Anthropogenic perturbations of tropospheric ion composition

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Abstract. This paper presents a simple model of the vertical distribution of the most abundant positive ions in the troposphere. The model is based on a simple ion chemical scheme, measured rate constants, and observed or calculated atmospheric densities of parent neutral compounds. It suggests that in many cases the most abundant gaseous ions are heavy protonated water cluster ions of pyridine, picoline and lutidine with ammonia molecules attached (pyridinated cluster ions) in the lower troposphere (below 7 km altitude), acetone cluster ions in the upper troposphere (between 7 and 15 km) and methyl cyanide cluster ions above 15 km. The relative abundance of heavy clustered aerosol ions is predicted to be highest near the surface. The model suggests that ion composition could be perturbed as a result of human activities (i.e., increasing emissions of parent neutral species including alkaline compounds), and that in particular, the relative atmospheric abundance of pyridinated water cluster ions is increasing dramatically and should further increase in the future.

Introduction

Electrical properties of the atmospheric medium, specifically the electrical conductivity, are directly influenced by the chemical nature of ions in the atmosphere. Ions have potential influences on neutral trace gases (via ion-molecule or ion-catalyzed reactions) and may trigger the formation of aerosols (via ion-induced nucleation).

Measurements of ion mobility in the lower troposphere [*Tammet et al.*, 1992] suggest that a large variety of ions with masses ranging from at least 25 to 1600 amu [*Kilpatrick*, 1971] are present near the Earth's surface. Many of these ion species, however, remain unidentified. Mass spectrometric measurements of atmospheric ion composition [*Arnold et al.*, 1984, *Arnold and Hauck*, 1985; *Eisele*, 1983; 1988; *Eisele and Tanner*, 1990; *Tanner and Eisele*, 1991] have shown that the protonated water cluster ions of ammonia, (NH_3) [proton affinity, PA = 204 kcal mol^{-1}], acetone (CH_3COCH_3)[PA = 193.6 kcal mol^{-1}], methyl cyanide (CH_3CN) [PA = 187 kcal mol^{-1}] and heterocyclic nitrogen-containing organic molecules such as pyridine (C_5H_5N) [PA = 220.8 kcal mol^{-1}], picoline (or methylpyridine C_5H_4 $(CH_3)N)$[PA $\simeq$ 225 kcal mol^{-1}], and lutidine (or dimethyl pyridine $C_5H_3(CH_3)_2N)$ [PA $\simeq$ 224-228 kcal mol^{-1}] are abundant ions of the troposphere. Other compounds (e.g., methyl substituted glucose amines or primary amines), have also been identified to form cluster ions by proton exchange [*Tanner and*

Eisele, 1991]. In addition, the attachment of ions on aerosols could lead to the formation of heavy aerosol cluster ions (with a mass of typically 10^3–10^4 amu) with very low atmospheric mobility. The abundance of most of the neutral parent compounds involved in the formation of the identified tropospheric cluster ions is directly affected by human activities.

In this paper, we present a simple model of ion chemistry applicable to the troposphere, and assess how ion composition could be changing as a result of anthropogenic activities.

Proposed Positive Ion Scheme for the Troposphere

The major source of ionization in the troposphere is provided by the action of galactic cosmic rays and of radioactivity (α, β and γ radiation from thoron and radon) on air molecules. The chemical scheme proposed in this work to describe the major ionic processes in the troposphere is summarized in Figure 1. The first ions formed are O_2^+ and N_2^+ which are immediately (less than 10^{-3} s) converted to proton hydrates $H^+(H_2O)_n$ after several intermediate steps [*Ferguson et al.*, 1979]. One or more water molecules included in these clusters can be substituted by other molecules with high proton affinity. As suggested by Eisele (1986, 1988), stable "pyridinated cluster ions" of the form $H^+(NH_3)_n(X)_m(H_2O)_l$ (where X represents either pyridine, picoline, or lutidine, and l, m, n may be equal to or greater than zero) are formed by a reaction path which is written symbolically:

