ION CHEMISTRY OF THE MIDDLE ATMOSPHERE

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1. INTRODUCTION

The ion chemistry of the middle atmosphere is a more difficult subject than that of the upper atmosphere; i.e., the ionosphere. It is more difficult to make in situ ion composition measurements because of the relatively high pressure which necessitates vacuum pumps associated with mass spectrometers. The measurement platforms are less satisfactory in the middle atmosphere as well; there are no middle atmosphere platforms of comparable utility to the AE satellites for example which have been used for comprehensive and precise E and F-region ion chemistry studies.

Laboratory studies of the relevant ion chemistry are also much more difficult for middle atmosphere ion chemistry, the relatively high pressure and low temperature leads to the importance of weakly bound cluster ions which are difficult to measure in the laboratory (as well as to sample in the atmosphere). The high pressure also leads to electron attachment which initiates a complex negative ion chemistry.

Our approach to middle atmosphere ion chemistry is to start with the positive ions of the D-region, which have been extensively studied, and extend this down to stratospheric altitudes where the first ion composition measurements have only recently been obtained. Then we do the same for the negative ion chemistry, starting with the D-region, which has been much less extensively measured for negative ions that for positive ions, and extend down to the stratosphere where the first ion composition measurements are only now being carried out. In each case the theoretical and laboratory extension of the ion chemistry from the D-region to the higher pressure stratosphere is primarily a matter of enquiring into the role of the minor constituents whose absolute concentrations become large enough to allow them to become involved in the ion chemistry.

The ion chemistry of the ionosphere and middle atmosphere have recently been reviewed in some detail (Ferguson, 1979; Ferguson et al., 1979).

2. D-REGION POSITIVE ION CHEMISTRY

Middle atmosphere ion chemistry was initiated with the rocket-borne mass spectrometer positive ion flights of Narcisi and Bailey (1965). Subsequently there have been numerous in situ measurements of the D-region positive ions (for examples, Goldberg and Akin, 1971; Narcisi et al., 1972; Arnold and Krankowsky, 1974; and Zbinden et al., 1975). Although there is considerable variation among the various flights, corresponding almost certainly to large atmospheric ion composition variations, these measurements conclusively show that the dominant ions of the lower E-region, O$_2^+$ and NO$, are replaced by the water cluster ions, H$_3$O$^+\cdot$nH$_2$O, in the D-region. Considerable
laboratory, theoretical, and in situ efforts have been directed toward identifying the D-region reaction paths that convert the primary $O_2^+$ and $NO^+$ ions into the observed $H_3O^+\cdot nH_2O$ ions. The reaction scheme that has emerged is given in Figure 1. Laboratory data are available for the rate constants and/or equilibrium constants for the reactions represented by solid lines and are currently unavailable for those represented by dashed lines. The details of this chemistry have been reviewed recently by Reid (1976). In addition, the hydration of $H_3O^+(H_2O)_n$ ions via intermediate $H_3O^+\cdot(H_2O)N_2$ and $H_3O^+(H_2O)CO_2$ clusters undoubtedly occurs (Chakrabarty, et al., 1978).

There has been no problem in explaining the conversion of the primary $O_2^+$ ions into the water cluster ions via the laboratory-verified paths shown in Figure 1 (Fehsenfeld and Ferguson, 1969). However, the major source of ionization in the undisturbed daytime D-region is photoionization of NO by solar Lyman-$\alpha$ radiation. The understanding of the conversion of the $NO^+$ ions into the water cluster ions has proven to be a more difficult problem. Because of the low mixing ratio of water in the D-region and the relatively low D-region pressures, it is necessary to invoke reactions of the type,

$$\text{NO}^+\cdot nH_2O + X + M \rightarrow \text{NO}^+\cdot nH_2O\cdot X + M,$$

(1)

where $n = 0, 1, 2$ and $X = N_2, CO_2$ for the conversion process (Ferguson, 1971). The weakly bound association complexes thus formed would then undergo a series of fast switching reactions,

$$\text{NO}^+\cdot nH_2O\cdot N_2 + CO_2 \rightarrow \text{NO}^+\cdot nH_2O\cdot CO_2 + N_2$$

(2)

$$\text{NO}^+\cdot nH_2O\cdot CO_2 + H_2O \rightarrow \text{NO}^+\cdot (n+1)H_2O + CO_2$$

(3)

that would greatly accelerate such hydration steps and hence the eventual production of the water cluster ions. These reaction paths are shown in the lower part of Figure 1. However, measurements of these reactions in the laboratory, or the detection of the key ions in the atmosphere, have presented a formidable experimental problem, since the intermediate $\text{NO}^+\cdot nH_2O\cdot X$ ions are extremely fragile.

