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The Atmospheric Chemistry of Hydrogen Cyanide (HCN)

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Since 1981, three groups have reported spectroscopic detections and measurements of hydrogen cyanide in the atmosphere. HCN concentrations (volume mixing ratios) of $(1.5–1.7) \times 10^{-10}$ appear to characterize the stratosphere and the northern hemisphere's nonurban troposphere. In this paper we explore the atmospheric behavior of HCN by examining its chemical and photochemical properties. Its principal sinks are reactions with atmospheric OH and $O(^1D)$; precipitation appears to be a negligible sink. In the stratosphere, vacuum UV photons also attack HCN. Atmospheric model calculations show that HCN should be relatively well mixed in the troposphere and that its concentration decreases slowly with altitude in the stratosphere. Its atmospheric residence time appears to be about 2.5 years, although 1–5 years is a possible range. To maintain the observed atmospheric burden of HCN, an annual source of about 2×10^{11} g nitrogen as HCN is required; we speculate as to the identity of these sources. Oxidation of HCN by OH, while the major sink for atmospheric HCN, is not simple or direct. Instead, oxidation proceeds from the HCN·OH adduct formed in HCN + OH reactions. These pathways and their uncertainties are outlined here.

1. INTRODUCTION

HCN was first seen in the earth's atmosphere by *Coffey et al.* [1981]. They employed infrared absorption instrumentation aboard an aircraft that flew between 5°N and 50°N latitude. Coffey et al. measured the total amount of HCN above 12 km altitude; their vertical column was 6.5×10^{14} cm^{-2}. Assuming that HCN is distributed uniformly with altitude above 12 km, they deduced a stratospheric mixing ratio of 1.55×10^{-10} by volume. These corrected HCN amounts are slightly lower (M. T. Coffey, private communication, 1982) than those reported by *Coffey et al.* [1981]. Similarly, *Carli et al.* [1982] discovered HCN by examining stratospheric microwave emission spectra. They obtained data between 20 and 40 km altitude. They state that the HCN mixing ratio was $(1.3–2.6) \times 10^{-10}$. More recently, *Rinsland et al.* [1982] detected HCN in the troposphere. With IR absorption measurements from Kitt Peak (altitude = 2.095 km), they found vertical column amounts of 2.73×10^{15} cm^{-2}, yielding an average tropospheric mixing ratio of 1.66×10^{-10} between 2.1 and 12 km. They were also able to estimate stratospheric HCN concentrations.

Because the earth's atmosphere is oxidizing, reasons for the presence of HCN are not entirely obvious. Questions as to the sources of this compound and the rate of oxidation arise immediately. Further, it is important to know if the oxidation of HCN represents a significant in situ source of gaseous nitrogen oxides or of NO_3^- and CN^- in precipitation and whether atmospheric HCN can interfere with attempts to measure NO_2 or peroxyacetyl nitrate, for example, by conversion to NO followed by chemiluminescent detection of NO. At concentrations of 170 ppt, HCN concentrations can exceed those of NO and NO_2 in the background troposphere [see *Kley et al.*, 1981], so the possibilities mentioned above should

be explored. It is also of interest to know whether the available HCN measurements shed any light on the origin and behavior of stratospheric CH_3CN detected by *Arnold et al.* [1978], *Arijs et al.* [1980], and *Böhringer and Arnold* [1981].

In this paper we explore the atmospheric chemistry of HCN by evaluating its properties and available kinetic and thermodynamic data; this discussion comprises section 2. Section 3 presents our atmospheric model calculations and estimates of HCN vertical profiles, source strengths, and atmospheric residence times.