$$H^+(H_2O)_r \xrightarrow{\ NH_3\ } H^+(NH_3)_x(H_2O)_z \xrightarrow{\ X\ } H^+(NH_3)_n(X)_m(H_2O)_l$$
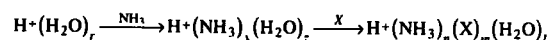
The scheme presented in Figure 1 also shows the formation of other non-proton hydrates (acetone cluster ions $[H^+(CH_3COCH_3)(H_2O)_n]$, methyl cyanide cluster ions $[H^+(CH_3CN)(H_2O)_n]$), and of aerosol cluster ions $[H^+(Aerosol)\ (Y)_p(H_2O)_n]$, where Y represents one of the parent neutral species. The reaction rates adopted in the model are shown in Table 1. Reactions (k_3, k_4, and k_5) in Table 1 are assumed to be irreversible due to the respective proton affinities of ammonia, acetone, and methyl cyanide. Since the proton affinity of pyridinated compounds is higher than that of ammonia, we have assumed that rate constants of the (probably endothermic) reactions (k_{12}, k_{13}, and k_{14}), are relatively small (10^{-11} cm^3 s^{-1}). Sensitivity calculations show, however, that the model results are not significantly modified when the values of these rate constants are changed from 0 to 10^{-9} cm^3 s^{-1}. The tropospheric ion pair production rate, and the concentration of aerosols (non volcanic conditions) are based on the work of *Rosen et al.* [1985] and the value adopted for the effective attachment coefficient of ion on aerosols (β = 5 x 10^{-6} cm^3 s^{-1}) is taken from *Datta et al.* (1987). The recombination rate for positive/negative ions is adopted from the study of *Arijs and Brasseur* [1986].
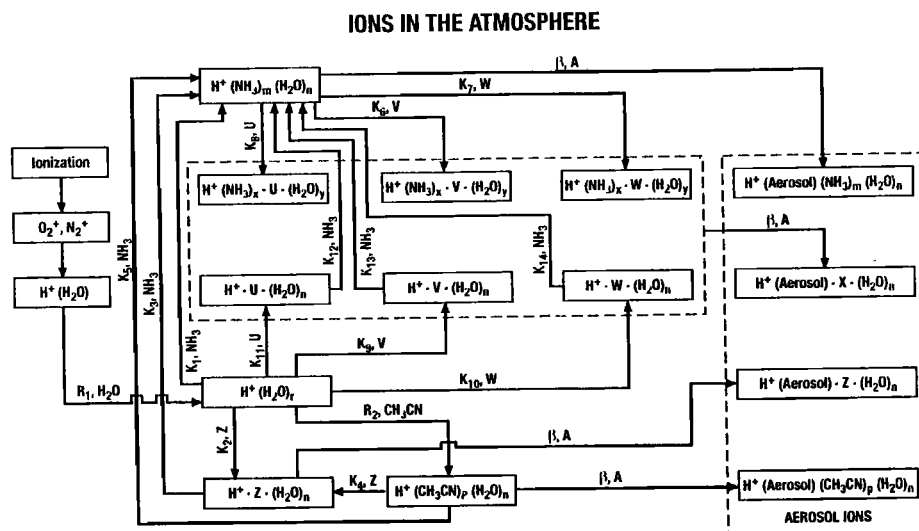
IONS IN THE ATMOSPHERE

Figure 1. Proposed chemical scheme for major positive ions in the troposphere with U representing pyridine, V picoline, W lutidine, X one of these three compounds (U, V, or W), and Z acetone. β represents the attachment coefficient on atmospheric aerosols (A).

Neutral Species Involved in Positive Ion Formation

The chemistry of the neutral species (especially the pyridinated compounds) that take part in ion chemistry and their proton exchange process are not yet properly known. It is believed that combustion is a major source for these compounds, and hence their atmospheric abundance is expected to be increasing substantially as a result of human activities. For example, methyl cyanide is known to be released in the atmosphere as a result of biomass burning, and has been observed in automobile exhaust gases and tobacco smoke [Hamm and Warneck, 1990]. It is also used as an industrial solvent. Estimates of the global CH_3CN emissions range from 0.16 Tg/yr [Arijs and Brasseur, 1986] to 1 Tg/yr [Hamm and Warneck, 1990]. The atmospheric loss of methyl cyanide is mainly due to the reaction with the hydroxyl (OH) radical. In addition to its emission by vegetation and biomass burning, acetone is produced mainly from the oxidation of anthropogenic hydrocarbons [Singh et al., 1994]. It is destroyed in the atmosphere by photolysis and reaction with OH. The sources of pyridinated compounds are believed to be primarily automobile exhaust, biomass burning, manufacturing and agricultural use, coal tars and tobacco smoke [Graedel,

1978]. Emission by the ocean could be an additional, but probably small atmospheric source. Destruction rates are not well established; however, the most likely processes are the reactions with OH.