Arnold and Krankowsky (1974, 1977) have had considerable success in solving the problem of sampling such weakly bound cluster ions in rocket-borne mass spectrometers. As a result, some key ions in this reaction scheme now have been observed in situ, for example $\text{NO}^+\cdot N_2$, $\text{NO}^+\cdot CO_2$, and $\text{NO}^+\cdot H_2O\cdot CO_2$. A sample of these results is shown in Figure 2. Progress has also been made in the laboratory. The rate constant and thermodynamic data for the clustering of $N_2$ to $\text{NO}^+$ (Reaction 1 with $X = N_2$, $n = 0$) are now available.

Although very few of these switching reactions have been measured in the laboratory, such reactions are known to be fast, $k \sim 10^{-9} \text{cm}^3\text{s}^{-1}$. Thus, this sequence of reactions seems to offer an efficient mechanism for the formation of $\text{NO}^+\cdot H_2O$ ions, particularly around 80 km where the D-region temperatures are the lowest. Reid (1977) has devised a reasonable extension of this cycle that can account for most of the observed D-region positive ion features. The nonpolar neutrals that are clustered to $\text{NO}^+$ are so weakly bound that these neutrals are collisionally dissociated to
some extent even at D-region temperatures. This is the case for NO⁺·N₂, which has a bond dissociation energy of 5 kcal/mole. Accordingly, when the temperature is above about 215 K, the collisional decomposition of NO⁺·N₂ will be larger than the switching reaction with CO₂.

For this reason, the conversion of NO⁺ ions to the observed water cluster ions is extremely sensitive to temperature, and the D-region positive ion composition will, therefore, manifest strong seasonal, latitudinal, and even irregular variations as a result of variations in the atmospheric temperature. Moreover, electron-ion recombination coefficients for these weakly bound cluster ions may be considerably larger than those for the unclustered NO⁺ and O₂⁺ ions, which may explain, at least in part, the strong variations in the electron density that are observed at about 80 km. While many of the details still await quantitative verification, the reaction scheme shown in Figure 1 has been shown (Reid, 1977) to qualitatively solve the long-standing D-region problem of the conversion of the primary NO⁺ ions into the observed water cluster ions.

3. STRATOSPHERIC POSITIVE ION CHEMISTRY

A positive ion reaction scheme for the stratosphere and troposphere is given in Figure 3 (Ferguson, et al., 1979). It is essentially the O₂⁺ reaction sequence of the D-region positive ion chemistry (Figure 1), augmented by reactions that involve some of the minor constituents of the lower atmosphere.

Galactic cosmic rays are the primary source of ionization in the stratosphere and upper troposphere. Radioactive decay is the primary source of ionization near the Earth's surface. Cole and Pierce (1965) have given a typical ionization production-rate altitude profile. Values of less than 1 to more than 20 ion pairs cm⁻³ s⁻¹ occur in the stratosphere. The ambient concentration of positive ions is determined by the recombination rate with negative ions. Measurements of the ion concentration have been typically about 5 × 10⁴ cm⁻³ in the lower stratosphere (Cole and Pierce, 1965; Paltridge, 1965, 1966). Positive ion lifetimes are on the order of a few thousand seconds.

As shown in Figure 3 the initial products of the ionization below 60 km are predominantly N₂⁺ and O₂⁺, with lesser amounts of O⁺ and N⁺. These ions are rapidly converted to O₂⁺, as well as an inconsequential amount of NO⁺, by well-established reactions. Once formed, the O₂⁺ ions associate with O₂:

\[ O₂⁺ + O₂ + M \rightarrow O₂cdotO₂⁺ + M, \]  (4)

The formation of O₂⁺·O₂ begins a series of fast switching reactions (Figure 1) that involve H₂O and leads to the formation of the water cluster ions, H₃O⁺·nH₂O.

