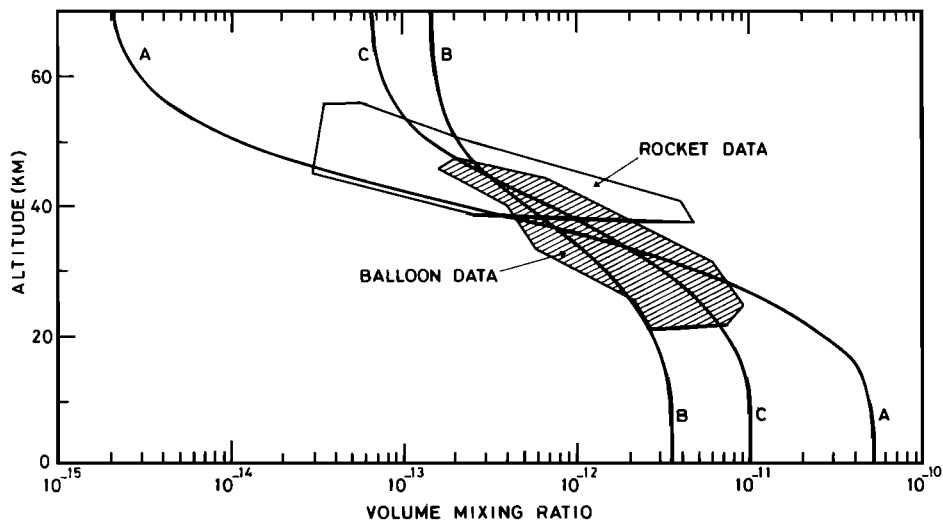
Fig. 6. Fitting of different vertical distributions of CH₃CN obtained through model calculations with present set of experimental data.

rate of about 6 x 10¹⁰ g. This value may be overestimated, since CH₃CN originating from industrial waste is mostly reaching the atmosphere through evaporation from surface waters in which it is released. Thereby degradation of the material by microorganisms cannot be excluded (Firmin and Gray, 1976).

Other important sources of atmospheric acetonitrile vapor are car exhaust gases, which contain about 1000 ppmv of organic material (Dulson, 1978). From this estimate, Becker et al. (1983) concluded that, for the Federal Republic of Germany, the annual production of organic gases by cars is about 10 kg per inhabitant. Converting this figure to the production per car and extrapolating for the total number of cars of the industrialized world leads to 6 x 10¹² g of organics. Accepting that about 1.3% of this is acetonitrile (Dulson, 1978), one obtains an extra global annual emission of CH₃CN of about 8 x 10¹⁰ g.

Biomass burning is clearly producing CH₃CN. According to Becker and Ionescu (1982), the concentration of acetonitrile at ground level raises by an order of magnitude during the burning of bush and grass. Although the absolute values of the data reported by these authors may be questioned, there clearly is an indication that wood and grass fires emit CH₃CN as suggested before (P.J. Crutzen, personal communication, 1983). It is also known that pyrolysis of proteins produce acetonitrile (Johnson and Kang, 1971) and that tobacco smoke (which is a special biomass burning process) contains relatively high concentrations of CH₃CN (Schmeltz and Hoffman, 1977). According to Greenberg et al. (1984) about 1.2-8.7 x 10¹³ g C/yr of nonmethane hydrocarbons are produced globally by biomass burning. About 2% of these are, at present, not identified (Greenberg et al., 1984). Assuming that 10% of the nonidentified hydrocarbons are acetonitrile, a global annual emission of 2.4-17.4 x 10¹⁰ g is obtained. The foregoing assumption, however, is rather crude and is based on the speculation that the acetonitrile content of biomass burning products should be less than 10⁻⁴ times the total

global carbon emission, which is estimated to be about 3.1 x 10¹⁵ g C/yr (Seiler and Crutzen, 1980). The factor 10⁻⁴ is derived from the fact that one cigarette (1 g of tobacco or about 0.75 g of C) produces about 100 µg of CH₃CN (Schmeltz and Hoffman, 1977) and that tobacco is a plant with a nitrogen content well above the average due to its alkaloid character.

