Atmospheric Pseudohalogen Chemistry

David John Lary

Hydrogen cyanide is not usually considered in atmospheric chemical models. The paper presents three reasons why hydrogen cyanide is likely to be significant for atmospheric chemistry. Firstly, HCN is a product and marker of biomass burning. Secondly, it is also likely that lightning is producing HCN, and as HCN is sparingly soluble it could be a useful long-lived "smoking gun" marker of lightning activity. Thirdly, the chemical decomposition of HCN leads to the production of small amounts of the cyanide (CN) and NCO radicals. The NCO radical can be photolyzed in the visible portion of the spectrum yielding nitrogen atoms (N). The production of nitrogen atoms is significant as it leads to the titration of total nitrogen from the atmosphere via $N+N->N_2$, where N_2 is molecular nitrogen.

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Abstract. There are at least three reasons why hydrogen cyanide is likely to be significant for atmospheric chemistry. The first is well known, HCN is a product and marker of biomass burning. However, if a detailed ion chemistry of lightning is considered then it is almost certain than in addition to lightning producing NO_x, it also produces HO_x and HCN. Unlike NO_x and HO_x, HCN is long-lived and could therefore be a useful marker of lightning activity. Observational evidence is considered to support this view. Thirdly, the chemical decomposition of HCN leads to the production of small amounts of CN and NCO. NCO can be photolyzed in the visible portion of the spectrum yielding N atoms. The production of N atoms is significant as it leads to the titration of nitrogen from the atmosphere via $N+N \rightarrow N_2$. Normally the only modelled source of N atoms is NO photolysis which happens largely in the UV Schumann-Runge bands. However, NCO photolysis occurs in the visible and so could be involved in titration of atmospheric nitrogen in the lower stratosphere and troposphere. HCN emission inventories are worthy of attention. The CN and NCO radicals have been termed pseudohalogens since the 1920s. They are strongly bound, univalent, radicals with an extensive and varied chemistry. The products of the atmospheric oxidation of HCN are NO, CO and O_3. $N+CH_4$ and $N+CH_3OH$ are found to be important sources of HCN. Including the pseudohalogen chemistry gives a small increase in ozone and total reactive nitrogen (NO_y).
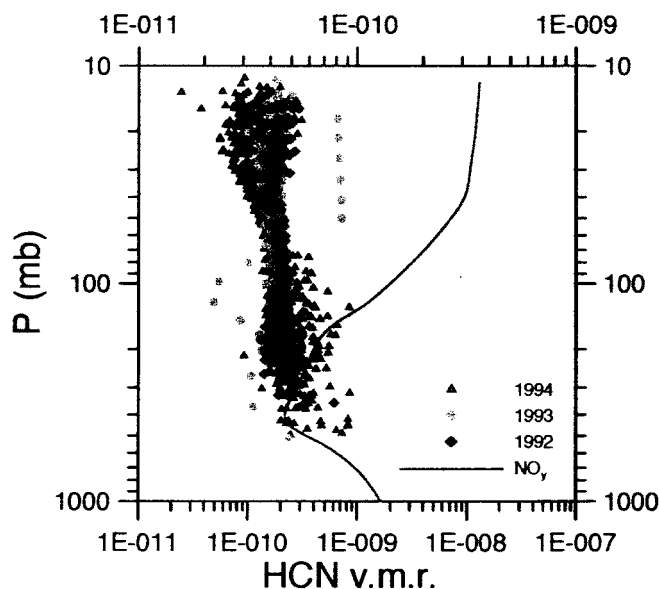
Fig. 1. All HCN observations made by the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) on the missions ATLAS-1 (1992), ATLAS-2 (1993), and ATLAS-3 (1994) shown together with a typical mid-latitude NO_y profile. The ATMOS data is publically available from the web site http://remus.jpl.nasa.gov/.

1 Introduction

Since the discovery of the Antarctic ozone hole by Farman et al. (1985) the importance of halogen radicals in determining the concentrations of atmospheric ozone has been clearly demonstrated. However, it was only in the mid 1970s that the

halogen radicals were first recognized as a potential threat to ozone. In like manner, there may be other radicals which play a rôle in ozone photochemistry. There are many natural and anthropogenic sources of compounds containing CN which can be released into the atmosphere. Many CN reactions are already considered when studying combustion chemistry and interstellar clouds. This paper considers their importance in our own atmosphere.