In the troposphere, where the H₂O mixing ratio is about 10⁻², the conversion of O₂⁺·O₂ to O₂⁺·H₂O proceeds so rapidly that there is no conceivable alternative to the path described above that leads to the water cluster ions. However, in the stratosphere, where the H₂O mixing ratio is only on the order of 10⁻⁶, other neutral constituents have comparable abundances. CO₂ has a much larger concentration and O₃ and CH₄ comparable with that of H₂O. If O₂⁺·O₂ reacts with any of these neutrals, then the ion chemistry outlined in Figure 3 might be significantly altered.
These O₂⁺•O₂ reactions have been examined recently (Dotan et al., 1978) and the results are given in Table I. The first entry is the fast reaction against which the alternative paths must compete. In contrast to it, the reaction of O₂⁺•O₂ with CH₄ is very slow. The reactions of O₂⁺•O₂ with CO₂ and O₂ were studied in equilibrium and the thermochemical constants are given. For CO₂, the equilibrium constant is about unity. The ratio of O₂ to CO₂ in the atmosphere is about 600; thus, the equilibrium will always strongly favor O₂⁺•O₂ rather than O₂⁺•CO₂. However, the exothermicity for the reaction involving O₃ is much larger; hence, the O₂⁺•CO₂ and O₂⁺•O₃ ion concentrations will be more comparable. The O₂⁺•O₃ ion concentrations are estimated to never drop below one-tenth of the O₂⁺•O₂ concentration and even equal it at 30 km. This means that the O₂⁺•O₃ chemistry must also be considered. The mass 80 ion in Figure 2, incidentally, almost certainly represents O₅⁺ rather than NO⁺•H₂O•O₂.

The reaction of O₂⁺•O₃ with CH₄ was found to be slow, k < 5 × 10⁻¹³ cm³ s⁻¹ (Dotan et al., 1978). In contrast, the reaction

\[ O₂⁺•O₃ + H₂O → O₂⁺•H₂O + O₂ \]  

(5)

is fast, \( k₅ = 1.2 \times 10^{-9} \) cm³ s⁻¹. However, the product of this reaction is O₂⁺•H₂O, which is the same ion produced by the reaction of O₂⁺•O₂ with H₂O, the reaction for which competitors were being sought. Therefore, as Figure 3 shows, the O₂⁺•O₃ chemistry simply represents a side excursion that loops the stratosphere positive ion chemistry back on the path involving O₂⁺•H₂O.

Lastly, it was observed that O₂⁺•H₂O does not react with CH₄, k < 5 × 10⁻¹³ cm³ s⁻¹. Thus, the neutrals CO₂, O₃, and CH₄ do not appear to disrupt the ion chemistry that leads to the water cluster ions and we assume that H₃O⁺ (H₂O)ₙ ions are formed in the stratosphere as well as in the D-region. With regard to possible reactions of neutrals with H₃O⁺ (H₂O)ₙ ions, we must now concern ourselves with much lower concentration species, since the lifetimes of H₃O⁺ (H₂O)ₙ ions greatly exceed the time it takes for O₂⁺ to lead to H₃O⁺ (H₂O)ₙ ions, (∼10³ sec compared to ∼10⁻³ sec). Rather than ppm concentrations we must be concerned with ppt concentrations. HNO₃ is one such species of interest, it is known to exist in both the stratosphere and troposphere. Its mixing ratio at 25 km is expected to be greater than 10⁻⁹ (Crutzen et al., 1978). Furthermore, the reaction

\[ H₃O⁺ + HNO₃ → H₂NO₃⁺ + H₂O \]  

(6)

is fast, \( k₆ = 1.6 \times 10^{-9} \) cm³ s⁻¹ (Fehsenfeld et al., 1975). However, HNO₃ does not create a new reaction path that leads away from the ultimate formation of the water cluster ions. A rather remarkable situation exists in that protonated nitric acid, H₂NO₃⁺, is chemically equivalent to hydrated NO₂⁺, i.e., NO₂⁺•H₂O as has been established by chemical reactivities (Fehsenfeld et al., 1975). When this ion is further hydrated in the atmosphere

\[ NO₂⁺•H₂O + H₂O + M → NO₂⁺•2H₂O + M, \]  

(7)

the product ion does not undergo additional hydration, but instead reacts via a fast binary reaction with H₂O,

\[ NO₂⁺•2H₂O + H₂O → H₃O⁺•H₂O + HNO₃. \]  

(8)
Thus, the NO$_2$•H$_2$O chemistry only leads back to the water cluster ions. As is shown in Figure 3, the same is also true for the possible path involving the trace constituent N$_2$O$_5$ (Davidson et al., 1978).

As indicated in Figure 3, both NH$_3$ and CH$_3$OH would destroy H$_3$O$^+$ (H$_2$O)$_n$ ions if present in sufficient concentrations. CH$_2$O on the other hand would not (Fehsenfeld, et al., 1978).