Summing up the emissions due to direct release (6 x 10¹⁰ g), car exhaust (8 x 10¹⁰ g), and biomass burning (2.4-17.4 x 10¹⁰ g), a total global annual estimated emission of about 1.64-3.14 x 10¹¹ g is obtained. This estimate is within the values defined by inequality (26).

The present estimations thus seem to be consistent, within the uncertainty limits, with those imposed by model calculations. This suggests that the proposed mechanism of CH₃CN being released at ground level and destroyed on its way up by oxidation reactions is most probably a valuable representation of reality.

However, some important remarks need to be made here. The two curves A and B, shown in Figure 6, were obtained from two extreme model calculations which, although suitable for estimations of an upper and lower limit for the emission strength of CH₃CN, are probably not realistic representations of reality. Curve B, for instance, starts from a very low emission rate, and curve A results from the use of a rather high rate coefficient k_{13} for the reaction of acetonitrile with hydroxyl radicals. In fact the expression used for k_{13} in this case leads to a value of 7.3 x 10⁻¹⁴ cm³ s⁻¹ at 300 K, whereas four of the five measurements of k_{13} (Zetzsch, 1981a, b; Fritz et al., 1982; Kurylo and Knable, 1984; Poulet et al., 1984) all indicate k_{13} = 2 x 10⁻¹⁴ cm³ s⁻¹ at 300 K. On the other hand the emission rate associated with curve A seems rather realistic, and curve A is in good agreement with a recent derivation of the CH₃CN mixing ratio (36 ppt at 11.3 km) of Arnold and Hauck (1985) and the figure of 56 pptv quoted as an average surface value by Snider and Dawson (1984, 1985). If the recent data of Arnold and Hauck are correct and if the value of k_{13} found by Harris

REACTION SCHEME FOR STRATOSPHERIC POSITIVE IONS

←—(N)—→ $12 \leqslant N \leqslant 29$ WATER CLUSTERING REACTIONS

$H^+X_i(H_2O)_m + H_2O + M \rightleftharpoons H^+X_i(H_2O)_{m+1} + M$

←—(R)—→ $30 \leqslant R \leqslant 43$ ACETONITRILE CLUSTERING REACTIONS

$H^+X_i(H_2O)_m + X + M \rightleftharpoons H^+X_{i+1}(H_2O)_m + M$

—(S)—→ $44 \leqslant s \leqslant 58$ SWITCHING REACTIONS

$H^+X_i(H_2O)_m + X \rightleftharpoons H^+X_{i+1}(H_2O)_{m-1} + H_2O$
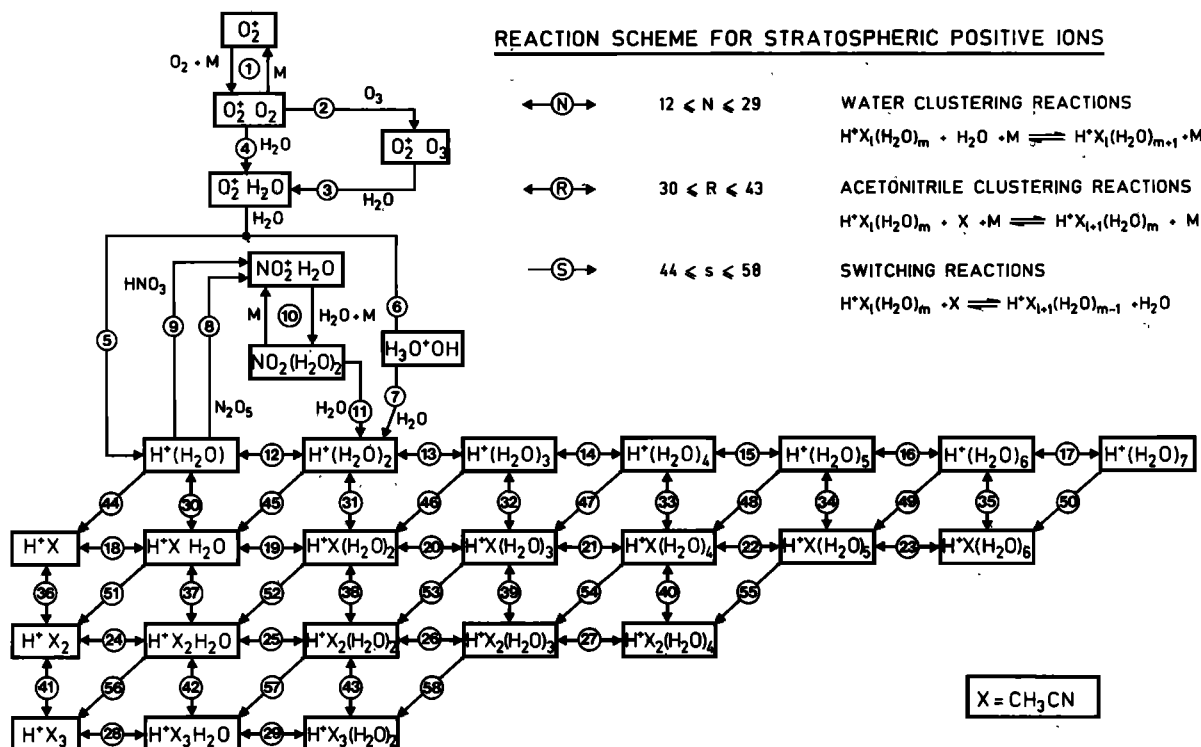
$X = CH_3CN$