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1.1 Properties

HCN (also called formonitrile) is a highly volatile, colorless, and extremely poisonous liquid (boiling point 26°C, freezing point -14°C). A solution of hydrogen cyanide in water is called hydrocyanic acid, or prussic acid. It was discovered in 1782 by the Swedish chemist, Carl Wilhelm Scheele, who prepared it from the pigment Prussian blue (Britannica, 2003).

1.2 Observations

It is surprising that HCN is so often overlooked as it has been observed on numerous occasions over the last two decades (Yokelson et al., 2003; Singh et al., 2003; Zhao et al., 2002; Rinsland et al., 2001, 2000; Zhao et al., 2000; Rinsland et al., 1999; Bradshaw et al., 1998; Rinsland et al., 1998a,b; Schneider et al., 1997; Mahieu et al., 1997; Rinsland et al., 1996; Notholt et al., 1995; Mahieu et al., 1995; Toon et al., 1992b,a; Kopp, 1990; Jaramillo et al., 1989; Zander, 1988; Carli and Park, 1988; Jaramillo et al., 1988; Abbas et al., 1987; Smith and Rinsland, 1985; Coffey et al., 1981). Recently it has sometimes been considered as an 'interference' for NO_y observations, for example, Bradshaw et al. (1998); Thompson et al. (1997); Kliner et al. (1997). However, regarding it as an 'interference' overlooks its potential importance in atmospheric chemistry, particularly as Cicerone and Zellner (1983) deduced that HCN has a very long residence time against rainout.

Figure 1 shows all the HCN observations made by the Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) on the missions ATLAS-1, ATLAS-2, and ATLAS-3 (Rinsland et al., 1998a,b, 1996) together with a typical mid-latitude NO_y profile. In the upper troposphere and lower stratosphere the HCN abundance is comparable to the NO_y present and should not be neglected. It is tantalizing that some of the tropical vertical profiles seem to have a large peak in HCN close to the tropopause which may be produced by lightning in regions of strong convective activity.

1.3 Likely Sources

HCN is produced by biomass burning (Lobert et al., 1990; Hurst et al., 1994b; Yokelson et al., 1997b; Holzinger et al., 1999; Rinsland et al., 1999, 2000; Barber et al., 2003; Li et al., 2003; Singh et al., 2003; Yokelson et al., 2003) since nitrogen in plant material is mostly present as amino acids and upon combustion this nitrogen is emitted as a variety of compounds including NH_3, NO, NO_2, N_2O, organic nitriles and nitrates (Holzinger et al., 1999; Yokelson et al., 1997a; Lee and Atkins, 1994; Hurst et al., 1994b,a; Kuhlbusch et al., 1991). There are many naturally occurring substances yielding cyanide in their seeds, such as the pit of the wild cherry. It usually occurs in combination with plant sugars. The tuberous edible plant of the spurge family called cassava (also known as manioc, mandioc, or yuca) were used by primitive peoples to produce HCN for poison darts and arrows. HCN is produced by other plants, bacteria and fungi.

In addition, aliphatic-amines are produced from animal husbandry and may be a source of HCN (Schade and Crutzen, 1995). Schade and Crutzen (1995) measured the emissions of volatile aliphatic amines and ammonia produced by the manure of beef cattle, dairy cows, swine, laying hens and horses in livestock buildings. The amine emissions consisted almost exclusively of the three methylamines and correlated with those of ammonia. Schade and Crutzen (1995) showed possible reaction pathways for atmospheric methylamines. These included the speculative but possible production of HCN.

There are many anthropogenic sources of compounds containing CN which can be released into the atmosphere. Cyanides are used in a variety of chemical processes including fumigation, case hardening of iron and steel, electroplating and in the concentration of ores. Hydrogen cyanide is a highly volatile and extremely poisonous gas that is used in fumigation, ore concentration, and various other industrial processes. Cyanogen, or oxalonitrile, $(CN)_2$, is also used as a chemical intermediate and a fumigant. Hydrogen cyanide is used to prepare polyacrylonitrile fibres (known by the generic name of acrylic) synthetic rubber, plastics, and in gas masers to produce a wavelength of 3.34 mm (Britannica, 2003). Acrylic fibres are spun from polymers consisting of at least 85% by weight of acrylonitrile units produced from ethylene oxide and hydrocyanic acid.