Recently the first stratospheric ion composition measurements have been made in rocket-borne mass-spectrometer flights (Arnold et al., 1977). Three high-latitude studies sampled the positive ions during descent through the altitudes 55 to 35 km, the lower of which is well into the stratosphere. Above 45 km, the substantial signal levels permitted high-resolution identification of the water cluster ions H$_3$O$^+$•nH$_2$O, with n = 0, 1, 2, and 3, as the dominant species in this region. Arnold and coworkers reported a rather sharp transition at about 45 km from the water cluster ions to ions with e/m ratios of 29 ± 2, 42 ± 2, 60 ± 2, and 80 ± 2. In the region below this altitude the non-water-cluster ions become the dominant species. More recently, balloon flights by Arijs et al., (1978) indicate that the water cluster ions are major species at 35 km. Other ions were observed in appreciable concentration, in particular, an ion with an e/m ratio of 96 ± 2.

The observation of the water cluster ions as the dominant species down to altitudes of 45 km or below, having been formed undoubtedly by the chemistry described in Figure 3, places useful upper limits on neutral molecules that react rapidly with H$_3$O$^+$•nH$_2$O ions. For example, laboratory studies (Fehsenfeld et al., 1978) find that these water cluster ions proton transfer rapidly with methanol with rate constants that are independent of temperature in the stratospheric range. Since Arnold et al. found no masses that could be associated with protonated methanol ions or their hydrates, an upper limit of 10$^{-11}$ on the CH$_3$OH mixing ratio could be deduced for this region of the atmosphere. This upper limit is several orders of magnitude less than might be inferred from the methane-oxidation chemistry with its present uncertainties.

The situation with ammonia appears to be quite similar. The reactions

$$H_3O^+•nH_2O + NH_3 \rightarrow NH_4^+•mH_2O + (n + 1 - m) H_2O$$

(where m = 0, 1, ..., n) have been found (Fehsenfeld and Ferguson, 1973) to be very fast for n = 0, 1, and 2. No detailed atmospheric profiles of NH$_3$ have been obtained. The concentration in the lower troposphere is believed to be significant, but is expected to fall off rapidly with altitude because of the large solubility of ammonia and its consequent rain-out of the atmosphere. Presumably NH$_4^+•nH_2$O ions do exist in the lower part of the troposphere and indeed may even be the dominant ions, but no ion composition measurements exist yet in this region.

Arnold et al., (1977) have tentatively identified the non-water-cluster ions that were observed in their flights as arising from reactions of the H$_3$O$^+$•nH$_2$O ions with formaldehyde and used their observations to deduce a CH$_2$O altitude profile. The reasonable choice of CH$_2$O as the trace neutral with which the water cluster ions were reacting was based on the fact that the proton affinity of CH$_2$O is greater than that of H$_2$O and that CH$_2$O is expected to be present in the atmosphere from the oxidation of methane. However, recent laboratory studies (Fehsenfeld et al., 1978) of the
CH$_2$O-H$_2$O ion chemistry do not support this interpretation. Unclustered H$_3$O$^+$ ions do indeed proton transfer with CH$_2$O but the reactions of the higher-order water cluster ions with CH$_2$O become endothermic. Even if the protonated formaldehyde ions were produced in some way in the stratosphere, they would be rapidly converted to H$_2$O$^+\cdot$nH$_2$O ions by reaction with H$_2$O.

The nonproton hydrates reported below about 40 km by Arnold et al. (1978) have recently been interpreted (Ferguson, 1978) as being due to the presence of protonated sodium hydroxide ions. The interpretation is given in Table II. It has been well known for over seventy years that a layer of atomic sodium exists in the atmosphere from its resonant scattering of sunlight which has been detected spectroscopically. This sodium exists in a layer near 90 km and is due to the ablation of meteorites in the atmosphere upon entry. It is argued that the sodium will be in the form of NaOH below about 40 km in the atmosphere. The proton affinity of NaOH is exceedingly high, $\sim$ 248 kcal mol$^{-1}$ (Kebarle, 1977). It is presumed therefore that reactions

$$H_3O^+(H_2O)_n + NaOH \rightarrow NaOH_2^+(H_2O)_m + (n - m + 1)H_2O \quad (10)$$

