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IS HYDROGEN CYANIDE (HCN) A PROGENITOR OF ACETONITRILE (CH_3CN) IN THE ATMOSPHERE?

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Abstract. The possibility of a link between HCN and CH_3CN in the atmosphere has been suggested recently. A new chemical analysis of this problem as well as model calculations indicate that, most probably, these gases are produced at the Earth's surface and destroyed by oxidation in the middle atmosphere. The strength of the photodestruction of these 2 molecules seems to be weak. It is unlikely that HCN is an atmospheric source of CH_3CN.

Introduction

According to mass spectrometric observations (Arnold et al., 1978; Arnold and Henschen, 1982; Arijs et al, 1982; 1983a, 1983b) acetonitrile is one of the ligands of positive stratospheric cluster ions. To validate this assumption, a comprehensive understanding of the behavior of CH_3CN is required. Brasseur et al (1983) have suggested that acetonitrile could be produced at the Earth's surface, essentially by biomass and industrial burning and destroyed in the troposphere and the stratosphere by oxidation reactions, mainly with OH radicals. The overall budget of this molecule is nevertheless not yet completely understood, due to quantitative uncertainties in the CH_3CN release and the mixing ratio in the lower troposphere. The two available observations of the acetonitrile surface mixing ratio (Becker and Ionescu, 1982; Snider and Dawson, 1984) differ by about a factor of 100, although the measurements by Snider and Dawson (1984) seem to be more representative of a background atmosphere.

Very recently, Murad et al (1984) suggested that hydrogen cyanide (HCN) might be a source of acetonitrile in the stratosphere through a chain of reactions initiated by reaction

$$HCN + CH_2O + M \rightarrow CH_2OH\text{-}CN + M. \qquad (1)$$

Another end-product of this mechanism would be CH_3OH which also plays a role in the stratospheric ion chemistry (Henschen and Arnold, 1981a; Arijs et al, 1982). Moreover, Murad et al (1984) introduced the reaction with proton hydrates as a fast destruction process for CH_3CN.

Cicerone and Zellner (1983) have examined the chemical and photochemical behavior of HCN without considering the suggestion by Murad. Their model calculations of the vertical distribution compare quite well with available observations (Coffey et al, 1981; Carli et al, 1982; Rinsland et al, 1982). Cicerone and Zellner (1983) derived that hydrogen cyanide has an atmospheric residence time of about 1-5 years, that this species is relatively well mixed in the troposphere but that its mixing ratio decreases slowly with altitude in the stratosphere.

In order to test the suggestion of a link between HCN and CH_3CN, new model calculations have been performed. These consider the latest field measurements of CH_3CN as well as recent laboratory data for some rate constants.

Brief Model Description

The model which is used in the present study is one-dimensional and similar to the one used by Brasseur et al (1983). The vertical transport is parameterized by an "eddy diffusion coefficient" (referred as K_1 in Brasseur et al, 1983). A large number of reactions involving oxygen, hydrogen, nitrogen, carbon and chlorine species are considered simultaneously (Brasseur et al., 1982) but only the processes directly related to the present study are listed in Tables 1 and 2. Two cases are considered : in the first run (table 1), CH_3CN is assumed to be destroyed by OH, $O(^1D)$ and Cl and, in the upper layers, by photodissociation process. The corresponding absorption cross section however has been measured (Zetzsch, private communication) only in a limited range of the spectrum, so that the related photodissociation frequency can only be approximate and depends on interpolations, made where data are missing. The precipitation scavenging of CH_3CN in the troposphere appears to be small compared to other loss processes, except maybe at very low altitude (z < 3 km) because of the low value of the Henry's law constant (Snider and Dawson, 1984). Indeed, when following the method suggested by Crutzen and Gidel (1983) to parametrize the effect of scavenging, we find that the corresponding loss coefficient is lower than 10^{-7} s^{-1} at ground level and decreases rapidly with increasing altitude (Arijs and Brasseur, in preparation). The corresponding average tropospheric lifetime is in reasonable agreement with the recent estimation of Hamm et al (1984).

Hydrogen cyanide is assumed to be produced at the surface and destroyed in the atmosphere by reaction with OH and $O(^1D)$ (Cicerone and Zellner, 1983). The photodissociation rate is not known and will be considered as negligible ($J_{HCN} = 0$) to obtain an upper limit of the concentration or as being equal to the photodissociation rate of hydrogen chloride ($J_{HCN} = J_{HCl}$). This last assumption has been adopted by Cicerone and Zellner but their adopted value of the HCl photodissociation coefficient (J_{HCl}) is significantly lower than the currently accepted values for J_{HCl}. Precipitation of HCN in the troposphere is considered to be a negligible sink.

The reactions considered in the second case, in addition to the chemistry used in case 1 are

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TABLE 1.- Reactions and corresponding rate constants adopted in case 1.