2. ATMOSPHERIC CHEMISTRY OF HCN

HCN is a strongly bound molecule. Its bond dissociation energy D has been determined by *Davis and Okabe* [1968]; $D(H-CN) = 5.20$ eV or 120 kcal/mol. This D value corresponds to a long-wavelength cutoff of 238.4 nm for photodissociation. In reality, the dissociation of HCN at wavelengths near 238 nm has not been observed. Instead, *Hilgendorff* [1935] observed a regular band series absorption between 178 and 200 nm, with an onset to continuous absorption below 178 nm. *Herzberg and Innes* [1957] observed predissociation for $\lambda < 178.5$ nm (6.93 eV), although they admitted that weak predissociation absorption might have escaped their detection. In their research, Herzberg and Innes found that

$$HCN + h\nu \rightarrow H(^2S) + CN(^2\pi)$$

the $^2\pi$ state of CN is 1.15 eV above the $X^2\Sigma$ ground state. In *Davis and Okabe's* [1968] work, they actually excited HCN with much shorter wavelengths and observed fluorescence of $CN(B^2\Sigma)$, an excited state of CN that is 3.20 eV above ground. There are no available data on photodissociation of HCN for 175 nm $< \lambda <$ 238 nm, a wavelength region of some interest for the stratosphere but of no consequence for tropospheric HCN. The strong H-CN bond cannot be broken by photons available in the troposphere or lower stratosphere. In our atmospheric model calculations we calculated HCN photolysis rates as described in section 3.

TABLE 1. Enthalpy of Reaction ΔH_R for Possible Reactions of HCN With 14 Atmospheric Gases

Reactants → Products	ΔH_R, kcal/mol
$HCN + O_2 \rightarrow HOCN + O$	+14
$\rightarrow HNCO + O$	+20
$HCN + OH \rightarrow HOCN + H$	>+2
$HCN + O_3 \rightarrow OH + CN + O_2$	+43
$HCN + HO_2 \rightarrow H_2 + O_2 + CN$	+66
$\rightarrow H_2O_2 + CN$	+35
$HCN + H_2O_2 \rightarrow H_2 + HO_2 + CN$	+102
$HCN + NO_2 \rightarrow HNO_2 + CN$	+43
$HCN + HNO_2 \rightarrow H_2 + NO_2 + CN$	+94
$HCN + CH_2O \rightarrow H_2 + CN + CHO$	+104
$HCN + SO_2 \rightarrow NCO + HSO$	+101
$HCN + O \rightarrow OH + CN$	+19
$HCN + Cl \rightarrow HCl + CN$	+18
$HCN + H \rightarrow H_2 + CN$	+17
$HCN + HCl \rightarrow H_2 + ClCN$	+23
$HCN + CO \rightarrow CHO + CN$	+105

Heats of formation for these calculations are taken from Okabe [1978] and apply for 0°K except for HO_2 for which we took Howard's [1980] value of 2.5 ± 1 kcal/mol and for NCO we adopted 48 kcal/mol from Sullivan et al. [1983]. Note that all these potential reactions are endothermic ($\Delta H_R > 0$); rates of these reactions in the atmosphere would be negligibly slow.

Contrary to extrapolations from information in several popular handbooks, HCN is not very soluble in water when low partial pressures (for example, <1 torr) of HCN are in question. Henry's constant $K_H = P/X$, where P is the partial pressure (torr) of HCN and X is the mole fraction of HCN in the liquid, is $K_H = 4000$ at 18°C and 0.01 atm HCN [International Critical Tables of Numerical Data, 1928]. At the same temperature the Ostwald solubility coefficient (see, e.g., Wilhelm et al., 1977] is about 252 [Linke, 1958]. Further confirming data are found in the works by Lewis and Randall [1923] and Landolt-Börnstein [1962]. On the basis of this solubility and the fact that HCN is a very weak acid

$$HCN_{aq} \rightleftharpoons H^+ + CN^- \qquad (K = 1.3 \times 10^{-9})$$

one deduces that HCN has a very long atmospheric residence time against rainout. If 1 m of rain falls per unit area each year and it were saturated with HCN (with respect to, say, 200 ppt of gaseous HCN) it would take 34 years of average rainfall to remove the 200 ppt of HCN. This calculation is not very sensitive to rainfall pH; we took pH = 4 here.