Figure 2 shows the vertical distribution of the neutral pyridinated species and methyl cyanide as calculated by the two-dimensional model of Brasseur et al. [1990] for the surface boundary conditions specified in Table 1. In the case of pyridine, a surface mixing ratio of 4 pptv has been adopted, which is an average between the different values suggested by Eisele [1988] and Tanner and Eisele [1991]. The adopted vertical profile for ammonia, also shown in Figure 2, is based on the indirect observations of Ziereis and Arnold [1986]. In the case of acetone, we adopt a vertical profile that is representative of the gas chromatography measurements of Singh et al. (1994) at mid-latitudes during the Arctic Boundary Layer Expedition (ABLE 3B). The adopted vertical profiles in the present study should be regarded as examples of possible values, but could vary with location since the atmospheric lifetime of most of the neutral compounds is relatively short (typically 1 month for acetone, 20 days for pyridine, and 2 days for picoline and lutidine, if the concentration of OH is assumed to be 10^6 cm^{-3}), and their surface emissions vary strongly from one location to another.

Table 1. Reaction Rates Used in Tropospheric Positive Ion Chemical Scheme

Reaction	Rate constant (cm^3 s^{-1})	Reference
$H^+(H_2O) + H_2O + M \rightarrow H^+(H_2O)_r$	$R_1 = 3.5 \times 10^{-27} (300/T)^2$ [M]	Lau et al., 1982
$H^+(H_2O)_r + CH_3CN \rightarrow H^+(CH_3CN)_p(H_2O)_n$	$R_2 = 3.06 \times 10^{-9} (300/T)$	Viggiano et al., 1988b
$H^+(H_2O)_r + NH_3 \rightarrow H^+(NH_3)_m(H_2O)_n$	$k_1 = 1.91 \times 10^{-9} (300/T)^{0.39}$	Viggiano et al., 1988b
$H^+(H_2O)_r + CH_3COCH_3 \rightarrow H^+(CH_3COCH_3)(H_2O)_n$	$k_2 = 2.04 \times 10^{-9} (300/T)^{0.59}$	Viggiano et al., 1988b
$H^+(CH_3COCH_3)(H_2O)_n + NH_3 \rightarrow H^+(NH_3)_m(H_2O)_n$	$k_3 = 2 \times 10^{-9}$	Hauch and Arnold, 1984
$H^+(CH_3CN)_p(H_2O)_n + CH_3COCH_3 \rightarrow H^+(CH_3COCH_3)(H_2O)_n$	$k_4 = 1.8 \times 10^{-9}$	Hauch and Arnold, 1984
$H^+(CH_3CN)_p(H_2O)_n + NH_3 \rightarrow H^+(NH_3)_m(H_2O)_n$	$k_5 = 1.8 \times 10^{-9}$	Schlager et al., 1983
$H^+(NH_3)_m(H_2O)_n + picoline \rightarrow H^+(NH_3)_x(picoline)(H_2O)_y$	$k_6 = 2.6 \times 10^{-9} (300/T)^{0.7}$	Viggiano et al, 1988a
$H^+(NH_3)_m(H_2O)_n + lutidine \rightarrow H^+(NH_3)_x(lutidine)(H_2O)_y$	$k_7 = 2 \times 10^{-9}$	Assumed
$H^+(NH_3)_m(H_2O)_n + pyridine \rightarrow H^+(NH_3)_x(pyridine)(H_2O)_y$	$k_8 = 2.1 \times 10^{-9} (300/T)^{0.7}$	Viggiano et al., 1988a
$H^+(H_2O)_r + picoline \rightarrow H^+(picoline)(H_2O)_n$	$k_9 = 2 \times 10^{-9}$	Assumed
$H^+(H_2O)_r + lutidine \rightarrow H^+(lutidine)(H_2O)_n$	$k_{10} = 2 \times 10^{-9}$	Assumed
$H^+(H_2O)_r + pyridine \rightarrow H^+(pyridine)(H_2O)_n$	$k_{11} = 2.08 \times 10^{-9} (300/T)^{0.89}$	Viggiano et al., 1988b
$H^+X(H_2O)_n + NH_3 \rightarrow H^+(NH_3)_m(H_2O)_n$	$k_{12} = k_{13} = k_{14} = 1 \times 10^{-11}$	Assumed