Fig. 7. Chemical scheme adopted for the positive ions in the stratosphere.

et al (1981) is too high, it looks as if we would need a supplementary loss mechanism for CH_3CN at the tropopause level or slightly above. Such a mechanism might consist of ion-molecule reactions followed by recombination with stable ion pair formation as discussed in section 2.4. At present, however, it is very speculative to evaluate the importance of such a mechanism because no detailed information is available about positive as well as negative ion composition in the altitude range 0-20 km. Furthermore, the recent upper limit of 32 ppt for CH_3CN at 2 km deduced by Muller (1985) shows that the data of Arnold and Hauck might also be too high, and neither curve B or C can be excluded as representations for the CH_3CN profile. We thus seem to have a dilemma about the choice of a good profile for CH_3CN as well as with its understanding. The way to a solution for this problem would be (1) more measurements of CH_3CN below 20 km, (2) a detailed study of the source strength of CH_3CN, (3) a refinement of our knowledge of the reaction rate coefficients for the loss processes (especially OH), (4) an investigation of possible loss through ion-molecule reactions; in particular, experiments about the products of recombination of heavy cluster ions.

For the time being, however, we will use the three curves A, B, and C to investigate their implications on the positive ion composition in the altitude region 15-50 km in the next sections.

4. Implications For Stratospheric Positive Ion Composition

4.1. The Ion Scheme

The primary ionization source in the stratosphere is galactic cosmic radiation. The asso-

ciated ion pair formation rate Q can be described by a parameterization suggested by Heaps (1978) which, for the latitude where most observations were made ($44°N$), reduces to

$$Q = 7.1 \times 10^{-18} \, [M] \qquad (27)$$

for altitudes above 30 km and

$$Q = 1.7 \times 10^{-20} \, [M]^{1.15} \qquad (28)$$

for lower altitudes. In these expressions, [M] is the atmospheric density expressed in reciprocal cubic centimeters, and Q is given in cubic centimeters per second. Although, strictly speaking, formula (28) is only valid above 18 km, we have used it down to 15 km because of the still reasonable agreement with experimental data. The final loss process for ions is ion-ion recombination. The recombination coefficient adopted here is given by

$$\alpha = 6 \times 10^{-8} \left(\frac{300}{T} \right)^{0.5}$$
$$+ 1.25 \times 10^{-25} \, [M] \left(\frac{300}{T} \right)^4 \qquad (29)$$

This formula, resulting from a fitting of most recent data to an analytical expression (Arijs et al., 1983a), provides results lying between those given by Rosen and Hofman (1981), Bates (1982), and Smith and Adams (1982).