would occur at the collision rate, $k_{10} \sim 2 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$. A concentration of NaOH $\sim 10^8 \text{cm}^{-3}$ at 40 km is required for (10) to compete with positive ion-negative ion recombination and this agrees well with calculations of Liu and Reid (1979) on the total expected sodium concentration in this altitude range. It is also predicted that at somewhat lower altitudes KOH$_2^+$ clusters will become dominant since the proton affinity of KOH $\sim$ 263 kcal mol$^{-1}$ (Kebarle, 1977) exceeds that of NaOH. The atmospheric abundance of K is an order of magnitude or more less than that of Na so that at 40 km the K concentration is too low to be involved in the ion chemistry. MgO has a large proton affinity, $\sim$ 212 kcal mol$^{-1}$ and it may well be that MgOH$^+$ clusters are formed by

$$H_3O^+(H_2O)_n + MgO \rightarrow MgOH^+(H_2O)_m + (n - m + 1)H_2O \quad (11)$$

since Mg is an order of magnitude more abundant than Na in meteorites. However, the MgOH$^+$ hydrates would presumable proton transfer to NaOH,

$$MgOH^+ + NaOH \rightarrow NaOH_2^+ + MgO \quad (12)$$

so that Mg, while relatively abundant, probably does not contribute to the ion composition. Mixed clusters involving both NaOH and KOH will also occur at some concentration level.

There is a clear need for more detailed measurements of stratospheric positive ions, including measurements at higher mass resolution. There is also a need for measurements of the critical neutral constituents for the ion chemistry, such as NaOH.

4. D-REGION NEGATIVE ION CHEMISTRY

In contrast to the D-region positive ion chemistry, where in situ measurements discovered the unexpected water cluster ions, the negative ion chemistry of the D-region has been derived predominantly from laboratory studies. This chemistry is shown schematically in Figure 4. The arrows represent reactions whose rate constants have been measured in the laboratory. Many of the details of D-region negative ion chemistry have been reviewed recently by Reid (1976).
The primary negative ion of the D-region is largely $O_2^-$, which is formed by the termolecular attachment of electrons to $O_2$. To a much less extent, $O^-$ is formed by dissociative attachment to $O_3$. The relatively unstable $O_2^-$ ions undergo a series of ion-molecule reactions with the D-region minor molecular neutral constituents to form progressively the more stable ions shown in Figure 4. In competition with this progression at each intermediate step are reactions with the minor D-region atomic neutral constituents that lead back eventually to the release of the electrons. The terminal ions $NO_3^-$ and $HCO_3^-$ are sufficiently stable to resist attack by the atomic species. For example, the electron affinity of $NO_3$ is 4.0 eV, one of the largest known for simple molecules.

The first few steps in the reaction sequence of Figure 4 are fast in comparison to the conversion of $CO_3^-$ to $NO_2^-$ by reaction with NO. The relatively small rate constant for this reaction and the low NO concentration implies that this is the limiting step in the $NO_3^-$ production sequence in Figure 4. However, this $CO_3^-$ bottleneck does not mean that there will be a large $CO_3^-$ concentration in the D-region, but rather it implies an overall low negative ion concentration. The rapid conversion of $CO_3^-$ back to $O_2^-$ via reaction with O and thence detachment of the electron by reaction with O holds the $CO_3^-$ concentration in check. The rate constants and densities involved in this loop are such that it will occur many times before a $CO_3^-$ ion is converted to an $NO_2^-$ ion. The step from $NO_2^-$ to $NO_3^-$ is fast compared to the preceding one, thus the steady-state $NO_3^-$ concentration is determined largely by the ratio of the $NO_2^-$ production rate, and the $NO_3^-$ loss by ion-ion recombination. Hence, this model predicts a rather large $[NO_3^-]/[CO_3^-]$ ratio in the D-region.

Thus, to a large extent the negative ion chemistry of the D-region is controlled by the neutral composition, and its variability is linked directly with the large variations in the minor species $O$, $O_3$, $NO$, and $H$. It is clear from Figure 4 that high pressure, hence lower altitude, favors the attachment of electrons to $O_2$, thereby initiating the negative ion chemistry, and the termolecular reactions that lead toward more-stable negative ions. Furthermore, the increasing concentrations of $O_3$ and NO and the decreasing concentration of $O$ at the lower altitudes all imply a rather sharp upper boundary for the D-region negative ions at 75 to 80 km, with the free electrons showing a complementary variation with altitude. Diurnal effects are expected to be large, since the $O$ atom concentration, for example, increases throughout the D-region during the day. At the same time, the less-stable negative ions are subject to photodestruction (Huber et al., 1977).