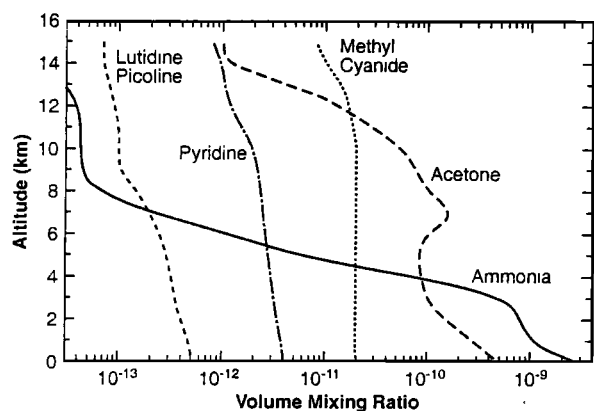Note: X represents either pyridine, picoline or lutidine.

Figure 2. Vertical distribution of key neutral compounds involved in the formation of ion clusters in the troposphere. Pyridine, picoline, lutidine and methyl cyanide mixing ratios are calculated by the two-dimensional model of *Brasseur et al.* (1990) for mid-latitude conditions. Vertical profiles of ammonia and acetone are representative of mean observations (see text).

Table 2. Surface Volume Mixing Ratio of Some of the Neutral Compounds Considered in the Present Work for Different Scenarios

	Normal	Scenario A	Scenario B	Scenario C
Ammonia (ppbv)	3.2	32	3.2	3.2
Acetone (ppbv)	1.5	15	1.5	1.5
Methyl cyanide (pptv)	20	200	200	20
Pyridine (pptv)	4.0	40	40	40
Picoline (pptv)	0.4	4	4	4
Lutidine (pptv)	0.4	4	4	4

remains the pydridinated cluster ions $[H^+(NH_3)_n X_m(H_2O)_i]$ (35% at the surface, 50% at 5 km, and 4% at 10 km) (not shown) and the simple ammonia cluster ions $[H^+(NH_3)_y(H_2O)_z]$ now account for typically 30% of the positive ions at 5–6 km. If it is assumed that pyridinated compounds are not present, the model shows the dominance of simple ammonia cluster ions $[H^+(NH_3)_y(H_2O)_z]$ between 1 and 7 km altitude. In all these idealized cases, acetone cluster ions are the most abundant family in the upper troposphere and heavy aerosol cluster ions are dominant near the surface.

Vertical Distribution of Ion Composition

The percentage abundance of the major ion families is shown in Figure 3. (The total ion density varies from 700 ions cm^{-3} near the surface to 3800 ions cm^{-3} at 15 km altitude). For the conditions described above, the most abundant ions below 7 km altitude are pyridinated cluster ions (45% at the surface, 75% at 5 km, 10% at 10 km) and aerosol cluster ions (55% at the surface, 15% at 5 km). Acetone cluster ions, which account for only 5% of the total ion density at 5 km, become the most abundant between 7 km and 14 km (more than 80% at 10 km). Methyl cyanide cluster ions (whose relative abundance is less than 1% below 10 km) become the dominant ions above 15 km (in agreement with earlier stratospheric model results reported for example by *Beig et al.*, 1993). Note that simple ammonia cluster ions $[H^+(NH_3)y(H_2O)_z]$ are not the dominant ions in the troposphere (percentage abundance never larger than 6%) due to their fast conversion to heavy cluster ions $[H^+(NH_3)_n(X)_m(H_2O)_i]$, as shown in reaction paths (1) and (2).

If the concentrations of pyridine, picoline and lutidine molecules are arbitrarily divided by a factor of 10 (representative of remote regions like the ocean), the dominant ion family
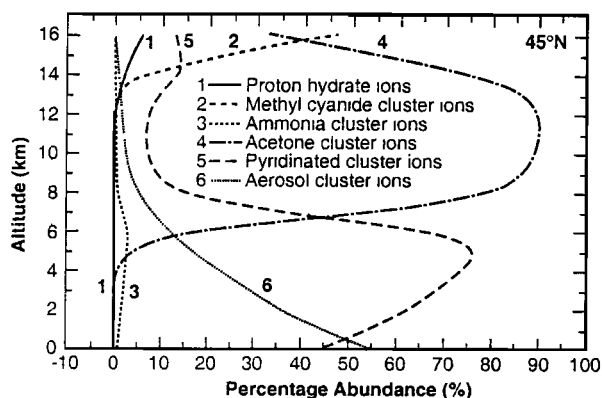
Anthropogenic Perturbations in Ion Composition