From the electroneutrality condition the total positive and negative ion concentration can then be derived through

$$n^+ = n^- = (Q/\alpha)^{1/2} \qquad (30)$$

The major primary ions created by cosmic rays are N_2^+ and O_2^+. Since N_2^+, however, exchanges its electrical charge instantaneously with O_2, one

TABLE 2. Ion Molecule Reaction Rates Used in the Model

Reaction	Forward Reaction Rate Constant[1]	$- \Delta H_o^2$	$- \Delta S_o^3$	Reference
(1) $O_2^+ + O_2 + M \rightarrow O_2^+O_2 + M$	2.6×10^{-30} $(300/T)^{3.2}$			Payzant et al. (1973)
		10.8	25	Conway and Janik (1973)
(2) $O_2^+O_2 + O_3 \rightarrow O_2^+O_3 + O_2$	1×10^{-10}	3.7	~ 4.5	Dotan et al. (1978)
(3) $O_2^+O_3 + H_2O \rightarrow O_2^+H_2O + O_3$	1.2×10^{-9}	---	---	Dotan et al. (1978)
(4) $O_2^+O_2 + H_2O \rightarrow O_2^+ \cdot H_2O + O_2$	1.5×10^{-9}	---	---	Howard et al. (1972)
(5) $O_2^+H_2O + H_2O \rightarrow H^+(H_2O) + OH + O_2$	2×10^{-10}	---	---	Howard et al. (1972)
(6) $\rightarrow H_3O^+ \cdot OH + O_2$	1×10^{-9}	---	---	Howard et al. (1972)
(7) $H_3O^+ \cdot OH + H_2O \rightarrow H^+(H_2O)_2 + OH$	1.4×10^{-9}	---	---	Howard et al. (1972)
(8) $H^+H_2O + N_2O_5 \rightarrow NO_2^+ \cdot H_2O + HNO_3$	1.3×10^{-9}	~23	---	Davidson et al.(1978)
(9) $H^+H_2O + HNO_3 \rightarrow NO_2^+ \cdot H_2O + H_2O$	1.6×10^{-9}	-	-	Fehsenfeld et al.(1975)
(10) $NO_2^+ \cdot H_2O + H_2O + M \rightarrow$ $NO_2^+(H_2O)_2 + M$	2×10^{-27}	[16]	[22]	Fehsenfeld et al.(1975)
(11) $NO_2^+(H_2O)_2 + H_2O \rightarrow$ $H^+(H_2O)_2 + HNO_3$	2×10^{-10}	---	---	Fehsenfeld et al.(1975)

[1] Rate constant in cubic centimeters per second for two-body reactions and in $cm^6 s^{-1}$ for three-body reactions
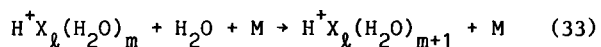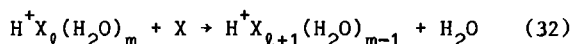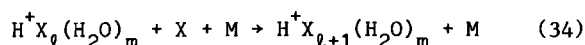
[2] kcal/mol.

[3] cal/(mol x deg.) or eu.

can consider that each ionization leads to the formation of an ionized oxygen molecule O_2^+. The subsequent ion chemistry leading to the terminal ions has been described in several papers and in particular by Ferguson et al. (1979) and Ferguson and Arnold (1981). The primary O_2^+ ions react with O_2 to form O_4^+, which can be hydrated to produce $O_2^+ \cdot H_2O$ and, subsequently, the $H^+(H_2O)$. The mechanism, which leads to the low-order proton hydrates (PH) is shown in the upper part of Figure 7 (reactions 1-11), and the appropriate reaction rate coefficients are given in Table 2. The higher-order PH are then obtained by supplementary three-body reactions (reactions 12-17 of Figure 7) :

$$H^+(H_2O)_n + H_2O + M \rightarrow H^+(H_2O)_{n+1} + M \qquad (31)$$
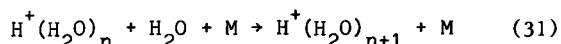
The reaction rate coefficients and thermochemical constants (ΔH_o and ΔS_o) used for these kinds of reactions in the present model are taken from Lau et al. (1982). The conversion of PH to nonproton hydrates (NPH) proceeds through