Hydrogen cyanide is a combustion product which is a human hazard during domestic and industrial fires. Some catalytic converters in bad repair can produce large amounts of Hydrogen cyanide. Hydrogen cyanide is produced in large quantities for laboratory and commercial use by three principal methods: Treatment of sodium cyanide with sulphuric acid, catalytic oxidation of a methane-ammonia mixture, and decomposition of formamide ($HCONH_2$).

We suggest that it is timely to compile HCN emission inventories.

It is interesting to note that the atmospheric measurements of HCN reported by Zander (1988) gave a mixing ratio for HCN in the Southern Hemisphere which was approximately 5% higher than that for the Northern Hemisphere. This may be due to biomass burning. It seems that in addition to HCN being a marker of biomass burning it is also a marker for lightning.

1.4 HCN, HO_x and Lightning

Emissions from CN radicals are occasionally observed from lightning disturbed air (Cicerone and Zellner, 1983). In the atmosphere of Jupiter HCN is present with a concentration of about 2 ppbv and is thought to be produced by lightning in the convective regions of Jupiter's atmosphere (Britannica, 2003; Borucki et al., 1988, 1991). On Titan HCN is also
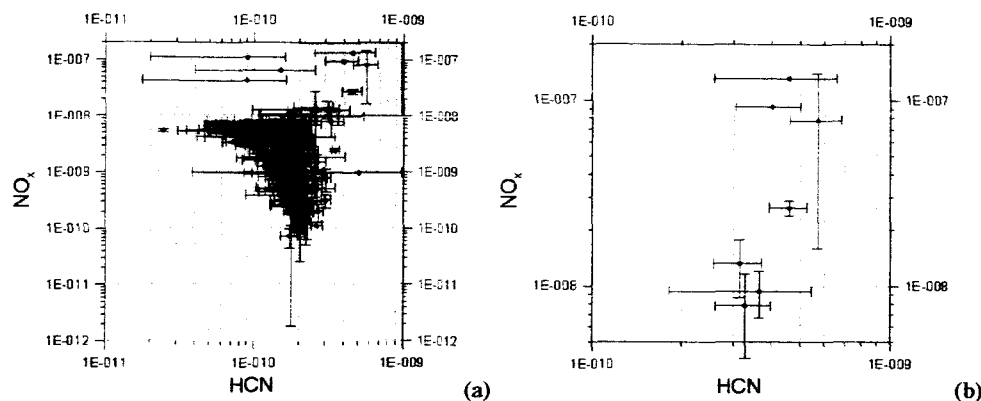
Fig. 2. Scatter diagram of the HCN and NO_x concentrations observed by ATMOS ATLAS3. Panel (a) shows all the available HCN and NO_x observations made. Panel (b) is an enlargement showing just the high NO_x and HCN concentrations which are probably associated with lightning (notice the log-log scale).

thought to be produced by lightning (Borucki et al., 1988). It may well be that lightning is a significant source of HCN, particularly due to its resistance to uptake by aqueous media.

Lightning produces large scale ionisation in the atmosphere with temperatures of around 30,000 K produced within a few microseconds. Both the ionisation and high temperatures are significant for atmospheric chemistry, and the full implications are usually completely overlooked, with attention paid almost exclusively to NO_x. Ionisation produced by cosmic rays and precipitating particles is well known to produce NO_x and HO_x(Brasseur and Solomon, 1987). The ionisation associated with lightning is between six and fifteen orders of magnitude greater than that associated with cosmic rays (Boldi, 1992). It is therefore likely that elevated HO_x should be associated with lightning (Hill, 1992). This has been both calculated (Boldi, 1992) and hinted at by observations of elevated HO_x in the vicinity of convective outflow (Jaegle et al., 1999). Calculations suggest that there is a 5-6% increase in global lightning for every 1°C of warming (Price and Rind, 1994), so if there is a lightning source of HO_x global warming could lead to a significant change in the oxidizing capacity of the atmosphere due to lightning produced HO_x alone.

