

STRATOSPHERIC ION CHEMISTRY: PRESENT UNDERSTANDING AND OUTSTANDING PROBLEMS

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Abstract—Our present knowledge on stratospheric ion chemistry is reviewed. Available experimental data as well as modelling efforts are discussed and the needs for further research are pointed out.

1. INTRODUCTION

Until 1977 our knowledge of the stratospheric ion chemistry was limited to tentative models. As a consequence of the pioneering work of Narcisi and co-workers (Narcisi and Bailey, 1965; Narcisi, 1974), which revealed a D region ion composition not expected by previous studies (Nicolet and Aikin, 1960), numerous laboratory experiments were performed and a wealth of ion molecule reaction rates and thermodynamic data (Ferguson, 1973) became available, enabling the generation of adequate ion reaction schemes (Ferguson, 1974) and ion chemistry models (Fehsenfeld and Ferguson, 1969; Thomas, 1974) for this region. Based upon this knowledge, some crude models (Ferguson, 1974; Mohnen, 1971) were extrapolated to speculate on the ion chemistry of the stratosphere. However, no experimental data about the ion composition in the Earth's atmosphere below 65 km altitude were available to confirm these predictions. This lack of *in situ* ion composition measurements was partly due to the large experimental problems associated with the sampling of ions from relatively high pressure regions such as the stratosphere. Furthermore the low number density of charged particles was expected to have minor effects on radio wave propagation and therefore there was limited motivation to tackle this considerable instrumental problem.

Nevertheless the knowledge of the ion composition and an understanding of the ion chemistry in the stratosphere is required to fully comprehend atmospheric electricity problems. It has also been realized that stratospheric ions might play an important role in aerosol formation and that ion composition probing

could lead to the detection of some trace gases so far unknown. Therefore efforts were undertaken in the mid-1970s by different groups to develop balloon-borne ion mass spectrometers. Up to now several *in situ* stratospheric ion composition measurements have been performed in the altitude region from 15 to 45 km mainly by two groups: the Max-Planck-Institut für Kernphysik in Heidelberg (MPIH) and the Belgian Institute for Space Aeronomy (BISA).

It is the purpose of the present paper to review our present knowledge of stratospheric ion chemistry as it has emerged from this work and from subsequent laboratory measurements and modelling efforts. Some outstanding problems, which require further research, will also be pointed out.

2. ION SOURCES, SINKS AND ION CONCENTRATIONS

The topic of ionization, recombination and ion density in the stratosphere has been reviewed to a considerable extent in a previous paper (Arijs, 1983) and will therefore only be discussed briefly hereafter.

Under normal conditions the principal and practically only ionization source in the stratosphere is galactic cosmic rays. The cosmic ray intensity decreases with increasing solar activity and exhibits no diurnal variation. It varies with geomagnetic latitude, being about three times greater at the poles than at the equator. Due to the high energy of the cosmic radiation its ionization effect is non-selective and virtually no absorption occurs in the stratosphere. Therefore the ion production rate Q merely depends on the neutral gas number density. At 35 km altitude the ion production rate varies between 1 and 3 ion-pairs cm^{-3} , whereas at 13 km a maximum is reached between 15 and 40 ion-pairs cm^{-3} , depending on the solar activity. Below 15 km, mass absorption of the cosmic rays starts to be effective and the ion pro-

Dedicated to Professor Dr Marcel Nicolet in honour of his 80th birthday and his numerous contributions to Aeronomy.

duction decreases with decreasing altitudes. The ionization in the stratosphere is well documented (Neher, 1967; Pommerantz and Duggal, 1974; Heaps, 1978) and no major contradictions or disputes seem to exist in this area.

Due to the high stratospheric neutral density the electrons formed by the ionization process rapidly attach mainly to oxygen molecules and form negative ions. Thus the resulting "plasma" consists of positive and negative ions, equal in number density. The final fate of these ions is loss through ion-ion recombination. Unfortunately very few laboratory data are available for the recombination coefficient α of the ions having the same nature as those found in the stratosphere (Smith *et al.*, 1981). However, recent parametrization efforts (Smith and Adams, 1982), computer simulations (Bates, 1982) as well as simultaneous *in situ* measurements of ion densities and ionization rates (Rosen and Hofman, 1981b) resulted in values for the ion-ion recombination coefficient which are in reasonable agreement for the altitude region from 10 to 45 km. The values of α thus obtained vary from $2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ at 10 km to $5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 45 km. At the present time the ion-ion recombination coefficient in the stratosphere can be considered as known within a factor of 2.

An additional loss mechanism of stratospheric ions may be attachment to aerosol particles (Zikmunda and Mohnen, 1972). However, little is known about this process and it is generally believed that under normal conditions it is not very efficient in the stratosphere. One of the major problems remaining so far in the field of stratospheric ion chemistry is that of ion-ion recombination products. This problem will be discussed again later on.

From the knowledge of the ionization rate Q and the ion-ion recombination coefficient α , the ion concentration n in the stratosphere can be easily calculated using the simple formula

$$Q = \alpha \times n^2, \quad (1)$$

which leads to ion concentrations in the stratosphere of the order of 3000 cm^{-3} , varying little with altitude. Numerous *in situ* measurements of the ion concentration with Guerdian condensers have been performed in the stratosphere (Paltridge, 1965; Bragin *et al.*, 1968; Rose *et al.*, 1972) and severe discrepancies have been noticed between the different measurements. It is now believed however that these are due to poorly understood and variable air flow in the Guerdian condensers, and more reliable results have been obtained with better-designed instruments (Rosen and Hofman, 1981a).

3. STRATOSPHERIC ION COMPOSITION MEASUREMENTS

3.1. Experimental techniques

Before describing the stratospheric ion composition results obtained hitherto, a description of the experimental methods used seems appropriate. Since, however, the major instrumental characteristics have been explained extensively elsewhere (Ingels *et al.*, 1978; Nevejans *et al.*, 1982, 1985), this description can be very brief.

All data reported in the open literature so far have been obtained with balloon-borne quadrupole mass spectrometers. Such instruments consist mainly of a quadrupole mass filter and associated detector built into a cryopump cooled by liquid helium (Ingels *et al.*, 1978) or liquid neon, and of the associated electronics package (Nevejans *et al.*, 1982, 1985). In all configurations flown up to now, the ions are sampled into the mass spectrometer through a single hole (of 0.2–0.4 mm diameter), drilled in a thin flange biased a few volts (typically 5 V) with respect to the metal structure of the balloon gondola. Two methods have been used to guide the ions into the mass filter itself. Whereas the Belgian group uses a small electrostatic lens mounted in front of the quadrupole for this purpose, the *MPIH* group omits this and uses an open front end of the quadrupole, taking advantage of the electric field created by the quadrupole field-axis bias potential with respect to the sampling plate (Schlager and Arnold, 1987a). In both cases, however, rather high electric fields exist in the gas jet expansion region just behind the sampling aperture. This electric field can, together with the high neutral density in the gas jet, give rise to collision-induced dissociation resulting in possible errors in the data interpretations.