The temperature of the D-region and lower atmosphere is less than 300 K and varies with time, place, and altitude and particularly with season and latitude. It is therefore also necessary to have temperature dependences for the reaction rate constants in order to understand the negative ion chemistry in detail.

Figure 4 does not include the effects of neutral molecules clustering to the negative ions. The rate constants of such termolecular association reactions typically increase with decreasing temperature and the breakup rates of weakly bound cluster ions decrease. Thus, at the relatively low D-region temperatures, all of the negative ions are subject to clustering, which is not very chemically specific. The terminal, i.e., long-lived, ions like $NO_3^-$ are certainly expected to be hydrated, hence $NO_3^-\cdot nH_2O$ ions are predicted to be the dominant ions in the D-region. If the intermediate ions cluster in their shorter lifetimes, the question arises as to whether this would significantly alter their subsequent chemistry. A limited study carried out a few years ago (Fehsenfeld and Ferguson, 1974)
indicated that water clusters would not significantly effect the reaction scheme of Figure 4. For example, one and two water molecules do not significantly alter the rate of $O_2^{-}$ charge transfer with $O_3$. One water molecule does not significantly effect the rate of $O_3^{-}$ reaction with $CO_2$ but two water molecules quenches this reaction, probably by making the reaction effectively endothermic. However, because of the large abundance of $CO_2$, the $O_3^{-}$ ions will not have time to cluster twice, so that this should have little effect. Clustering to $CO_3^{-}$ may somewhat alleviate the $CO_3^{-}$ bottleneck if it inhibits the reaction of $CO_3^{-}$ with $O$ relative to that with $NO$. At D-region temperatures, there could be important negative-ion association reactions with $O_2$, $N_2$, $CO_2$, and $H_2O$, followed by switching, exactly analogous to the D-region $NO^+$ association sequence proposed in the lower part of Figure 1. Only one such D-region negative-ion reaction path has been studied in the laboratory, namely, the one involving $CO_3^{-}+H_2O$ shown in Figure 4. With the improved ability to study individual cluster ions that now exists, more extensive studies of the effects of clustering on chemical reactivity are being undertaken.

The first in situ measurements of the D-region negative ion composition were made by Narcisi et al., (1971) and Arnold et al., (1971). Figure 5 shows the ion concentration recorded in a later flight by Narcisi and coworkers. The dominant ions below 90 km are those with e/m ratios of $62 + n18$ ($n = 1-5$). An interpretation of these ions as $NO_3^{-}·nH_2O$ is consistent with the model shown in Figure 4. However, the persistence of e/m ratios of 16 and 32, which are presumably $O^{-}$ and $O_2^{-}$, at the higher altitudes is not in accord with the chemistry of Figure 4 which predicts an upper boundary for the negative ions at lower altitudes. The flights of Arnold and coworkers found somewhat different results. Namely, they report a rather sharp upper boundary to the D-region negative ions, in accord with the predictions based on laboratory measurements, but the $NO_3^{-}·nH_2O$ sequence was not observed. The major ion species in these flights were identified as $CO_3^{-}$, $Cl^{-}$, and $HCO_3^{-}$.

In view of the sparcity and differences between the atmospheric negative ion measurements, the substantial uncertainties in the concentrations of certain critical minor neutral species, and the need for more laboratory reaction studies, a quantitative understanding of D-region negative ion chemistry cannot be claimed at the present.

5. STRATOSPHERIC NEGATIVE ION CHEMISTRY

The negative ion chemistry of the stratosphere and troposphere are even more speculative than the positive ion chemistry of these regions. In addition to there being few measurements of the trace neutrals involved, only one negative ion composition measurement has so far been reported (Arnold and Henschen, 1978). Furthermore, the D-region measurements, from which one could draw guidance, are relatively sparse and somewhat ambiguous at present, as pointed out above. Thus, our present understanding of the negative ion processes in the stratosphere stems largely from laboratory studies.