Equilibrium thermodynamic calculations (Boldi, 1992) show that for the conditions associated with a lightning strike in the terrestrial atmosphere we would expect between 0.7 to 1 ppbv of HCN. If HCN is produced by lightning, then in the surrounding air we would simultaneously expect elevated concentrations of both NO_x and NO_y. This is exactly what ATMOS observed (ATMOS). For example, around a thousand observations of HCN were made during November 1994 as part of ATLAS3 (ATMOS). Among these observations there were six anomalously high HCN observations of greater than 0.7 ppbv, for which elevated concentrations of both NO_x and NO_y were also observed. If one plots a scatter diagram of the HCN against NO_x concentrations (Figure 2), we find that there is a strong correlation between HCN and

NO_x for high HCN concentrations. This corresponds to the air parcels that have probably recently encountered lightning. There is not a strong correlation for the lower HCN and NO_x concentrations as NO_x and HCN are not in chemical equilibrium.

There are several satellites which observe global lightning, but these had not been launched at the time of the last ATMOS mission. However, for the six locations with HCN concentrations greater than 0.7 ppbv visible satellite images show cloud cover as do the NCEP analyses (NCEP). Each of the six locations were in a coastal region or over land which is where most lightning activity occurs. The vertical structure of the HCN profile may provide a good test for the hypothesis that HCN is produced by lightning. During thunderstorms we expect a 'C' shaped NO_x profile (Pickering et al., 1998), and so should also expect a 'C' shaped HCN profile with enhanced HCN in the region between 5 and 14 km.

1.5 Previous modelling work

The only previous modelling studies of atmospheric HCN appear to be those of Cicerone and Zellner (1983); Brasseur et al. (1985); Li et al. (2003); Singh et al. (2003) who considered the earth's current atmosphere and the studies of Zahnle (1986a,b) who presented a study of the likely HCN chemistry in the earth's early atmosphere. Cicerone and Zellner (1983) identified the major atmospheric losses of HCN. Li et al. (2003) and Singh et al. (2003) showed that the main HCN loss is due to oceanic uptake.

This study expands the previous work by considering many N, CN and NCO reactions which are known to be important in flame chemistry. These reactions are considered for conditions relevant to the current atmosphere. Including these reactions provides additional sources of HCN, not included by Cicerone and Zellner (1983); Brasseur et al. (1985), and some of which were not included by Zahnle (1986a,b) either. HCN photolysis is shown to be a minor

loss for HCN.

2 Reasons to Consider HCN

Before systematically examining atmospheric CN_x chemistry let us examine at least three reasons why we should consider atmospheric HCN chemistry.

2.1 Abundance

Figure 1 shows that in the upper troposphere and lower stratosphere the HCN abundance is comparable to the NO_y present.

2.2 Tracer

HCN is a long lived, low solubility (Cicerone and Zellner, 1983) gas. If as it seems HCN is produced by lightning (Britannica, 2003; Cicerone and Zellner, 1983; Borucki et al., 1988, 1991) then as it is not rained out it may well prove to be an effective tracer of lightning activity. Such a marker could be extremely valuable to complement observations (Huntrieser et al., 1998; Kawakami et al., 1997; Hauf et al., 1995).

2.3 N atom source

The main stratospheric sink of NO_y is the reaction of N with NO

$$N + NO \longrightarrow N_2 + O(^3P) \tag{1}$$

with the main source of N atoms generally accepted to be the photolysis of NO

$$NO + h\nu \longrightarrow N + O(^3P) \quad \lambda \leq 189 \text{ nm} \tag{2}$$
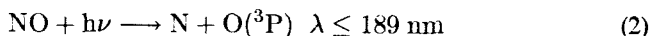
However, the photolysis of NCO is also a source of N atoms. The rate of N production due to NCO photolysis is calculated to be faster than that due to NO photolysis below about 10 km.

$$NCO + h\nu \longrightarrow N + CO \quad \lambda \leq 342 \text{ nm}$$
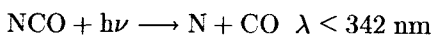
Consequently, when pseudohalogen chemistry is included in the model there is a significant increase (more than an order of magnitude) in the N atom concentration below 10 km (Figure 4).