3.2. Positive ion composition data

The very first results on stratospheric ion composition were obtained by Arnold *et al.* (1977) with a rocket-borne instrument, merely as a by-product of their mesospheric measurements. As was expected from previous models (Ferguson, 1974), hydronium ions of the type $\text{H}^+(\text{H}_2\text{O})_n$, also called proton hydrates (PHs), were detected. However a second group of ions, called non-proton hydrates (NPHs), containing the masses 29 ± 2 , 42 ± 2 , 60 ± 2 and 80 ± 2 , was also observed. It was established that this ion family resulted from ion-molecule reactions of the PHs with an unknown trace gas X, having a larger proton affinity than that of water.

The major inconveniences of rocket-borne instruments are the short integration time and the possible break up of the ions due to the shock wave in front

of the instrument. Balloons do not have these disadvantages and therefore are well suited for ion-probing in the stratosphere. The first positive ion mass spectra obtained in the stratosphere with balloon-borne instruments (Arijs *et al.*, 1978; Arnold *et al.*, 1978) confirmed the existence of the NPHs and showed that they could be represented by the formula $H^+X_n(H_2O)_m$, where X had a mass of 41 ± 1 . After these findings, there have been several speculations on the nature of X (Arnold *et al.*, 1978; Ferguson, 1978; Murad and Swider, 1979), but a definite identification of X became possible only after the first high-resolution mass spectra obtained by Arijs *et al.* (1980). From these it was concluded unambiguously that the mass of X was 41 and that this molecule most probably was acetonitrile (CH_3CN), as originally suggested by Arnold *et al.* (1978). Whereas at first this hypothesis had been considered as unlikely in view of the difficulty of explaining the presence of acetonitrile in the stratosphere, more credibility to it was given later on by laboratory measurements (Smith *et al.*, 1981; Böhringer and Arnold, 1981; Viggiano *et al.*, 1988), careful inspection of mass spectra with regard to fractional and isotopic abundance (Arnold *et al.*, 1981a; Arijs *et al.*, 1982a; Ingels *et al.*, 1986) and break-up products (Schlager and Arnold, 1985). Since 1977 several positive ion composition measurements have been performed with instruments with increased resolution and thanks to the progress in ballooning techniques; the altitude domain presently investigated with balloon-borne ion mass spectrometers ranges from about 20 to 45 km. All measurements revealed two major ion families, PHs and NPHs, the fractional abundances of which are shown versus altitude in Fig. 1.

Apart from the two major positive ion families detected in the stratosphere, several minor mass peaks have also been observed (Arijs *et al.*, 1982a; Henschen and Arnold, 1981). Their analysis, however, is at present merely speculative, and a final identification has to await balloon flights with more sensitive instruments (Moor *et al.*, 1989). Furthermore it should be noted that care must be taken in the interpretation of small ion mass peaks, since contamination can be a serious problem in balloon-borne *in situ* instruments and can easily falsify ion signals (Nevejans *et al.*, 1985).

The altitude region covered by stratospheric ion composition measurements has recently been extended by the MPIH group in two ways. By means of a Falcon 20 research airplane and a new aircraft-borne instrument, measurements were performed in the uppermost part of the troposphere and the lowermost part of the stratosphere (Hauck and Arnold,

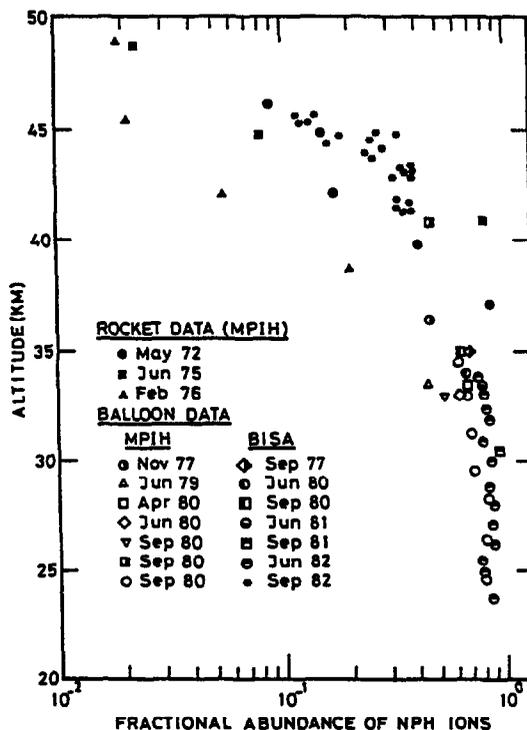


FIG. 1. FRACTIONAL ABUNDANCE OF NON-PROTON HYDRATE IONS VERSUS ALTITUDE AS OBTAINED IN DIFFERENT BALLOON AND ROCKET EXPERIMENTS.

BISA: Belgian Institute for Space Aeronomy; MPIH: Max-Planck-Institut für Kernphysik of Heidelberg (after Arijs *et al.*, 1984).

1984). Again two major ion families have been observed; but due to the low resolution used in favour of signal strength, it is very difficult to identify the families unambiguously. The first group probably consists of PHs, although hydrated ammonium cannot be excluded and the second one most likely is due to protonated acetone-water clusters. Further measurements will be required to fully interpret these data.

Recently the first measurement results obtained with a new parachute-borne drop sonde mass spectrometer, designed for ion composition studies around the stratopause, were published (Pfeilsticker and Arnold, 1989). Positive ion mass spectra recorded at 55.9 and 48.3 km were reported. The mass peaks observed (37, 55 and 73) indicated the presence of PHs, but apart from peaks induced by telemetry-induced radio-wave ionization (mass 32 and 50, O_2^+ and $O_2^+H_2O$, respectively) (Pfeilsticker and Arnold, 1987) no major NPH signals could be identified.

Again, low resolution was used and more experiments will be necessary to identify the ions at these altitudes.

3.3. Negative ion composition data

From the reaction schemes, developed for the D region and the neutral composition data of the stratosphere, it was expected that the most dominant negative ions in this region would be NO_3^- and its hydrates (Ferguson, 1974). Soon after the first mass analysis of positive ions, negative stratospheric ion composition measurements became available (Arnold and Henschen, 1978). These data, recorded around 35 km altitude, showed the presence of two major negative ion families. According to previous laboratory experiments (Fehsenfeld *et al.*, 1975), one could be identified as $\text{NO}_3^- (\text{HNO}_3)_n$, whereas the other could be represented by $\text{R}^- (\text{HR})_m (\text{HNO}_3)_l$. As a most likely candidate for HR, sulphuric acid was put forward by Arnold and Henschen. Although unexpected, this assignment seemed more acceptable than the CH_3CN hypothesis, because the presence of H_2SO_4 in the stratosphere was expected as a result of the photochemical oxidation of sulphur compounds such as SO_2 and COS (see Turco *et al.* (1979) and references therein). The assumption of HR being H_2SO_4 was rather quickly supported by laboratory measurements of ion-molecule reactions of H_2SO_4 with $\text{NO}_3^- (\text{HNO}_3)_n$ cluster ions by Viggiano *et al.* (1980) and was later confirmed by the first high-resolution negative ion mass spectra, obtained near 35 km altitude by Arijs *et al.* (1981).