$$H^+X_\ell(H_2O)_m + X \rightarrow H^+X_{\ell+1}(H_2O)_{m-1} + H_2O \qquad (32)$$

$$H^+X_\ell(H_2O)_m + H_2O + M \rightarrow H^+X_\ell(H_2O)_{m+1} + M \qquad (33)$$

and

$$H^+X_\ell(H_2O)_m + X + M \rightarrow H^+X_{\ell+1}(H_2O)_m + M \qquad (34)$$

where $X \equiv CH_3CN$. Switching reactions represented by equation (32) -- reactions (44)-(58) in Figure 7 -- have been measured in the laboratory

by Smith et al. (1981) for $\ell = 0$ and $m = 1, 2, 3, 4$. The results are in good agreement with calculations based on the ADO (average dipole orientation) theory of Su and Bowers (1975). Since the latter allows the computation of all unknown rate constants for these types of reactions, we use the ADO values for the forward reaction rates throughout the whole model. For the clustering reactions represented by equations (33) and (34), no measurements of the rate constants are available. In this case we put the forward reaction rate constants equal to the corresponding rate constant (clustering with the same number of ligands involved) for PH water clustering (equation (32)) corrected by a factor taking into account the difference in reduced masses of the ions and molecules. The values of ΔH_o and ΔS_o are adopted from laboratory measurements of Meot-Ner (1978) for reactions (36) and (41) of Figure 7, Meot-Ner (1984) for reactions (18)-(23), and from recent unpublished data (M. Meot-Ner, private communication, 1984) for reactions (24), (25), (26), (29), (37), (40), and (42).

For all reactions (two-body and three-body) a forward (k_f) and a reverse reaction (k_r) are used where possible. The reverse reaction rate is calculated through

$$k_r = k_f/K_{eq} \qquad (35)$$

and

$$- RT \ln K_{eq} = \Delta H_o - T\Delta S_o \qquad (36)$$

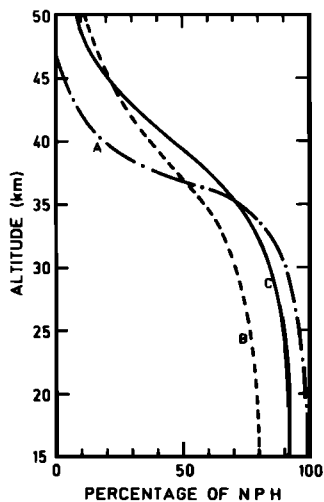If no appropriate values for ΔH_o and ΔS_o are

Fig. 8. Relative amount of the non proton hydrate ions calculated for the different vertical distributions of CH_3CN shown in Figure 6.

available from the literature, they are calculated from a thermodynamic cycle. For cases where this was impossible, such as for reactions (3), (4), (5), (6), (7), (8), (9), and (11), k_r is put to zero. All reaction rate coefficients for three-body reactions are computed from

$$k_f^{(3)} = k_{fo}^{(3)} /(1 + k_{fo}^{(3)}[M]/k_c) \qquad (37)$$

where $k_{fo}^{(3)}$ is the three-body rate constant (in $cm^6 \, s^{-1}$) as cited in the literature for low pressures and the collisional rate constant k_c is obtained from the ADO theory of Su and Bowers (1975). The use of formula (37) guarantees a saturation of $k_f^{(3)}$ at lower altitudes. A priori we have not ruled out the possibility of the competition of association reactions represented by equation (34) with switching reactions (equation (32)). Since, however, the total effective bimolecular rate coefficient for a reaction involving both switching and association in parallel will not exceed the collisional rate coefficient k_c and since the switching reaction rate coefficient at low pressures turns out to be about equal to k_c (Smith et al., 1981), we put

$$k_f^{(2)} = k_c - k_f^{(3)} [M] \qquad (38)$$

where $k_f^{(2)}$ is the forward reaction rate coefficient for reactions of the type of equation (32), k_c is obtained with the ADO theory, and $k_f^{(3)}$ is the forward rate coefficient for association reactions (equation (34)) as obtained with formula (37).