The approach here has been to start with the D-region negative ion chemistry given in Figure 4 and modify it to be in accord with the expected differences in neutral composition of the two regions. These considerations fall into two classes. First, to look for possible changes in the chemistry that leads to the $NO_3^{-}$ ions and secondly to consider whether these ions would react with trace neutral species that are suspected in the lower atmosphere to form even more stable ions.
The first necessary modification of the D-region scheme is to disregard the reactions of atomic oxygen, whose concentration below 50 km is negligible in comparison to that of \( \text{O}_3 \). In addition, \( \text{NO} \) will no longer play a role. Furthermore, the rapid formation of cluster ions can strongly alter the evolution of ion chemistry. For example, the reaction of \( \text{O}_3^- \) with \( \text{CO}_2 \) is known to decrease rapidly with \( \text{O}_3^- \) hydration (Fehsenfeld and Ferguson, 1974). Because \( \text{H}_2\text{O} \) bonds more strongly to \( \text{O}_3^- \) than to \( \text{CO}_3^- \), this reaction may become endothermic when \( \text{O}_3^- \) becomes heavily hydrated (Dotan et al., 1977). In the lower atmosphere, \( \text{O}_3^- \) hydration is likely to occur before the reaction of \( \text{O}_3^- \) with \( \text{CO}_2 \).

The reaction scheme based on these considerations is shown in Figure 6. The dashed lines represent places of considerable uncertainty. For example, it is not clear whether \( \text{O}_2^-\cdot\text{nH}_2\text{O} \) ions will react with \( \text{O}_3 \), as do the unclustered \( \text{O}_2^- \) ions. The situation with \( \text{O}_3^-\cdot\text{nH}_2\text{O}, \text{O}_3^- \), and \( \text{CO}_2 \) is the same; namely, the hydrated ions may not follow the same reaction paths as the unhydrated ions.

However, even if the paths that lead to \( \text{NO}_3^- \) are somewhat uncertain, its eventual formation does not appear to be in doubt. Both \( \text{HNO}_3 \) and \( \text{N}_2\text{O}_5 \) provide effective \( \text{NO}_3^- \) production routes. Some of these reactions are listed in Table III. Furthermore, it has been shown that \( \text{HNO}_3 \) exothermically displaces \( \text{H}_2\text{O} \) in hydrated negative ions (Fehsenfeld et al., 1975); therefore, the agent for \( \text{NO}_3^- \) formation can always enter the cluster.

The high stability of \( \text{NO}_3^- \) seems to insure its role in the terminal negative ions of the lower atmosphere. At the present, no neutral species expected to have a significant atmospheric concentration has been found to react with \( \text{NO}_3^- \). The ion will, of course, hydrate and it is known that there are several molecules that can displace \( \text{H}_2\text{O} \) from a hydrated \( \text{NO}_3^- \) cluster. The molecules \( \text{SO}_2 \) (Fehsenfeld and Ferguson, 1973) and \( \text{HNO}_3 \) (Fehsenfeld et al., 1975; Davidson et al., 1978) are examples. Thus, it is likely that the terminal negative ions of the lower atmosphere are complex cluster ions, like \( \text{NO}_3^-\cdot2\text{H}_2\text{O}\cdot\text{mSO}_2\cdot\text{nHNO}_3 \), with \( \text{NO}_3^- \) as the core ion. Recently, Arnold and Henschen (1978) have reported the first stratospheric negative ion observations. They report ions which are tentatively identified as \( \text{NO}_3^-\cdot(\text{HNO}_3)_1 \) and \( \text{NO}_3^-\cdot(\text{HCl})\cdot(\text{HNO}_3)_n \) with \( n = 1, 2, 3 \) in each case, as well as some ions which may possibly involve \( \text{HSO}_4^- \) cores and \( \text{H}_2\text{SO}_4 \) neutrals. The negative ion chemistry of the Middle Atmosphere is clearly in a rather elementary state of understanding. This can only be improved by more extensive \textit{in situ} ion composition measurements.

REFERENCES


Figure 1. D-region positive ion chemistry.

Figure 2. Altitude profiles of NO$^+$ cluster ions (from Arnold and Krankowsky, 1974). The identification of mass 80 ± 1 and 88 ± 1 amu are less certain.
Figure 3. Stratospheric positive ion chemistry.

Figure 4. Reaction scheme for D-region negative ion chemistry.
Figure 5. D-region negative ion composition measurements during total eclipse (from Narcisi et al., 1972).