From 1980 on, a considerable number of balloon experiments have been devoted to the measurement of the stratospheric negative ion composition (Viggiano and Arnold, 1981a; Arijs *et al.*, 1982b, 1983a, 1985a; Arnold *et al.*, 1981b, 1982; Viggiano *et al.*, 1983; Arnold and Qiu, 1984; Schlager and Arnold, 1986, 1987b; Ingels *et al.*, 1987). Data are now available between 15 and 45 km, including detailed height profiles of the different observed ion species (Viggiano *et al.*, 1983). These data showed that all major negative ions are clusters with either NO_3^- or HSO_4^- as core ions and having HNO_3 , H_2SO_4 and H_2O as ligands. Typical fractional count rates, which are a measure of the fractional abundances of the NO_3^- and HSO_4^- ions versus altitude, are shown in Fig. 2.

Apart from the HSO_4^- and NO_3^- ions, other ion clusters were detected in the minor mass peaks of some spectra (McCrum and Arnold, 1981; Arijs *et al.*, 1982b), but again their definite identification is by no means certain and will require further measurements.

Recently negative ion mass spectra recorded with the *DROPAS* instrument (Pfeilsticker and Arnold,

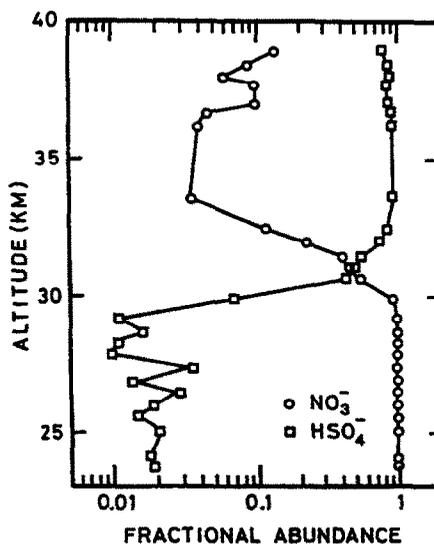


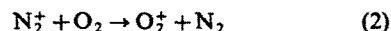
FIG. 2. FRACTIONAL ION SIGNAL OF NO_3^- AND HSO_4^- CORE IONS AS A FUNCTION OF ALTITUDE AS OBSERVED IN A BALLOON FLIGHT BY THE HEIDELBERG GROUP (AFTER VIGGIANO AND ARNOLD, 1981).

1989) between 35 and 55 km, revealed that near the stratopause the major negative ions contain CO_3^- and HCO_3^- core ions as well as NO_3^- and HSO_4^- ions with not more than one HNO_3 ligand.

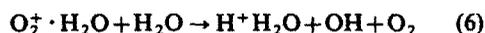
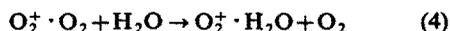
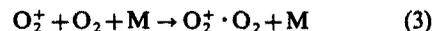
4. STRATOSPHERIC ION CHEMISTRY

4.1. Positive ion chemistry

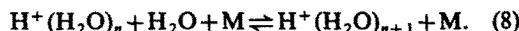
As a result of the laboratory measurements, performed to unravel the D region ion chemistry, the formation of hydronium ions or proton hydrates in the stratosphere could be easily explained. The ion reaction chain leading to PHs starts with the O_2^+ ion, which is either directly formed by galactic cosmic ray ionization or by charge transfer:



from N_2^+ , also formed by cosmic rays. Subsequently the following ion-molecule reactions occur:

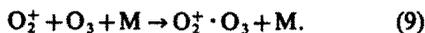


Further hydration then proceeds through:

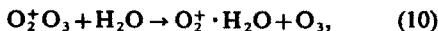


The previous ion-molecule reactions have been studied extensively in the laboratory and their rate constants are known within about 40% (for a review of ion-molecule reaction rates see Ikezoe *et al.*, 1987). Reactions (2)–(8) are terminated in a few milliseconds and therefore the whole reaction chain is fast compared to the total lifetime of the ions, which is determined by ion-ion recombination and is normally of the order of a few hours. Non-proton hydrates can only be formed in two different ways: either the reaction chain (2)–(8) is interrupted somewhere before the PHs are formed or the terminal PHs react with some trace gas of the stratosphere. The first possibility has been investigated by Dotan *et al.* (1978) by studying the ion chemistry of gases equally abundant as water vapour in the stratosphere, namely CO_2 , CH_4 and ozone.

Only ozone was found to be able to compete with water vapour through the reaction



However, the resulting cluster ion $\text{O}_2^+ \cdot \text{O}_3$ reacts very fast with water through



and therefore has no influence.

As a conclusion it can be safely stated that the formation of NPHs through an interruption of the PH formation cycle is very unlikely, and that therefore PHs are expected to be terminal ions in the stratosphere and also in the troposphere where water vapour is much more abundant. The PH reaction scheme accepted hitherto is represented in Fig. 3.

The presence of NPHs in the stratosphere must therefore be explained by the reaction of some trace gas X with PHs. As was explained by Ferguson and Arnold (1981) the number of candidates for X must be limited to those gases having a larger proton affinity than that of water (165 kcal/mol). Because of the long lifetime of the ions ($\sim 10^4$ s), we have to look for gases for which the ion molecule reaction rate with PHs multiplied by their concentration is of the order of 10^{-4} s^{-1} , which for rate constants of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ translates into number densities of minimum 10^5 cm^{-3} . There are several trace gases having a higher number density than 10^5 cm^{-3} and with a proton affinity larger than 170 kcal/mol present in the stratosphere, such as HNO_3 and N_2O_5 . As is shown in Fig. 2 these species perform a "do nothing cycle" through the reactions (for rate constants and references see Ikezoe *et al.*, 1987):

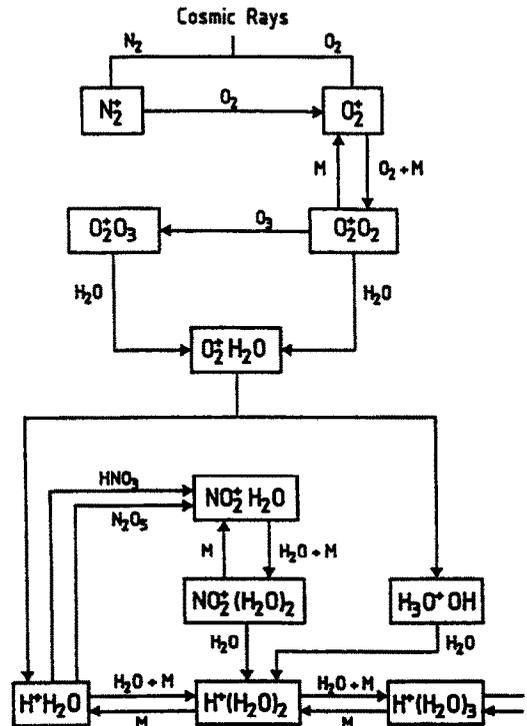
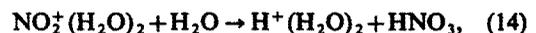
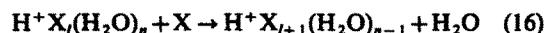