Reaction	Rate constant ($cm^3\ s^{-1}$) (T in K; n(M) in cm^{-3})	Reference
HCN + OH → products	see below $(k)^*$	Cicerone and Zellner (1983)
HCN + $O(^1D)$ → OH + CN	1×10^{-10}	Cicerone and Zellner (1983)
HCN + hν → H + CN		See text
CH_3CN + OH → products	6.3×10^{-13} exp(- 1030/T)	Kurylo (1984)
$CH_3CN + O(^1D) \rightarrow CH_2CN + OH$	1×10^{-10}	Working value
$CH_3CN + Cl \rightarrow CH_2CN + HCl$	8.0×10^{-11} exp(- 3000/T)	Olbregts et al. (1984)
CH_3CN + hν → products	see text	Zetsch, private communication
CH_3CN + wash-out	$\beta_w = 4.5 \times 10^{-8}\ \exp(-\ z^2/15.4) s^{-1}$	Calculated with method of Crutzen and Gidel (1983)
$^*k = \dfrac{k_o\ n(M)}{1 + k_o\ n(M)/k_\infty}\ 0.8^{[1 + \log^2 (k_o\ n(M)/k_\infty)]^{-1}}$	$k_o = 1.5 \times 10^{-31}\ \exp(-\ 875/T)\ cm^6\ s^{-1}$ $k_\infty = 1.16 \times 10^{-13}\ \exp(-\ 400/T)\ cm^3\ s^{-1}$	Adopted from Cicerone and Zellner (1983)

given in Table 2. The important modifications are the link introduced between HCN and CH_3CN as well as the fast destruction process of acetonitrile by proton hydrates.

For both molecules, a mixing ratio is prescribed as lower boundary condition at the surface, namely 10 ppt and 170 ppt for CH_3CN and HCN respectively and a zero flux is assumed as upper boundary condition at 100 km altitude.

Model Results and Discussion

Figure 1 shows the vertical distribution of the HCN and CH_3CN mixing ratio obtained with the reactions of Table 1 (case 1). These theoretical profiles are compared with available observations. As already indicated by Cicerone and Zellner (1983), the mixing ratio of hydrogen cyanide is almost constant in the troposphere and decreases progressively in the stratosphere. The corresponding slope however is steeper than in the paper by Cicerone and Zellner (1983) due to a difference in the adopted J_{HCN} value. When J_{HCN} is put equal to zero, the relative concentration is considerably increased in the upper stratosphere and is in much better agreement with the available observations. In both cases, the model suggests a residence time of about 2.7 yrs and an integrated loss in balance with an atmospheric release of the order of 0.26 MT/yr.

TABLE 2.- Additional reactions with their corresponding rate constants considered in case 2.

Reaction	Rate constant ($cm^3\ s^{-1}$)	Reference
$HCN + CH_2O \rightarrow CH_2OH\text{-}CN$	A : = 2×10^{-31} n(M)	Murad et al (1984)
	B : see below	Working value
$CH_2OH\text{-}CN$ + hν → CH_2CN + OH	yield : 50%	Estimate; Murad et al (1984)
$CH_2OH\text{-}CN$ + hν → CH_2OH + CN	yield : 50%	Estimate; Murad et al (1984)
$CH_2OH + HO_2 \rightarrow CH_3OH + O_2$	Fast	Assumed, Murad et al (1984)
$CH_2CN + HO_2 \rightarrow CH_3CN + O_2$	Fast	Assumed, Murad et al (1984)
$CH_3OH + H^+(H_2O)_n \rightarrow H^+.CH_3OH.(H_2O)_{n-1} + H_2O$	2×10^{-9}	Bohme et al (1979)
$CH_3CN + H^+(H_2O)_n \rightarrow H^+.CH_3CN.(H_2O)_{n-1} + H_2O$	2×10^{-9}	Estimate, Murad et al (1984)
$H^+.CH_3OH.(H_2O)_n + y^- \rightarrow$ products	2×10^{-7}	Smith and Adams (1982)
$H^+.CH_3CN.(H_2O)_n + y^- \rightarrow$ products	2×10^{-7}	Smith and Adams (1982)

B = same expression as k (table 1) but $k_o = 1 \times 10^{-35}\ cm^6\ s^{-1}$ and $k_\infty = 5 \times 10^{-13}$ exp(- 2500/T)