Figure 6. Stratospheric and tropospheric negative ion chemistry.
Table I
$O_2^+ + O_2$ Reactions with $H_2O$, $CH_4$, $CO_2$, and $O_3$ (300 K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Result$^a$</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>1. $O_2^+ + H_2O + O_2 + H_2O + O_2$</td>
<td>$k = 1.5(-9)$ cm$^3$ s$^{-1}$</td>
<td>Howard et al. (1972)</td>
</tr>
<tr>
<td>2. $O_2^+ + CH_4 +$ products</td>
<td>$k &lt; 3(-12)$ cm$^3$ s$^{-1}$</td>
<td>Dotan et al. (1978)</td>
</tr>
<tr>
<td>3. $O_2^+ + CO_2 + O_2 + CO_2 + O_2$</td>
<td>$\Delta H = 0.3\pm1.0$ kcal mole$^{-1}$</td>
<td>Dotan et al. (1978)</td>
</tr>
<tr>
<td></td>
<td>$\Delta S = 4.3\pm2.6$ cal mole$^{-1}$K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>4. $O_2^+ + O_3 + O_3 + O_2$</td>
<td>$\Delta H = -3.7\pm1.0$ kcal mole$^{-1}$</td>
<td>Dotan et al. (1978)</td>
</tr>
<tr>
<td></td>
<td>$\Delta S = 4.5\pm2.6$ cal mole$^{-1}$K$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $1.5(-9)$ implies $1.5 \times 10^{-9}$. 
### Table II
Mass Spectra of Stratospheric Positive Ions

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Proposed NaOH Ion Clusters</th>
<th>Proposed KOH Ion Clusters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
</tr>
<tr>
<td>29±2</td>
<td></td>
<td>41 NaOH₂⁺</td>
<td>57 KOH₂⁺</td>
</tr>
<tr>
<td>42±2</td>
<td></td>
<td>60 NaOH₂⁺·H₂O</td>
<td>81 NaOH₂⁺·NaOH</td>
</tr>
<tr>
<td>60±2</td>
<td>80±2</td>
<td>78±2 77 NaOH₂⁺·2H₂O</td>
<td>95 NaOH₂⁺·3H₂O</td>
</tr>
<tr>
<td>82±2</td>
<td>96±2</td>
<td>96±1 99 NaOH₂⁺·NaOH·H₂O</td>
<td>93 KOH₂⁺·2H₂O</td>
</tr>
<tr>
<td>99±2</td>
<td>114±2</td>
<td>113 NaOH₂⁺·4H₂O</td>
<td>111 KOH₂⁺·3H₂O</td>
</tr>
<tr>
<td></td>
<td>118±1</td>
<td>117 NaOH₂⁺·NaOH·2H₂O</td>
<td>113 KOH₂⁺·KOH</td>
</tr>
<tr>
<td></td>
<td>136±1</td>
<td>135 NaOH₂⁺·NaOH·3H₂O</td>
<td>129 KOH₂⁺·4H₂O</td>
</tr>
<tr>
<td></td>
<td>140±1</td>
<td>139 NaOH₂⁺·2NaOH·H₂O</td>
<td>131 KOH₂⁺·KOH·H₂O</td>
</tr>
</tbody>
</table>


Arijs, private communication


Table III
Negative Ion Reactions with HNO$_3$ and N$_2$O$_5$ (300 K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate Constant$^a$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^3$ s$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>1. CO$_3^-$ + HNO$_3$ → NO$_3^-$ + HCO$_3$(?)</td>
<td>8.0(-10)</td>
<td>Fehsenfeld et al. (1975)</td>
</tr>
<tr>
<td>2. NO$_2^-$ + HNO$_3$ → NO$_3^-$ + HNO$_2$</td>
<td>1.6(-9)</td>
<td>Fehsenfeld et al. (1975)</td>
</tr>
<tr>
<td>3. Cl$^-$ + HNO$_3$ → NO$_3^-$ + HCl</td>
<td>1.6(-9)</td>
<td>Fehsenfeld et al. (1975)</td>
</tr>
<tr>
<td>4. CO$_3^-$ + N$_2$O$_5$ → NO$_3^-$ + NO$_3$ + CO$_2$</td>
<td>2.8(-10)</td>
<td>Davidson et al. (1978)</td>
</tr>
<tr>
<td>5. NO$_2^-$ + N$_2$O$_5$ → NO$_3^-$ + 2NO$_2$</td>
<td>7.0(-10)</td>
<td>Davidson et al. (1978)</td>
</tr>
<tr>
<td>6. Cl$^-$ + N$_2$O$_5$ → NO$_3^-$ + ClNO$_2$</td>
<td>9.4(-10)</td>
<td>Davidson et al. (1978)</td>
</tr>
</tbody>
</table>

$^a$ 8.0(-10) implies 8.0 x 10$^{-10}$. 