Let us proceed now to examine possible gas phase reactions that can affect the atmospheric behavior of HCN. We will conclude that the principal sinks for HCN are reactions with OH and $O(^1D)$ and in the upper stratosphere, photolysis. First we will examine and dismiss other potential reactions. Table 1 lists enthalpies of reaction, ΔH_R, for potential reactions between HCN and 14 atmospheric gases. The significantly positive values of ΔH_R shown in Table 1 indicate that each of these reactions would proceed very slowly if at all at atmospheric temperatures. Once again, the impression arises that HCN can be a relatively stable gas in the atmosphere, as was suggested by Crutzen et al. [1979].

It is possible to propose exothermic gas phase atmospheric reactions of HCN. Table 2 lists seven such reactants that branch into 14 sets of reaction products. Close inspection of molecular structures leads one to the conclusion that most of these reactions are unlikely to proceed in the atmosphere. For example, $HCN + ClO \rightarrow NCO + HCl$ would be a four-centered reaction; four-centered reactions involving closed-

electron shell reactants exhibit relatively large activation energies [see, e.g., Kneba and Wolfrum, 1980].

In other cases from Table 2, for example, $HCN + O_3 \rightarrow HOCN + O_2$, while one can imagine reasonable pathways like

$$HCN + O_3 \rightarrow HOCN + O_2$$

primary attacks on a closed electron shell molecule (HCN) are required. For example, the reaction of CO (isoelectronic with HCN) and O_3 is unmeasureably slow ($k < 10^{-23}$ cm³/molecule s). In several of the possible reactions listed in Table 2, extensive rearrangements are also required. Finally, there is no available evidence that any of the possible reactions in Table 2 actually occur except for one of the pathways with OH.

There are two likely atmospheric reactants of significance in the atmospheric chemistry of HCN: $O(^1D)$ and OH. Indeed, the reaction of OH and HCN has been studied in the laboratory [Phillips, 1978, 1979; Fritz et al., 1983; R. Zellner and B. Fritz, unpublished manuscript, 1983]. From these laboratory experiments, it appears that an adduct is formed; the thermochemistry of the possible reaction pathways is shown in Table 2. The central values of $\Delta H_{298}°$ for HCN, OH, CN, and H_2O lead to the conclusion that $HCN + OH \rightarrow CN + H_2O$ is slightly endothermic ($\Delta H_R = +1.5$ kcal/mol). Further, for a hydrogen abstraction reaction like this, BEBO calculations indicate that there should be an activation energy of at least 9 kcal/mol (R. Zellner and B. Fritz, unpublished manuscript, 1983). The experiments of Fritz et al. [1983] imply that this reaction path is not followed at atmospheric temperatures. Further, the exchange reaction path ($OH + HCN \rightarrow HOCN + H$) which has been suggested to be one of the dominant HCN oxidation routes in flames [Haynes, 1977] is endothermic by 2.4 kcal/mol, and it is probably prevented by an additional dissociation barrier between $HCN \cdot OH$ and $HOCN + H$. Formation of $HNCO + H$ is less likely than $HOCN$ due to an additional isomerization of the heavy atom moiety.

TABLE 2. Possible Exothermic Reactions of HCN With Atmospheric Gases

Reactants → Products	ΔH_R, kcal/mol
$HCN + O_3 \rightarrow HO_2 + NCO$	−16
$\rightarrow HNCO + O_2$	−81
$\rightarrow HOCN + O_2$	−75
$HCN + NO \rightarrow N_2 + CHO$	−45
$HCN + NO_2 \rightarrow N_2O + CHO$	−11
$\rightarrow HNCO + NO$	−33
$\rightarrow HOCN + NO$	−27
$HCN + O_2(^1\Delta) \rightarrow OH + NCO$	−14
$HCN + ClO \rightarrow HCl + NCO$	−30
$HCN + H_2O_2 \rightarrow HNCO + H_2O$	−71
$\rightarrow HOCN + H_2O$	−66
$HCN + OH \rightarrow H_2O + CN$	$-1.5 < \Delta H_R < +4.5$
$\rightarrow HNCO + H$	−4
$\rightarrow HCNOH$	−35(+4)