3 Atmospheric CN_x chemistry

Let us now consider the HCN chemistry depicted in Figure 3 as simulated using the extensively validated AutoChem model (Lary et al., 1995; Fisher and Lary, 1995; Lary, 1996; Lary et al., 2003). The model is explicit and uses the adaptive-timestep, error monitoring, Stoer and Bulirsch (1980) time integration scheme designed by Press et al.
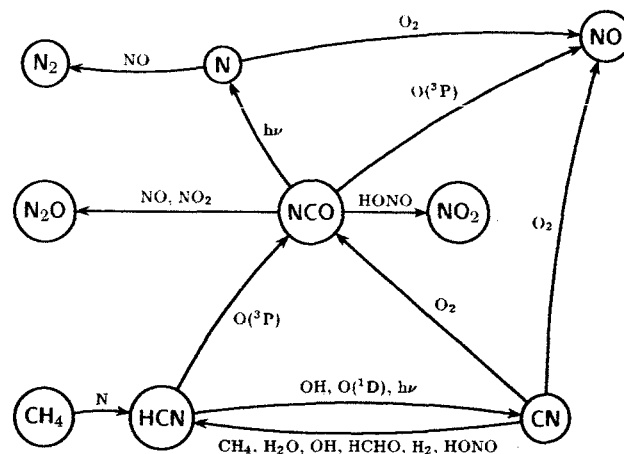
Fig. 3. The CN, NCO, HCN reaction scheme used in the model.

(1992) for stiff systems of equations. Photolysis rates are calculated using full spherical geometry and multiple scattering (Anderson, 1983; Lary and Pyle, 1991a,b; Meier et al., 1982; Nicolet et al., 1982) corrected after Becker et al. (2000). The photolysis rate used for each time step is obtained by ten point Gaussian-Legendre integration (Press et al., 1992). In this study the model described a total of 49 species including CN, NCO and HCN. The model kinetic data is based on DeMore et al. (2000) with the cyanide reactions coming from a variety of sources.

The eventual fate of most HCN released into the atmosphere is NO. Since HCN has a long lifetime against rainout (Cicerone and Zellner, 1983), whereas NO_x does not, HCN can be transported from the regions where it is emitted and slowly release NO_x away from the source regions. The net effect of HCN oxidation is summarized by the following reaction sequence shown in Table 1. Therefore including HCN
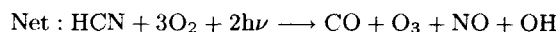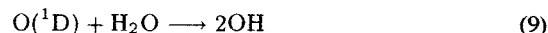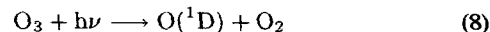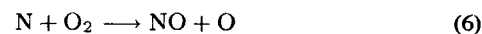
$$HCN + OH \longrightarrow H_2O + CN \tag{3}$$
$$CN + O_2 \longrightarrow NCO + O \tag{4}$$
$$NCO + h\nu \longrightarrow N + CO \tag{5}$$
$$N + O_2 \longrightarrow NO + O \tag{6}$$
$$2O + 2O_2 \longrightarrow 2O_3 \tag{7}$$
$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \tag{8}$$
$$O(^1D) + H_2O \longrightarrow 2OH \tag{9}$$
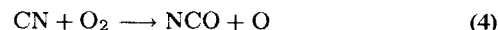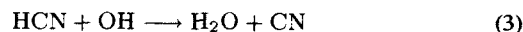
Net : $HCN + 3O_2 + 2h\nu \longrightarrow CO + O_3 + NO + OH$

Table 1. HCN oxidation sequence.

chemistry provides a small additional source of NO_x, O_3 and CO. If there is a heterogeneous conversion (oxidation)

of HCN then it may be more important than described here, particularly in the upper troposphere.

3.1 HCN

Figure 1 shows the observed HCN profiles from ATMOS. Cicerone and Zellner (1983) and Brasseur et al. (1985) were able to reproduce the tropospheric portion of the profile but not the stratospheric portion. They suggested that the discrepancy may be due to an inappropriate OH concentration or HCN photolysis rate. The HCN photolysis rate calculated by assuming HCN has the same absorption cross-section as HCl will be too fast as Herzberg and Innes (1957) report a predissociation limit of 179 nm for HCN, which means that the HCN photolysis rate is very small. This is confirmed by the calculations of Huebner et al. (1992).