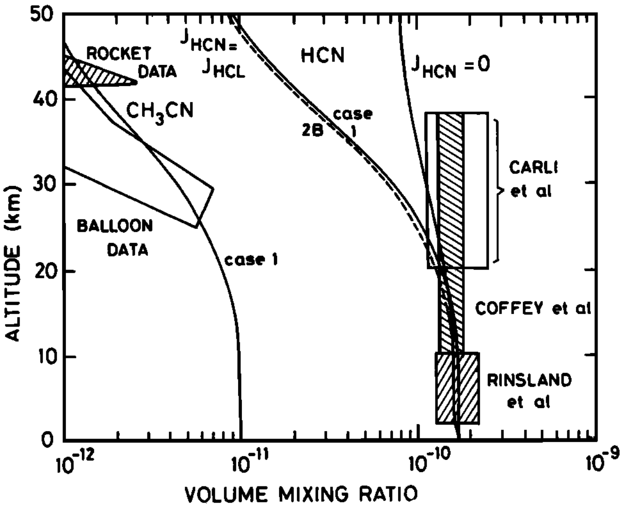

Fig. 1. Vertical distributions of HCN and CH_3CN predicted with a 1-D model and compared with observational data. Case 1 refers to the chemistry described in Table 1. Two extreme values of the photodissociation frequency of HCN are adopted ($J_{HCN} = 0$ and $J_{HCN} = J_{HCl}$). The dashed line refers to case 2 (Table 2) when reaction rate B is adopted for the destruction of HCN by CH_2O. Other curves obtained for case 2 and which are too far away from experimental data are not plotted.

The calculated vertical distribution of CH_3CN is in fairly good agreement with the observed data derived from balloon borne ion mass spectrometers, if a mixing ratio of 10 pptv is adopted at the surface. The data obtained from high altitude balloon observations (Arijs et al., 1983b) and rocket experiments (Arnold et al, 1977) seem however to be lower than the theoretical predictions, suggesting a possible additional loss mechanism in the upper stratosphere and in the mesosphere. The calculated lifetime of CH_3CN is 1.5 yrs and the ground level emission required to balance the atmospheric sink is 0.045 MT/yr.

When considering the second reaction scheme (case 2), the main loss process for HCN becomes its reaction with formaldehyde, if the rate constant suggested by Murad et al (2×10^{-31} cm^6 s^{-1}) is adopted. Consequently, with this assumption, hydrogen cyanide whose lifetime in the lower troposphere is as short as 20 seconds, is almost entirely destroyed near the ground and cannot be involved as a source for CH_3CN in the stratosphere. With this chemical scheme, it thus seems difficult to reconcile model calculations with the idea of HCN being a progenitor of CH_3CN.

We have also considered the reaction of proton hydrates with CH_3CN as a sink mechanism for acetonitrile, as suggested by Murad et al (1984). Using a total ion density derived from the parametrization of Heaps (1978) above 18 km and from in situ measurements of Rosen and Hofman (1981) below this altitude and a relative abundance of non proton hydrates compatible with recent ion composition data (Arijs et al., 1983a and b; Henschen and Arnold, 1981b), one obtains a mixing ratio of less than 10^{-2} pptv above 20 km, in disagreement with the observations.

This indicates that, although the formation of $H^+(CH_3CN)_\ell(H_2O)_m$ ions through reaction of acetonitrile with proton hydrates is irreversible, the latter is not an effective sink for CH_3CN. This can only be explained by the fact that CH_3CN is released again upon most of the recombinations of the $H^+(CH_3CN)_\ell(H_2O)_m$ ions with negative ions.

Another argument to reject a strong HCN/CH_3CN coupling is based on chemical considerations. Reaction

$$CH_2CN + HO_2 \rightarrow CH_3CN + O_2 \qquad (2)$$

which is assumed as the final process for the acetonitrile formation competes with reaction

$$CH_2CN + O_2 + M \rightarrow OOCH_2CN + M \qquad (3)$$

The rate constant of this mechanism is not known. However, if a value similar to the rate constant for the $CH_3 + O_2 + M$ reaction is adopted (2.6×10^{-31} $(T/300)^{-3.0}$ cm^6 s^{-1} - Baulch et al, 1982), reaction (3) should be dominant.

In this case, reaction (1) still acts as a sink for HCN but not as a source for CH_3CN. The rate constant of reaction (1) however is most probably lower than the value derived by Murad et al (1984) since the association of hydrogen cyanide and formaldehyde is a 4- center process between closed shell molecules. Anticipating for such a reaction an activation energy of 5 kcal/mole for the high pressure rate constant and assuming in the case of a reaction of such complexity a rate constant at 10 mbar which is 10-20 percent of the high pressure limit, the rate constant labelled B in Table 2 can be adopted as a working value. The loss rate in this case is reduced by 4 orders of magnitude and the resulting HCN profile, shown by a dashed line (2B) in figure 1, does not depart significantly from the curve obtained when reaction (1) is omitted. However, the lifetime of HCN is reduced to 0.4 yr and the required emission rate is 1.75 MT HCN/yr.

Conclusion

Model calculations as well as an analysis of the chemical scheme involved indicate that the link between HCN and CH_3CN seems very unlikely. The best hypothesis for these two gases at present is that they are produced at the Earth's surface and destroyed in the atmosphere by chemical reactions. A number of uncertainties however remain and should be elucidated in the future. For example a quantitative analysis of all sources of these gases is required together with a study of the photodestruction and the heterogeneous removal of these species.

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