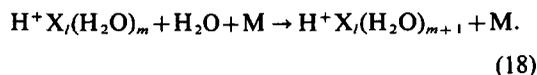
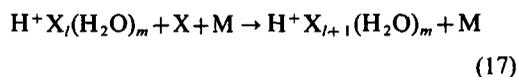
FIG. 3. REACTION SCHEME SHOWING THE CONVERSION OF PRIMARY POSITIVE IONS FORMED BY COSMIC RAYS INTO HYDRONIUM IONS OR PROTON HYDRATES (PHs).



which convert $\text{H}^+ \cdot \text{H}_2\text{O}$ into $\text{H}^+ (\text{H}_2\text{O})_2$. Several other candidates can be considered for X, among which NaOH appeared to be the most likely (Ferguson, 1978; Liu and Reid, 1979) until high-resolution ion mass spectra, which excluded this hypothesis, had been recorded (Arijs *et al.*, 1980). A very important conclusion of the elimination of NaOH as a possible candidate for X is that sodium or its compounds, which are according to Liu and Reid (1979) expected as a result of meteor ablation in the stratosphere, must disappear in some way before it participates in the stratospheric ion chemistry. It is most likely that this sink for sodium compounds is adsorption in aerosols (Turco *et al.*, 1981). It is now generally accepted that X is acetonitrile (see Section 3.2) and that the NPHs are formed through the ligand-switching reactions



and the three body association reactions



This continuation of the reaction-scheme of Fig. 3 is shown in Fig. 4.

Assuming that reactions (16) are the source for the NPHs and that the sink is ion-ion recombination, we may write

$$k[\text{X}][\text{PH}] = \alpha[\text{NPH}][n^-], \quad (19)$$

where square brackets denote number densities, k is the rate coefficient for reactions (16), $[n^-]$ is the total negative ion concentration and α the ion-ion recombination coefficient. Since the ratio R ($[\text{NPH}]/[\text{PH}]$) can be deduced from the fractional abundances as shown in Fig. 1 and the values of k , α and $[n^-]$ can be obtained from other sources, equation (19) principally allows the derivation of the mixing ratio of acetonitrile versus altitude in the stratosphere. A compilation of the CH_3CN mixing ratios as inferred in this way from the presently available set of positive ion composition data is shown in Fig. 5, together with model calculations. As was justified before (Arijs *et al.*, 1987) a value of $3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for k has been adopted, $[n^-]$ was calculated using formula (1) and the parametrization of Heaps (1978) for Q , and for α a parametrization of the form

$$\alpha = 6 \times 10^{-8} \times (300/T)^{1/2} + 1.25 \times 10^{-25} \times [\text{M}] \times (300/T)^4 \quad (20)$$

was used.

A few remarks should be made here about the results summarized in Fig. 5. In all derivations of the CH_3CN mixing ratio published so far, the values of $[n^-]$ or α were either taken from the literature or from

parametrizations as described above. This may lead to considerable errors. The value of α used by the Belgian group for instance is, at high altitudes (around 30 km), closer to the theoretical value of Bates (1982), whereas for lower altitudes (around 20 km) it is closer to the parametrization of Smith and Adams (1982), which is about two times larger than the Bates values at this altitude. Presently the ion-ion recombination coefficient is known within a factor of 2 and as a result the same error may be present in the acetonitrile mixing ratio profiles. Furthermore the use of a value for $[n^-]$ calculated as explained before or adopted from other *in situ* measurements can also induce some errors, because the real ion density at the time of the recording of the mass spectra may be different. Ideally one would have to measure simultaneously the ion composition, the total ion concentration and the ionization rate to obtain exact values of $[\text{CH}_3\text{CN}]$.

A major error in the derived CH_3CN number densities, however, is caused by the collision-induced dissociation (CID) of the ions upon sampling into the mass spectrometer. As was explained in Section 3.1 rather high electric fields exist in the mass spectrometer in the gas jet expansion region. In this region the gas number density is still sufficient to allow many collisions of the sampled ions with neutrals. Due to the acceleration of the ions by the existing electric fields, some of these collisions can be energetic enough to break off ligands of the sampled ion clusters. As a consequence the observed distribution in an ion family can be strongly disturbed. This phenomenon has been recognized rather quickly for the PHs and in some cases was even corrected by laboratory calibrations (Arnold *et al.*, 1981b; Arijs *et al.*, 1982b). Only recently it was realized that CID may even result in knocking off the more strongly bound CH_3CN ligands and thus may reconvert NPHs in PHs in the mass spectrometer itself (Schlager and Arnold, 1987b; Arijs *et al.*, 1987; Graul and Squires, 1989). A theoretical investigation of the CID process (Fussen *et al.*,

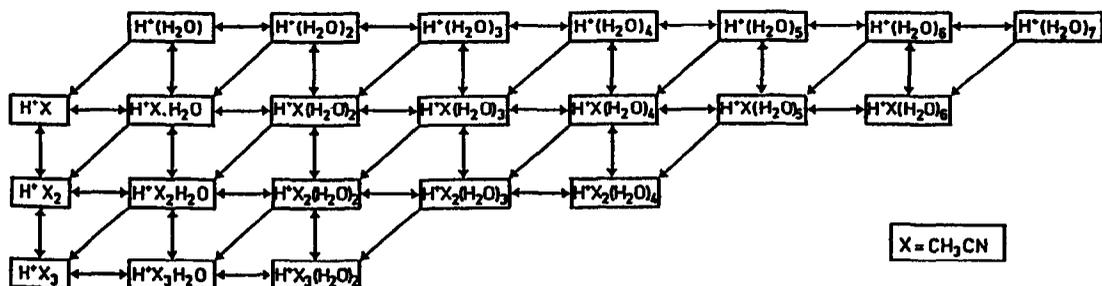


FIG. 4. REACTION SCHEME FOR THE CONVERSION OF PHs INTO NPHs.