Another likely possibility for the discrepancy is in-situ atmospheric production of HCN. Such production can occur by several routes, most of which are very slow as they involve the CN radical which is quickly removed by reaction with O_2. For this reason, an effective production will probably not involve CN. Zahnle (1986a) included the production of HCN caused by the reaction of N with CH_2 and CH_3. Since CH_2 is produced mainly by Lyman-α CH_4 photolysis, this source of HCN will be small in the troposphere and stratosphere (these source are included in the model). The reaction of N with CH_4 is the most important source of HCN in the model, and has a noticeable effect on the calculated HCN concentration above 25 km. It was not included by Cicerone and Zellner (1983); Brasseur et al. (1985); Zahnle (1986a,b). The rate constant was measured by Takahashi (1972) at 298 K with N_2 as the bath gas as 2.5×10^{-14} molecules^{-1} cm^3 s^{-1}.

$$N + CH_4 \longrightarrow HCN + H_2 + H \tag{10}$$
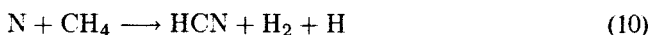
Ocean uptake is the dominant sink for HCN (Singh et al., 2003; Li et al., 2003). The main atmospheric loss of HCN is reaction with OH.

$$HCN + OH \longrightarrow H_2O + CN$$
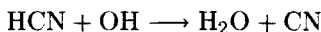
If the HCl cross-section is used to calculate the HCN photolysis rate as was done by Cicerone and Zellner (1983) and Brasseur et al. (1985) then above 35 km photolysis is the most important loss of HCN. However, Herzberg and Innes (1957) report a predissociation limit of 55900 cm^{-1}, 179 nm. This means that *no* photolysis would occur in the important UV window and HCN photolysis is very slow.

$$HCN + h\nu \longrightarrow H + CN \quad \lambda \leq 179 \, nm \tag{11}$$

There is also a minor loss due to reaction with $O(^3P)$ and $O(^1D)$ (Figure 4).

$$HCN + O(^3P) \longrightarrow H + NCO \tag{12}$$
$$HCN + O(^1D) \longrightarrow OH + CN \tag{13}$$

3.2 The cyanide radical, CN

In the sunlit atmosphere CN is in photochemical equilibrium. CN has a very short lifetime because of the very fast reaction of CN with O_2. The lifetime varies between about 10 ns and 60 μs. The calculated CN profile is shown in Figure 4.
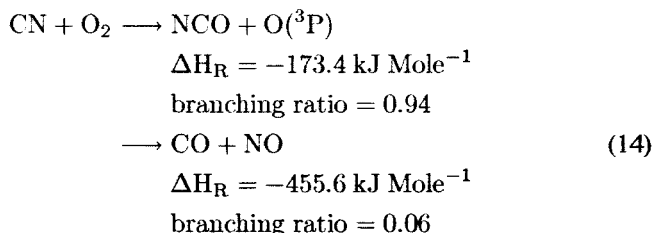
The most important production channel for CN in the model km is

$$HCN + OH \longrightarrow H_2O + CN$$

The reaction is slightly endothermic at 298 K, however, the reverse reaction is not a significant source of HCN. In the upper atmosphere the reaction of HCN with $O(^1D)$ and HCN photolysis each contribute a few percent to the overall production of CN.

$$HCN + O(^1D) \longrightarrow OH + CN$$
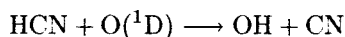
The main loss of CN at all altitudes in the model is the rapid reaction of CN with O_2 which has two channels

$$CN + O_2 \longrightarrow NCO + O(^3P)$$
$$\Delta H_R = -173.4 \, kJ \, Mole^{-1}$$
$$\text{branching ratio} = 0.94$$
$$\longrightarrow CO + NO \tag{14}$$
$$\Delta H_R = -455.6 \, kJ \, Mole^{-1}$$
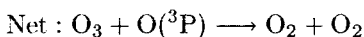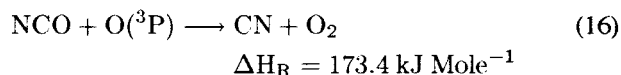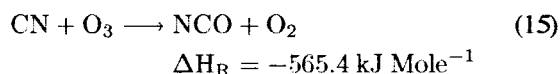$$\text{branching ratio} = 0.06$$

The branching ratio quoted was determined by Schmatjko and Wolfrum (1978). In the laboratory Basco (1965) found that there was a production of ozone due to the first channel of this reaction in an excess of oxygen because it can be followed by

$$O(^3P) + O_2 \xrightarrow{M} O3$$
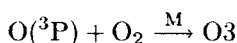
Such a production of O_3 does occur in the model to a very small extent, but it is only a small source of O_3 as the CN radicals are present in such small concentrations. In addition, the NO formed can then take part in catalytic destruction of O_3.