4.2. Brief Model Description

The model used here is based on the assumption that all ions are in steady state, and it is essentially the same as the one described in detail by Brasseur and Chatel (1983). The present calculations take into account 29

different ion species and 58 reactions (see Table 2 and Figure 7). The concentrations of the neutral trace species are taken from the 1-D model used in section 3, and the vertical distribution of the temperature is taken from the U.S. Standard Atmosphere (1966).

4.3. Model Results

The relative amount of the NPH, as predicted by the model for the three CH_3CN profiles as given in figure 6, is shown in figure 8. As will be discussed in a subsequent paper (Ingels et al., this issue), the experimental results obtained so far are in reasonable agreement with the model calculations but do not allow a definite choice of the appropriate profile of CH_3CN because of the large scatter in the experimental data. Figure 9 shows the relative amount of the most abundant ion species calculated for cases A, B, and C. The different ions are labeled with their mass number, and the corresponding chemical composition is specified in Table 3. Figure 9 indicates that very few differences occur for the three cases, except below 25 km, where the ion composition is directly controlled by the amount of CH_3CN.

To illustrate the effect of temperature variation, a model run was performed for case C with a temperature profile that differs from the U.S. Standard Atmosphere by about 10 K (adopted temperature is 10° lower). The results are shown by the dotted lines in Figure 9c.

It is also interesting to investigate the influence on the different ion abundances of possible association reactions of the type of equation (33). Therefore several model runs have been performed for case C. In a first run, all reaction rate constants are used as described in section 4.1. In a second run, forward rate constants for three-body reactions (30)-(43) in Figure 7 are put equal to zero. In a third run, only those for reactions (30) to (35) are imposed to be zero. All runs give exactly the same relative ion abundances as shown in Figure 9c. This is to be expected, since equilibrium conditions are rapidly established in the water clustering reactions, shown along the horizontal lines in the lower part of Figure 7.

A detailed comparison of the ion abundances emerging from the model with the experimental data obtained so far is beyond the scope of this paper and is presented in a companion paper (Ingels et al., this isssue). Nevertheless it is noted that the results of the present model calculation are in better agreement with the available measurements than those of a previous model prediction (Brasseur and Chatel, 1983), where the effect of CH_3CN on the ion chemistry was also considered but where a more simplified reaction scheme was used. The most abundant NPH ion in the altitude region 25-40 km found now is the ion with mass 96, in accord with all positive ion spectra published so far. Above 40 km, the most abundant ions have a mass 73 and 55 amu, which is also in agreement with published data. However, care should be taken in comparing the model calculations with observed abundances in view of contamination, cluster break-up, and uncertainties in the temperature (Ingels et al., 1985).
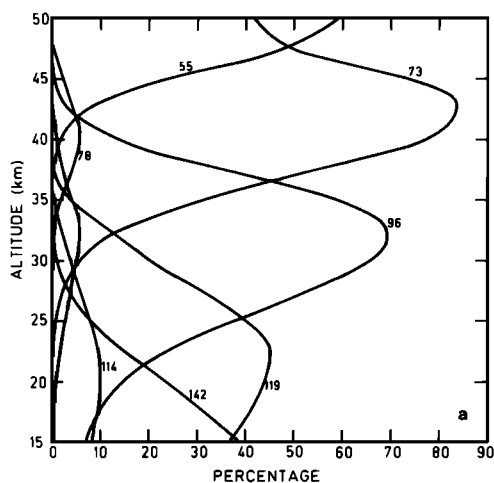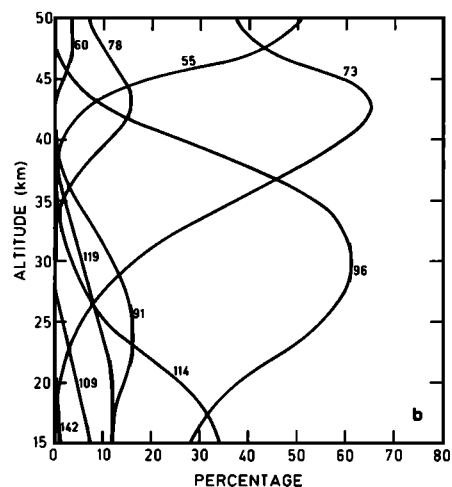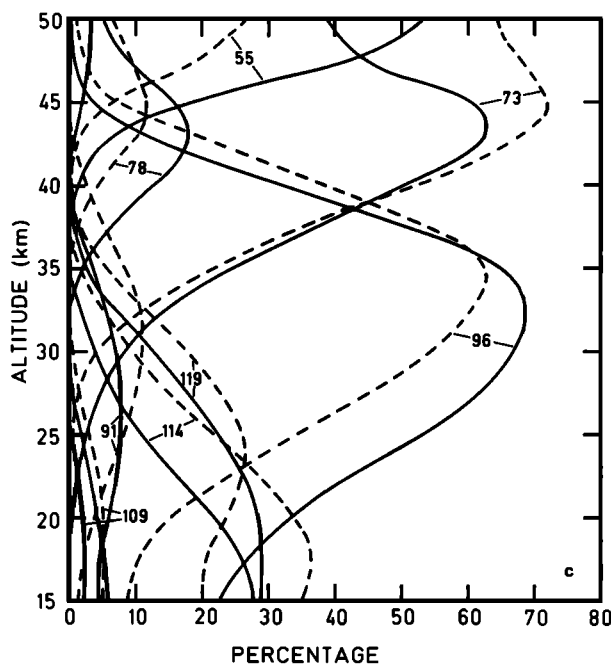
Fig. 9a