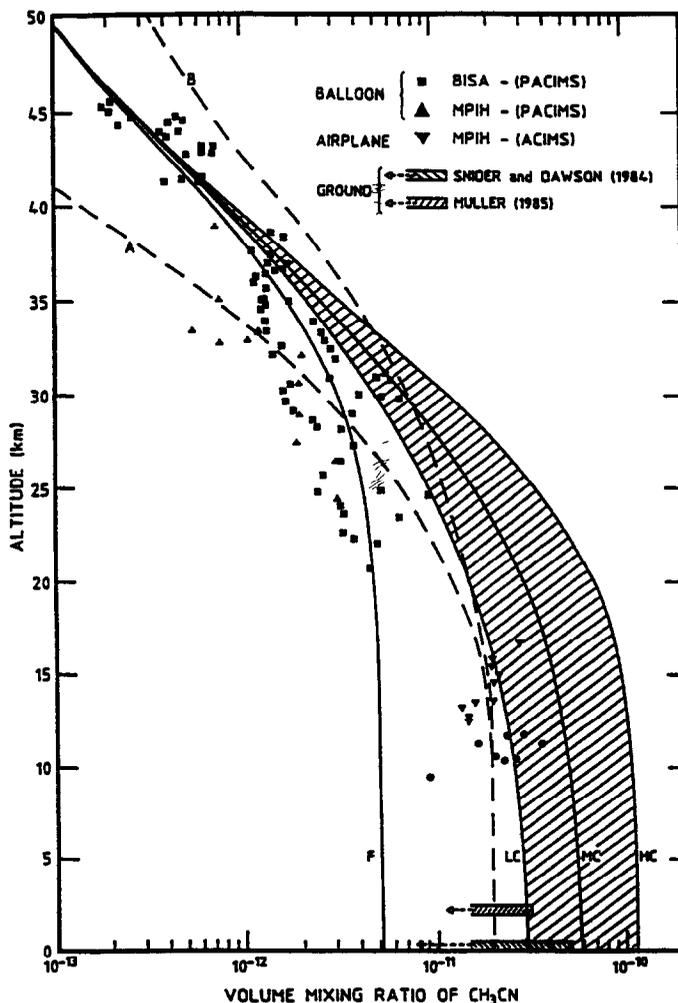


FIG. 5. VOLUME MIXING RATIO PROFILE OF ACETONITRILE AS DERIVED FROM DIFFERENT EXPERIMENTS AND MODELS.

Lines A and B are two typical model calculations. Line F is a non-linear fit through the balloon data and lines LC, MC and HC are possible corrections for collision-induced dissociation (after Fussen *et al.*, 1989).

1989) showed that the error induced by CID may be as large as a factor of 4 at an altitude of 25 km. It is also accepted now that CID is responsible for the discrepancies between the CH_3CN mixing ratios derived from natural ion composition measurements and those inferred from *ACIMS* (Active Chemical Ionization Mass Spectrometry) experiments (Knopp and Arnold, 1987; Arnold and Knopp, 1987) (see also Fig. 5).

As a result it is very difficult to compare the CH_3CN profile above 20 km as shown in Fig. 5 with model calculations. This is rather unfortunate because a good check of our understanding of the stratospheric

positive ion chemistry would be the building up of a model of acetonitrile and coupling it to an ion-chemical model to compare the results with the ion composition data, such as ion distribution profiles and derived CH_3CN profiles. Although some attempts to realize this have been made (Brasseur *et al.*, 1983; Arijs and Brasseur, 1986) and the results are encouraging, more refinements are required to finalize this work.

Establishing an ion-chemical model requires the knowledge of an acetonitrile profile as well as information concerning the rate constants and thermochemical data of the ion-molecule reactions

involved. Apart from the *ACIMS* results, which cover a limited altitude range, and a few ground measurements (Snider and Dawson, 1984; Muller, 1985) all data on the CH_3CN concentrations versus height are derived from ion composition measurements. Therefore a neutral model for acetonitrile must be set up first. It is believed that this molecule is injected into the atmosphere by human activities, partly washed out in the troposphere and destroyed on its way up by chemical reaction (mainly with OH) and at higher altitudes by photodissociation. For the diffusion and wash-out appropriate data can be found (see Arijs and Brasseur (1986) and references therein) and new values of the photodissociation of acetonitrile have recently been published (Masako and Lee, 1985). As was shown in previous modelling efforts the major uncertainties for CH_3CN modelling were the rate constant for the reaction with hydroxyl radicals and the acetonitrile budget (sources and sinks). Meanwhile, some new laboratory experiments have been performed by Hynes and Wine (1991) and new ground-based measurements of acetonitrile have become available (Hamm *et al.*, 1989; Hamm and Warneck, 1990). Continued *in situ* measurements using the *ACIMS* method, which is much less sensitive to CID, and renewed modelling using the up-to-date information can make our insight into the problem of atmospheric acetonitrile distribution more consistent.

For modelling the positive ion composition a great deal of laboratory data had been previously collected in order to describe the D region ion chemistry, and some of this knowledge can be directly transferred to the stratospheric model. Reactions (1)–(7) have been studied in detail and their rate constants have been reported before (see Ikezoe *et al.*, 1987). The kinetics, equilibrium and the temperature dependence of the rate constants of the hydration reactions (8) are also well documented in the literature (Lau *et al.*, 1982).

Concerning the formation of NPH cluster ions, less laboratory data are available. The switching reactions (15) have been studied by Smith *et al.* (1981) for $n = 1, 2, 3$ and 4. These studies have been extended recently by Viggiano *et al.* (1988) for values of n up to 7. Thermochemical data, enthalpy (ΔH°) and entropy changes (ΔS°), of clustering reactions (17) and (18) were obtained recently by Deakynne *et al.* (1986). No data are available so far for the rate constants of reactions (16) and information is lacking concerning the competition of formation of $\text{H}^+(\text{CH}_3\text{CN})_n(\text{H}_2\text{O})_m$ through three body-association reactions ((17) and (18)) and two body-switching reactions (16). However, it is very unlikely that such information would be crucial for modelling purposes since the ion distributions will be mainly controlled

by equilibrium conditions (determined by ΔH° and ΔS°) in view of the long lifetime of the ions.

Although some details may be lacking, sufficient new data seem to be available to update the present positive ion models. The major problem however, will be the comparison of the calculated ion distributions with the measured ones in view of the disturbing role of CID, which is presently not fully understood.

4.2. Negative ion chemistry

Our insight into the formation mechanism of the NO_3^- cluster ions in the stratosphere is again based upon the foundations laid for the description of the D region ion chemistry. This mechanism, which due to the low concentration of atomic oxygen in the stratosphere is somewhat simpler than in the D region, is schematically represented in Fig. 6. The electrons formed by cosmic rays rapidly attach to the abundant oxygen molecules to form O_2^- , which reacts very fast with oxygen and the most abundant trace gases H_2O , CO_2 and ozone in the following way:

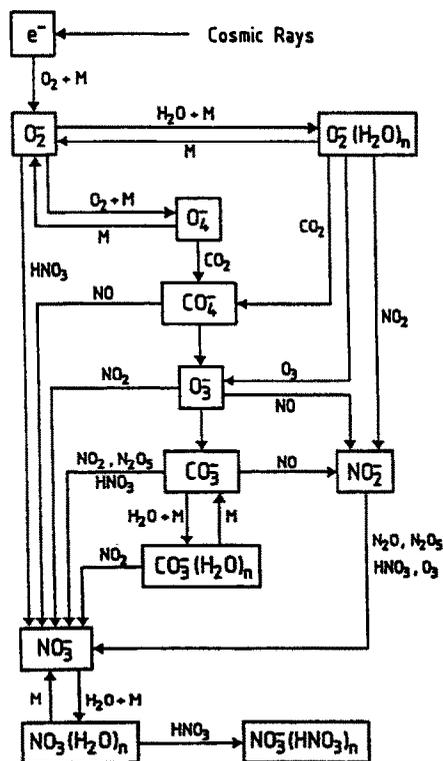
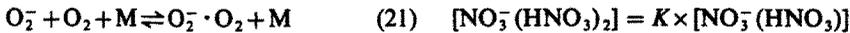
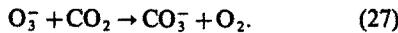
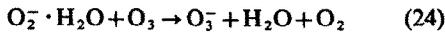