Since CN is a pseudohalogen it might be expected that, like the halogens, it could take part in the catalytic destruction of ozone, for example

$$CN + O_3 \longrightarrow NCO + O_2 \tag{15}$$
$$\Delta H_R = -565.4 \, kJ \, Mole^{-1}$$
$$NCO + O(^3P) \longrightarrow CN + O_2 \tag{16}$$
$$\Delta H_R = 173.4 \, kJ \, Mole^{-1}$$

$$Net : O_3 + O(^3P) \longrightarrow O_2 + O_2$$

Clearly the important difference between the pseudo-halogen CN and halogens such as Cl and Br, involved in stratospheric
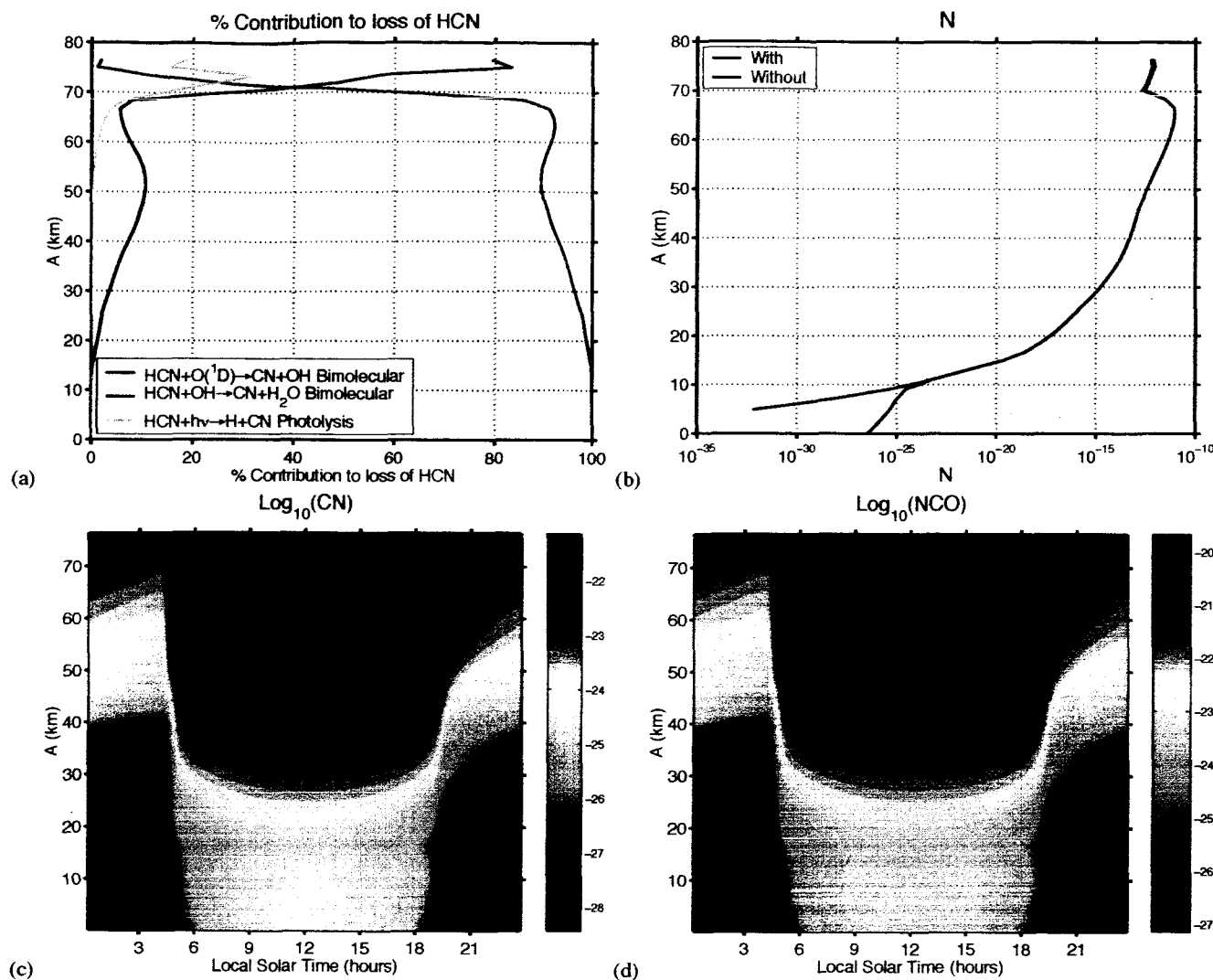
Fig. 4. Panel (a) shows the calculated contributions for the various loss terms of HCN. Panel (b) shows the effect on the nitrogen atom v.m.r. when cyanide chemistry is included. The red line shows the calculation with pseudohalogen chemistry the blue line shows the calculation without pseudohalogen chemistry. Panels (c) and (d) show calculated diurnal cycles for CN and NCO.