Fig. 9b

Fig. 9c

Fig. 9. Vertical distribution of the relative amount of the most abundant positive ions in the stratosphere: (a), (b) and (c) are the results obtained with the CH_3CN profiles A, B, and C, respectively, of Figure 6.

5. Summary and Conclusions

The vertical distribution of acetonitrile in the atmosphere has been calculated with a one-dimensional model on the basis of an assumption that CH_3CN is released at the earth's surface and removed from the atmosphere by scavenging through precipitation and chemical reactions (mainly with hydroxyl radicals in the stratosphere and atomic oxygen in the mesosphere). The rate of precipitation scavenging is computed by using laboratory data of the equilibrium vapor pressure above water-acetonitrile solutions, and the result obtained is in good agreement with a recent independent determination (Hamm et al., 1984). It is also

demonstrated that the loss of CH_3CN by ion-molecule reactions is probably only important in some altitude regions, although more experimental data are needed to evaluate their importance. For the chemical loss reactions, most recent rate constants measured in the laboratory were adopted. The use of different values for these reaction rate constants and for the eddy diffusion coefficient leads to a variety of possible CH_3CN profiles.

The combination of the extreme model results and the experimental vertical profiles of CH_3CN, resulting from ion mass spectrometry, leads to an estimation for the bounds on the global annual surface emission of acetonitrile. These bounds (1.5×10^{10} g and 5×10^{11} g) seem

TABLE 3. Mass Number and Chemical Composition of Most Abundant Ions (X $\equiv$ CH$_3$CN)

Mass Number, amu		Formula
PH	NPH	
55		$H^+(H_2O)_3$
73		$H^+(H_2O)_4$
91		$H^+(H_2O)_5$
109		$H^+(H_2O)_6$
	60	$(H^+ \cdot X \cdot H_2O)$
	78	$H^+X(H_2O)_2$
	96	$H^+X(H_2O)_3$
	114	$H^+X(H_2O)_4$
	142	$H^+ \cdot X_3 \cdot H_2O$

consistent with the strength of the actual known sources of CH$_3$CN (direct emission, car exhaust gases, and biomass burning), which supports the basic idea of the model.

Finally, it is shown through a model calculation of the ion composition, based on most recent laboratory data about ion-molecule reactions and ion-clustering of CH$_3$CN, that the obtained acetonitrile profiles lead to ion abundances, which are in good agreement with most recent experimental results in the altitude region 20-45 km.

An extension of the experimental data over a larger altitude region, as well as refined laboratory measurements concerning the chemical processes involved, especially ion-molecule reaction losses, are needed to elucidate the problem.

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