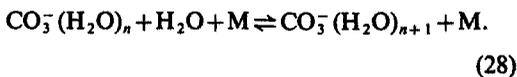
FIG. 6. ION-MOLECULE REACTION SCHEME SHOWING THE CONVERSION OF THE PRIMARY NEGATIVE IONS INTO NO_3^- CORE IONS IN THE STRATOSPHERE.



and further hydration of O_2^- . These hydrates of O_2^- and $\text{O}_2^- \cdot \text{O}_2$ subsequently disappear through



The CO_3^- ions are then hydrated through

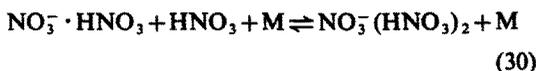


The previous reactions are mostly well known and their rate constants have been measured in the laboratory (see Ikezoe *et al.*, 1987). The conversion of CO_3^- into NO_3^- ions can be explained through the reactions of CO_3^- with NO_2 , HNO_3 and N_2O_5 , the rate constants of which have also been determined in the laboratory. Additionally some by-pass reactions of NO_x gases, also shown in Fig. 6, give rise to NO_3^- ions. The transformation of the hydrates of CO_3^- ions into NO_3^- ions or its clusters are less well understood. It is generally accepted that this also happens by reactions with NO_x compounds, but so far only the reaction



has been reported as rapidly in the literature (Fehsenfeld and Ferguson, 1974). Recently published laboratory measurements of the *MPIH* group (Möhler and Arnold, 1991) have shown that the reaction of $\text{CO}_3^- (\text{H}_2\text{O})_n$ ions with HNO_3 leads to $\text{NO}_3^- (\text{HNO}_3)_n$ clusters via so far unknown intermediate steps.

Once formed, NO_3^- will be very quickly hydrated in the stratosphere. However, according to Fehsenfeld *et al.* (1975) nitric acid will rapidly displace water, and $\text{NO}_3^- (\text{HNO}_3)_n$ ions will be formed. In conclusion it can be stated that although not all details are yet fully known, the presence of NO_3^- ions and its clusters in the stratosphere can be understood. In fact the observed distribution of the $\text{NO}_3^- (\text{HNO}_3)_n$ ions can be used to derive HNO_3 concentrations. Assuming near equilibrium for



we may write

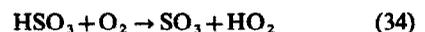
where $P(\text{HNO}_3)$ is the partial pressure of nitric acid and the equilibrium constant K is given by

$$RT \ln K = -\Delta H_{1,2}^\circ + \Delta S_{1,2}^\circ \times T. \quad (32)$$

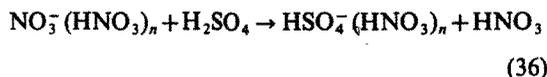
Using the thermodynamic data ($\Delta H_{1,2}^\circ$ and $\Delta S_{1,2}^\circ$) obtained by Davidson *et al.* (1978) in the laboratory, and the relative abundances of mass 125 ($\text{NO}_3^- \cdot \text{HNO}_3$) and mass 188 ($\text{NO}_3^- (\text{HNO}_3)_2$), as observed in negative ion spectra recorded in the stratosphere, the partial pressure of nitric acid was determined by the Heidelberg team (*MPIH*) (Arnold *et al.*, 1980) as well as by the Belgian group (Arijs *et al.*, 1981, 1985). However, due to the disturbing role of CID, which reconverts $\text{NO}_3^- (\text{HNO}_3)_2$ into $\text{NO}_3^- \cdot \text{HNO}_3$ in the instrument, these data are thought to be only reliable above about 30 km altitude.

It should also be noted that the assumption of equilibrium for the forward and reverse reactions (30) may be wrong if there are considerable loss or sink terms for the ions other than HNO_3 attachment or dissociation. If for instance the production of $\text{NO}_3^- \cdot \text{HNO}_3$ from a ligand-switching of HNO_3 and $\text{NO}_3^- \cdot \text{H}_2\text{O}$ would be larger than the production via the dissociation of $\text{NO}_3^- (\text{HNO}_3)_2$, then equation (31) is not valid any more and the application of the above-described method also leads to false results for the nitric acid concentration. This effect may contribute to the observed discrepancies between the nitric acid mixing ratios inferred as explained above and those obtained by optical methods (Arijs *et al.*, 1984). In order to assess the effect of this non-equilibrium, the detailed formation mechanism of the $\text{NO}_3^- (\text{HNO}_3)_n$ ions should be known, and more laboratory measurements of the appropriate ion-molecule reactions are required.

The transition of NO_3^- ions to other R^- core ions, as observed (Section 3.3), can only be explained by the presence of a trace gas with an electron affinity larger than that of HNO_3 . With the observed mass 97 for R, Arnold and Henschen (1978) suggested that the trace gas HR was sulphuric acid, which was expected to be the result of the oxidation cycle



This suggestion was quickly confirmed by laboratory experiments of Viggiano and colleagues (1980, 1982), who measured the reaction



for $n = 0, 1$ and 2 in a flowing afterglow apparatus. A possible continuation of the reaction scheme shown in Fig. 6 as proposed by Arijs *et al.* (1981) is given in Fig. 7. This scheme is probably not complete, and meanwhile other association reactions which can occur in the stratosphere, such as HCl clustering to HSO_4^- have been investigated in the laboratory (Viggiano, 1984).

As for CH_3CN the observed relative abundances of NO_3^- and HSO_4^- ions have been used to derive sulphuric acid concentration in the stratosphere in the altitude region 20–45 km (Arnold and Fabian, 1980; Viggiano and Arnold, 1981b, 1983; Arijs *et al.*, 1982, 1983; Arnold *et al.*, 1982; Arnold and Bührke, 1983; Qiu and Arnold, 1984; Pfeilsticker and Arnold, 1989) using the continuity equation

$$k_2[\text{H}_2\text{SO}_4][n_N] = \alpha[n_S][n^+], \quad (37)$$

where k_2 is the rate coefficient for reactions (36), n^+ is the total positive ion concentration and n_N and n_S are the NO_3^- and HSO_4^- ions respectively. The results

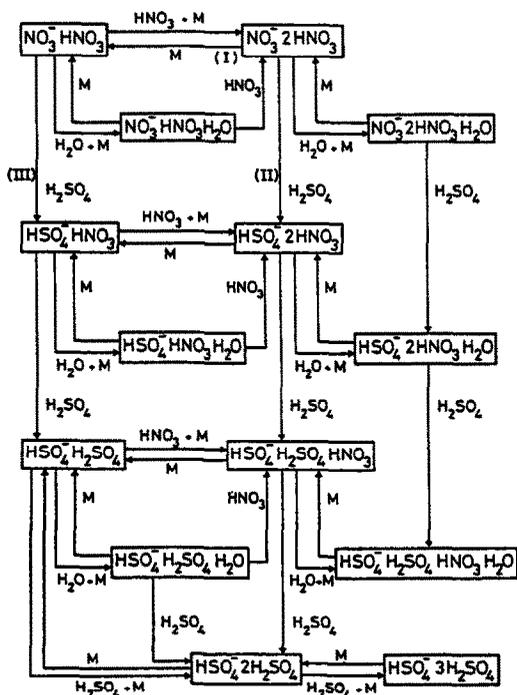


FIG. 7. POSSIBLE CONTINUATION OF THE REACTION SCHEME OF FIG. 6 (AFTER ARIJS *et al.*, 1981).