ozone destruction, is the very marked difference in their reactions with O_2. Chlorine and bromine form weakly bound peroxides on reaction with O_2

$$Cl + O_2 + M \leftrightarrow ClOO + M \tag{17}$$

$$Br + O_2 + M \leftrightarrow BrOO + M \tag{18}$$

which rapidly decompose to give back the halogen, whereas CN reacts rapidly with O2, as we have mentioned previously

$$CN + O_2 \longrightarrow NCO + O$$

$$CN + O_2 \longrightarrow CO + NO$$
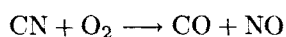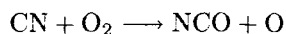
Yielding primarily NCO and O. If Cl or Br atoms reacted with O_2 in a similar way to CN, there would be no ozone loss. So the CN radical behaves in a crucially, very different manner to the halogens, preventing it from participating in an efficient ozone loss cycle.

The reaction CN + O_3 is thermodynamically very favorable but its rate constant has not been determined. The NCO + O reaction to give CN as a product occurs in flames (Tsang, 1992). This reaction is endothermic at room temperature by 173 KJ/Mole. So this reaction has not been included in the reaction scheme. Consequently, with the current chemical scheme the only way to convert the NCO formed by the reaction of CN with O_3 back to CN is via HCN photolysis. Since HCN has a lifetime of about 5 months (Singh et al., 2003; Li et al., 2003) and HCN photolysis is extremely slow this is not an effective loss of O_3.

The CN + O_2 reaction has a second channel which produces CO + NO and so can either enhance the NO/NO2 catalytic cycle, or enhance the production of odd oxygen if it is followed by the formation and photolysis of NO_2. Unlike the photolysis of NO_2 or ClO, the photolysis of NCO, does

not yield an oxygen atom

$$NCO + h\nu \longrightarrow N + CO$$
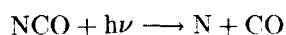
and so is not a source of odd oxygen. However, it is a source of N atoms.

3.3 The NCO radical

NCO is in photochemical equilibrium throughout the sunlit atmosphere. The lifetime varies from about 6 seconds at the surface down to about a second at 65 km. The calculated NCO profile can be seen in Figure 4. By far the most important production of NCO is due to the fast reaction

$$CN + O_2 \longrightarrow NCO + O(^3P)$$
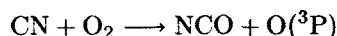
The main loss of NCO in the model is

$$NCO + O_2 \longrightarrow NO + CO_2 \tag{19}$$
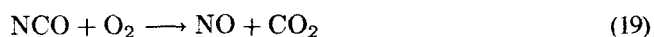
In the upper atmosphere the reaction with $O(^3P)$ also plays a role.

$$NCO + O(^3P) \longrightarrow CO + NO \tag{20}$$

4 Conclusions

In addition to NO_x lightning it is suggested that it is also producing significant amounts of HCN and possibly HO_x. HCN is a stable, long-lived, sparingly soluble molecule with a long residence time against rain-out. Unlike NO_x, HCN can act as a relatively inert 'marker' of lightning activity, and may thereby serve as a proxy for the total amount of lightning activity in the atmosphere. The vertical structure of HCN observed during thunderstorms may provide a good test for the hypothesis that HCN is produced by lightning.

NCO photolysis enhances the N atom concentration, and hence, enhances the rate of NO_y loss due to the reaction of N with NO. This additional source of N atoms is more important than NO photolysis below 10 km. The NCO absorption cross-section does not appear to have been measured and is one of the largest uncertainties in this study.

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