Abstract. The possibility of a link between HCN and CH$_3$CN 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$_3$CN.

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$_3$CN 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 of CH$_3$CN with OH radicals. The overall budget of this molecule is nevertheless not yet completely understood, due to quantitative uncertainties in the CH$_3$CN 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

\[ \text{HCN} + \text{CH}_2\text{O} + \text{M} \rightarrow \text{CH}_2\text{OH-CN} + \text{M}. \]  

Another end-product of this mechanism would be CH$_3$OH 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$_3$CN. 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; Hinsland 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$_3$CN, new model calculations have been performed. These consider the latest 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" (Cicerone and Zellner, 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), HCN is assumed to be destroyed by OH, O($^D$) and CI 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$_3$CN 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 less than $10^{-3}$ 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($^D$) (Cicerone and Zellner, 1983). The photodissociation rate is not known and will be considered as negligible ($Q_{\text{HCN}} = 0$) to obtain an upper limit of the concentration or as being equal to the photodissociation rate of hydrogen chloride ($Q_{\text{HCN}} = Q_{\text{HCl}}$). This last assumption has been adopted by Cicerone and Zellner but their adopted value of the HCl photodissociation coefficient ($J_{\text{HCl}}$) is significantly lower than the currently accepted values for $J_{\text{HCl}}$. 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...
TABLE 1.- Reactions and corresponding rate constants adopted in case 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant ( \text{cm}^3 \text{s}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCN} + \text{OH} \rightarrow \text{products} )</td>
<td>see below ((k))</td>
<td>Cicerone and Zellner (1983)</td>
</tr>
<tr>
<td>( \text{HCN} + \text{O}(^{1}D) \rightarrow \text{OH} + \text{CN} )</td>
<td>(1 \times 10^{-10})</td>
<td>Cicerone and Zellner (1983)</td>
</tr>
<tr>
<td>( \text{HCN} + \text{hv} \rightarrow \text{H} + \text{CN} )</td>
<td>see text</td>
<td>Working value</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{OH} \rightarrow \text{products} )</td>
<td>(6.3 \times 10^{-13} \exp(-1030/T))</td>
<td>Kurylo (1984)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{O}(^{1}D) \rightarrow \text{CH}_2\text{CN} + \text{OH} )</td>
<td>(1 \times 10^{-10})</td>
<td>Olbregts et al. (1984)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{Cl} \rightarrow \text{CH}_2\text{CN} + \text{HCl} )</td>
<td>(8.0 \times 10^{-11} \exp(-3000/T))</td>
<td>Zetsch, private communication</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{hv} \rightarrow \text{products} )</td>
<td>see text</td>
<td>Calculated with method of Crutzen and Gidel (1983)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{wash-out} )</td>
<td>(\beta_w = 4.5 \times 10^{-8} \exp(-z^2/15.4) \text{s}^{-1})</td>
<td>Adopted from Cicerone and Zellner (1983)</td>
</tr>
</tbody>
</table>

\[ k = \frac{k_0 n(M)}{1 + \log^2 (k_0 n(M)/k_\infty) / 0.8} \]

\[ k_0 = 1.5 \times 10^{-31} \exp(-875/T) \text{ cm}^6 \text{s}^{-1} \]

\[ k_\infty = 1.16 \times 10^{-13} \exp(-400/T) \text{ cm}^3 \text{s}^{-1} \]

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant ( \text{cm}^3 \text{s}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HCN} + \text{CH}_2\text{O} \rightarrow \text{CH}_2\text{OH-CN} )</td>
<td>(A : = 2 \times 10^{-31} n(M))</td>
<td>Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{OH-CN} + \text{hv} \rightarrow \text{CH}_2\text{CN} + \text{OH} )</td>
<td>yield : 50%</td>
<td>Estimate; Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CN} + \text{hv} \rightarrow \text{CN} + \text{CH}_2\text{CN} )</td>
<td>yield : 50%</td>
<td>Estimate; Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{OH} + \text{HO}_2 \rightarrow \text{CH}_3\text{OH} + \text{O}_2 )</td>
<td>Fast</td>
<td>Assumed, Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CN} + \text{HO}_2 \rightarrow \text{CH}_3\text{CN} + \text{O}_2 )</td>
<td>Fast</td>
<td>Assumed, Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{CH}_2\text{CN} + \text{H}^+(\text{H}_2\text{O}) \rightarrow \text{H}^+.\text{CH}_2\text{CN}.(\text{H}_2\text{O})_n-1 + \text{H}_2\text{O} )</td>
<td>(2 \times 10^{-9})</td>
<td>Bohme et al (1979)</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CN} + \text{H}^+(\text{H}_2\text{O})_n \rightarrow \text{H}^+.\text{CH}_3\text{CN}.(\text{H}_2\text{O})_n-1 + \text{H}_2\text{O} )</td>
<td>(2 \times 10^{-9})</td>
<td>Estimate, Murad et al (1984)</td>
</tr>
<tr>
<td>( \text{H}^+.\text{CH}_2\text{CN}.(\text{H}_2\text{O})_n + \gamma \rightarrow \text{products} )</td>
<td>(2 \times 10^{-7})</td>
<td>Smith and Adams (1982)</td>
</tr>
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</tr>
</tbody>
</table>

\( B = \text{same expression as } k \text{ (table 1)} \) but \(k_0 = 1 \times 10^{-35} \text{ cm}^6 \text{s}^{-1}\) and \(k_\infty = 5 \times 10^{-13} \exp(-2500/T)\)
50 + H (CHCN)(H₂O) ions through reaction of acetonitrile with proton hydrates is irreversible, the latter is not an effective sink for CH₃CN. This can only be explained by the fact that CH₃CN is released again upon most of the recombinations of the H⁺(CH₃CN)(H₂O) ions with negative ions.

Another argument to reject a strong HCN/CH₃CN coupling is based on chemical considerations. Reaction

\[ \text{CH}_2\text{CN} + \text{HO}_2 \rightarrow \text{CH}_3\text{CN} + \text{O}_2 (2) \]

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

\[ \text{CH}_2\text{CN} + \text{O}_2 + \text{M} + \text{OOCH}_2\text{CN} + \text{M} (3) \]

The rate constant of this mechanism is not known. However, if a value similar to the rate constant for the CH + O reaction adopted VOLUME MIXING RATIO for the CH + O reaction adopted Fig. 1. Vertical distributions of HCN and CH₃CN (2.6 x 10⁻³ /30 3' cm s⁻¹) is adopted (J-cN = 0 and JCN(TbeHC≈ I). The 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.

The calculated vertical distribution of CH₃CN 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 CH₃CN 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 x 10⁻³¹ cm⁶ 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 CH₃CN in the stratosphere. With this chemical scheme, it thus seems difficult to reconcile model calculations with the idea of HCN being a progenitor of CH₃CN.

We have also considered the reaction of proton hydrates with CH₃CN 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 10⁻⁶ pptv above 20 km, in disagreement with the observations.

This indicates that, although the formation of H⁺(CH₃CN)(H₂O) ions through reaction of acetonitrile with proton hydrates is irreversible, the latter is not an effective sink for CH₃CN. This can only be explained by the fact that CH₃CN is released again upon most of the recombinations of the H⁺(CH₃CN)(H₂O) ions with negative ions.

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Conclusion

Model calculations as well as an analysis of the chemical scheme involved indicate that the link between HCN and CH₃CN 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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References

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