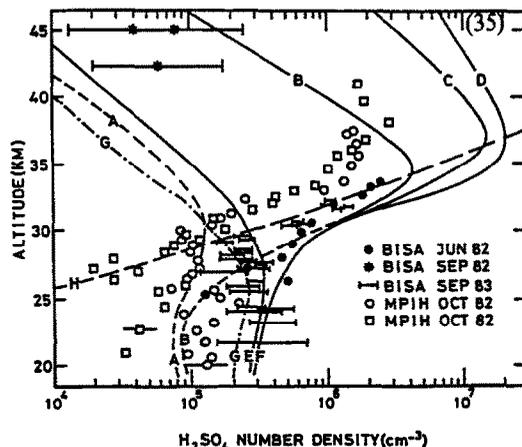


FIG. 8. SULPHURIC ACID NUMBER DENSITIES VERSUS ALTITUDE AS DERIVED FROM DIFFERENT BALLOON FLIGHTS COMPARED TO MODEL CALCULATIONS OF TURCO *et al.* (1981 AND A VAPOUR PRESSURE CALCULATION (LINE H) (AFTER ARIJS *et al.*, 1983b).

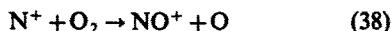
of these measurements are summarized in Fig. 8. Evidently the same remarks concerning possible errors resulting from inaccuracies in α and $[n^+]$ are valid as for the derivation of acetonitrile profiles.

The results of Fig. 8 can again not be compared to other experimental data, because no sulphuric acid vapour measurements with any other technique than ion composition probing are available. Therefore it is again only possible to rely upon model calculations for this molecule. Although sulphuric acid is a much more important trace gas than CH_3CN , because of its vital role in aerosol formation, the models available for this compound are much more speculative than for acetonitrile. The detailed chemical formation mechanism through the oxidation of SO_2 has only been established recently (Stockwell and Calvert, 1983; Margitan, 1984; Martin *et al.*, 1986); no measurements on its photodissociation are available and the modelling of heterogeneous processes in the photochemistry of H_2SO_4 is based upon many assumptions (Turco *et al.*, 1981, 1982; Hamill *et al.*, 1982). As a result, negative ion chemistry models, for which the knowledge of a sulphuric acid profile is essential, are only in an early stage (Brasseur and Chatel, 1983; Kawamoto and Ogawa, 1984). Therefore a comparison of the detailed height profiles of negative ion abundances, which also suffer from CID effects, will only be meaningful when the neutral chemistry of sulphuric acid is fully understood, more appropriate reaction rates of applicable ion–molecule reactions (such as reactions (36) for higher n values or hydration of HSO_4^- ions) will be measured and the role of CID can be quantitatively described.

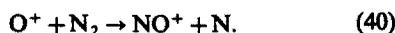
Although a detailed comparison of measurements and models has to await further laboratory experiments of reaction rates, H_2SO_4 photolysis and real effects of CID, some important conclusions follow from the negative ion composition data. These measurements have for the first time given experimental evidence for the presence of sulphuric acid vapour in the stratosphere. A comparison of the derived profile of Fig. 8 with vapour pressure calculations (Viggiano and Arnold, 1983; Arijs *et al.*, 1983b, 1985; Qiu and Arnold, 1984) of a mixture consisting of about 75% sulphuric acid and 25% water and represented by curve H in Fig. 8 shows a reasonable agreement in the altitude region 27–32 km. Assuming that the derived sulphuric acid concentrations are not too disturbed by CID at those altitudes, this indicates that the H_2SO_4 concentration is controlled by the evaporation–condensation equilibrium from aerosols and that previous ideas about aerosol composition were correct. Below about 27 km the H_2SO_4 number densities are substantially higher than expected from evaporation–condensation equilibria and are probably controlled by the photochemistry. Above 35 km, H_2SO_4 concentrations become lower than expected from curve H, suggesting another sink mechanism. It is not clear yet whether this is adsorption on so-called smoke particles (Turco *et al.*, 1981) originating from meteoric debris or photodissociation.

5. INFLUENCE ON NEUTRAL CHEMISTRY

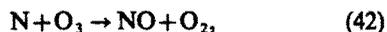
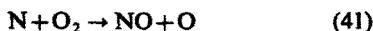
In Section 4 it was assumed that the major ionization products of cosmic rays in the stratosphere are N_2^+ and O_2^+ . In fact these species represent only 80% of the total primary ions (N_2^+ : 64% and O_2^+ : 16%). According to Dalgarno (1967) O^+ (4%) and N^+ (16%) are formed. These ions, however, are rapidly converted through the reactions



and



O_2^+ is transformed into PHs which converted as described before, and the conversion of NO^+ is also well known from the D region ion chemistry. Thus the production of N^+ and O^+ has no implications on the final stratospheric ion composition. However, the atomic nitrogen resulting from reactions (39) and (40) gives rise to the production of nitric oxide by:



although part of the N atoms disappear through



This additional NO source has been studied extensively (Nicolet, 1975; Rudderman and Chamberlain, 1975; Jackman *et al.*, 1980), and under normal stratospheric ionization conditions is lower than the normal production of NO by the oxidation of nitrous oxide (Nicolet and Peetermans, 1972):

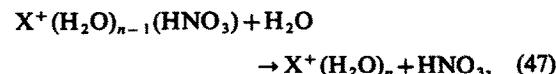
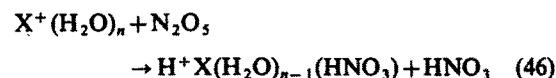


However, during so-called solar proton events or PCAs this production can become considerably enhanced and even give rise to ozone depletions through catalytic reactions. This phenomenon has been the subject of many modelling efforts and is described in detail in the literature (e.g. Crutzen *et al.*, 1975; Heath *et al.*, 1977; Rush *et al.*, 1981; Jackman *et al.*, 1990; Reid *et al.*, 1991).

Further influences of ion–molecule reactions on the stratospheric neutral chemistry under normal ionization conditions have generally been considered as negligible because of the low ion densities encountered in this part of the Earth's atmosphere. Nevertheless it is possible to imagine other processes where the ions can, in spite of their low number density, play a considerable role. Such a process was suggested by Böhrringer *et al.* (1983) to explain the so-called "Noxon-cliffs" (Noxon, 1979). It consists of the ion-assisted catalysis of the conversion:



which is extremely slow in the gas phase with $k_3 \leq 1.3$ (-20) $\text{cm}^3 \text{s}^{-1}$ (Morris and Niki, 1973), but might be considerably accelerated by the ion–molecule reactions:

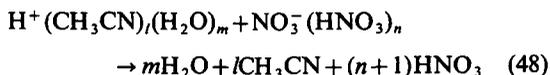


where X^+ is either H_3O^+ or $\text{H}^+(\text{CH}_3\text{CN})_n$ and the sum of equations (46) and (47) forms equation (45).