Several of the molecules involved in the formation of cluster ions are released at the Earth's surface as a result of anthropogenic processes including fossil fuel and biomass burning. The atmospheric abundance of these parent neutral compounds, and hence the ionic composition of the troposphere has most probably changed over the last decades as a result of human activities, and is expected to change further in the future. The magnitude of
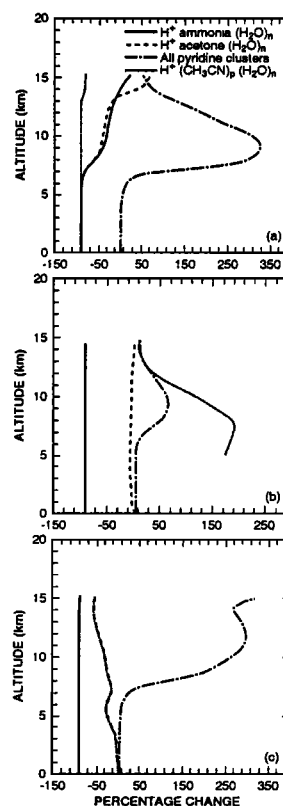

Figure 3. Percentage abundance of major positive ion families calculated between the surface and 16 km altitude (midlatitude conditions).

Figure 4. Vertical distribution of the percentage change in the abundance of major tropospheric positive ion families for scenarios A, B, and C, with respect to reference case.

these changes cannot be properly established due to the lack of systematic observations of these compounds and the uncertainties associated with their sources and sinks. In order to determine the potential response of the ionic composition of the troposphere to human activities, we have considered three simple scenarios for the concentration growth of the parent neutral compounds (shown in Table 2). In scenario A, the concentration of all compounds is increased by an arbitrary factor 10 from the background case, while in scenario B the atmospheric abundance of only the pyridinated compounds and of methyl cyanide is increased by an order of magnitude. Finally, in scenario C, an increase of a factor 10 is applied only to the concentration of the pyridinated compounds. The percentage changes in the ion concentration with respect to the background case are shown in Figure 4 for all three scenarios.

In the case of scenario A, the largest positive change (350% at 8 km) is found for the pyridinated ions in the upper troposphere. Changes in the abundance of these ions are, however, small below 5 km. The concentration of the other ions is reduced by a factor 2 below 5 km altitude (and up to 15 km in the case of methyl cyanide cluster ions). In the case of scenario B, the largest relative change is found to occur for methyl cyanide cluster ions, but it is without significant consequences, especially in the lower troposphere where the relative abundance of this ion family is extremely small. The percentage change in the concentration of pyridinated ions for scenario B is only significant above 7 km, and reaches a maximum value of 75% at 9 km. The concentration of ammonia cluster ions is reduced by approximately 90%, and that of methyl cyanide cluster ions is increased by 15% in the entire troposphere. Finally, for scenario C, the abundance of pyridinated ion clusters increases by 200-300% in the upper troposphere, while the concentration of ammonia is reduced by 90%. The reductions in the concentration of acetone and methyl cyanide cluster ions are almost identical (3% at the surface and 60% at 14 km).

Conclusions

In this paper, we have proposed a simple model of positive ions for the troposphere, which suggests that, in moderately or strongly polluted environments, pyridinated cluster ions are the most abundant ions below 7 km altitude, as also suggested by Eisele [1988]. Hence, alkaline species other than ammonia must be considered when assessing the alkalinity of lower tropospheric air. A large fraction of the total ions is found to be aerosol cluster ions near the ground; the concentration of this type of ions may increase substantially after volcanic eruptions . In the upper troposphere, the dominant ions appear to be acetone clusters.

The ion composition of the troposphere is expected to change in the future in response to human activities, and specifically in response to enhanced emissions of anthropogenic compounds including pyridine, picoline and lutidine. As future changes in the concentration of these alkaline neutral compounds are not known, accurate estimates of the ionic composition as a function of time cannot be provided. Model calculations suggest, however, that the atmospheric density of pyridinated cluster ions is fast rising.

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