Laboratory measurements of Böhrringer *et al.* (1983) have shown, however, that for the dominant positive ions as observed in stratosphere, the rate coefficient of reaction (46) is too low to enhance the conversion of equation (45).

Another possible role of stratospheric ions might be the formation of the so-called multi-ion clusters (MICs) as proposed by Arnold (1980). Whereas it is

normally assumed that ion-ion recombinations, such as



result in the return of original neutral molecules in the gas phase, Arnold has pointed out that under certain conditions, for large enough values of l , m and n , the recombination may lead to stable ion pairs or MICs. These species may then be the embryos of additional condensation nuclei for aerosol formation. If the MICs remain stable, the ion-ion recombinations leading to their formation give rise to an effective loss of the neutrals involved in the preceding ion formation. As was mentioned previously (Arijs and Brasseur, 1986) this sink mechanism can become quite efficient at certain altitudes for acetonitrile, if MIC formation is effective. In order to assess the magnitude of this possible sink for other trace gases involved in the ion chemistry, such as HNO_3 and H_2SO_4 , a knowledge of the conditions for MIC formation, the detailed positive as well as negative ion distributions and the thermochemical properties of these ions are required.

In order to prevent the dissociation after recombination the following criterion has to be fulfilled:

$$S^+ + S^- > IP + E_C - EA, \quad (49)$$

where S^+ is the total solvation energy of the positive ion, S^- the total solvation of the negative ion, IP is the ionization potential of the precursor neutral of the positive ion core, E_C the energy released upon the formation of a chemical bond and EA is the electron affinity of the precursor of the negative ion core. A critical investigation of condition (49) for the observed ions in the stratosphere leads to the following conclusions:

(1) for the positive ions, PHs and NPHs, the required thermochemical data have been measured in the laboratory (Lau *et al.*, 1982; Deakynne *et al.*, 1986). However, if several data sets are available for the same cluster family, considerable differences are noticed between them (Castleman, 1986).

(2) for the $\text{NO}_3^-(\text{HNO}_3)_n$ ions two laboratory data sets are published (Davidson *et al.*, 1978; Wlodeck *et al.*, 1980), which again differ substantially.

(3) for the $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m$ ions or mixed HSO_4^- clusters no laboratory data exist and the only known values for the solvation energies are estimations based on *in situ* ion composition data (Arnold *et al.*, 1982), which may suffer from CID. This situation clearly hampers any definite conclusions on MIC formation. In view of the presently available data, however, stable

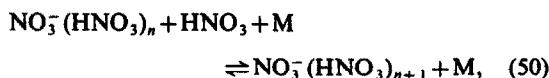
ion pair formation upon recombination between the dominant positive stratospheric ions and the most abundant $\text{NO}_3^-(\text{HNO}_3)_n$ ions seems unlikely. Therefore no substantial HNO_3 loss due to MIC formation is expected under normal ionization rates in the stratosphere. The situation may be somewhat different for the HSO_4^- ions. It is accepted that the bond dissociation energy of small clusters is mostly larger than the bulk phase vaporization energy ΔH_v° of the solvent molecules (Märk and Castleman, 1985). Since for sulphuric acid ΔH_v° is about 18 kcal/mol, the solvation energy of H_2SO_4 in the HSO_4^- ions is expected to be larger. Consequently the heavy $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m$ clusters with 4 or 5 ligands offer the potential to form stable ion pairs. Using the measured fractional abundances of these ions Arnold *et al.* (1982) estimated the fraction of ion-ion recombinations capable to form MICs to be 0.1–0.7 around 32–34 km altitude. If this is true, then a non-negligible loss term for H_2SO_4 and CH_3CN would appear in the neutral chemistry of these molecules, which should be taken into account in models. It should be emphasized however that the previous findings are based upon estimations and a simple model for MIC formation and that no laboratory data on the products of ion-ion recombination are at hand so far. Until these and experimental results on the thermochemical data of the HSO_4^- clusters become available the conclusions regarding multi-ion complexes remain speculative.

6. SUMMARY AND CONCLUSIONS

During the last 15 years considerable progress has been made in stratospheric ion composition measurements and in our understanding of the underlying ion chemistry. Thanks to the development of balloon-, airplane- and rocket-borne ion mass spectrometers, measurements have now been performed practically throughout the whole stratosphere, although the most reliable data set is still the one obtained with balloon-borne instruments. The data obtained in this way span the altitude range from roughly 20 to 45 km. For completeness' sake additional measurements are required below 20 and above 40 km. The available data for positive ions indicate that two major ion families dominate in the stratosphere. The first (proton hydrates) was expected from previous modelling efforts and the formation of these ions is reasonably well understood as a result of previous laboratory work, undertaken to explain the D region ion composition. The second group or non-proton hydrate family is believed to be the result of switching reactions of the PHs with acetonitrile. The formation of NPHs has been clarified by recent laboratory work,

although to construct a complete model, some additional measurements of reaction rates will be required. Furthermore some uncertainties concerning the budget and mixing ratio profile of acetonitrile need to be elucidated. To compare the experimental results with modelling efforts, a better insight into the problem of collision-induced dissociation, which distorts the measured ion distributions, is also needed. In general, though the present picture on the major positive ions seems to be a rather consistent one.

For negative ions an approximately equal amount of *in situ* data is available. Again there appear to be two major ion groups, namely the NO_3^- and the HSO_4^- clusters. Although the general lines of the formation of the NO_3^- ions and of the conversion of the latter ones into the HSO_4^- ions are understood, fewer details on the reaction scheme are available. The detailed mechanism of the conversion of the primary negative ions into the $\text{NO}_3^-(\text{HNO}_3)_n$ ions is still not completely known. In particular measurements are needed on the reactions of $\text{CO}_3^-(\text{H}_2\text{O})_n$ ions with HNO_3 . Furthermore it has to be noted that although thermochemical data exist about the three body associations



only one forward reaction rate has been measured as a function of pressure, namely the one for $n = 0$. It is clear that further measurements are a necessity. Also switching and clustering reactions with sulphuric acid need to be extended. In particular reliable thermochemical data are required for the mixed clusters of the type $\text{HSO}_4^-(\text{HNO}_3)_l(\text{H}_2\text{SO}_4)_m$, to allow a critical assessment of the stable ion pair formation upon ion-ion recombination and to investigate the possible role of such MIC formation in the neutral chemistry. Laboratory or theoretical guidance concerning the products of ion-ion recombination for heavy ion clusters would equally be most helpful.

It is most probable that the data of *in situ* negative ion mass spectrometric measurements are also disturbed by CID.

For the less abundant positive and negative ions, the information is at present very scarce. More sensitive instruments need to be built to shed some light onto this problem, although it is expected that contamination of the environment by the balloon gondola may lead to artificial ion-molecule reactions that will complicate the interpretation of the data to a large extent. Nevertheless more sensitive instruments may allow sampling of the major ions with lower electric fields and thus provide data which are not influenced

by CID. Efforts in this direction should therefore be continued.

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