See Table 1 for definitions and sources of thermodynamic data; a heat of formation, ΔH_f, of 9 kcal/mol has been taken for CHO [Benson, 1976]. We have taken $\Delta H_f \geq -14$ and ≥ -8 kcal/mol for HNCO and HOCN, respectively [Sullivan et al., 1983; Benson, 1978]. Although exothermic, most of these reactions are concluded to be highly unlikely as discussed in the text. The only likely reactions affecting atmospheric HCN is with OH in which an adduct is formed and reaction with $O(^1D)$.
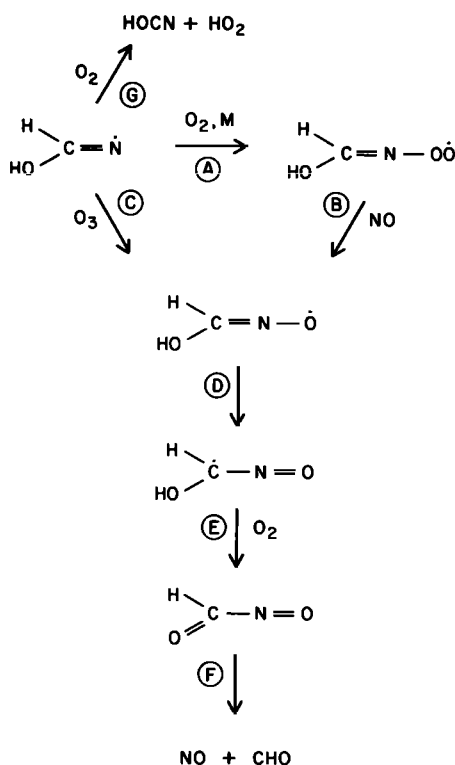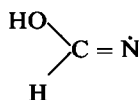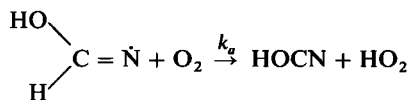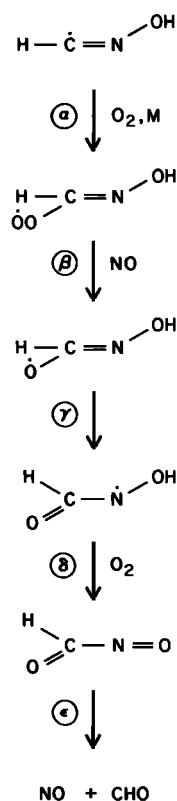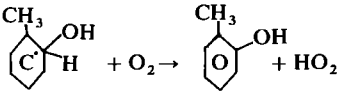
Fig. 1. Atmospheric oxidation pathway of the HCN·OH adduct assuming that the OH is associated with the carbon atom. Processes labeled A–G are discussed in the text, for example, F is the decomposition of nitrosoformaldehyde. This overall oxidation pathway is by analogy with that of hydrocarbons and is essentially that of *Fritz et al.* [1983].

We cannot dismiss this possibility, but we consider it unlikely that this bimolecular abstraction reaction can compete with termolecular O_2 addition, especially in the troposphere. To compete successfully, k_a must exceed the effective second-order rate constant, k_{II}, for the O_2 addition shown at point A in Figure 1. At ambient pressures k_{II} should be near 10^{-12} cm^3/molecule s. Several lines of reasoning indicate that k_a cannot be this fast. First, new experiments in Göttingen have tested the influence of O_2 by adding O_2 and NO to the reaction mixture. The apparent rate constant for OH + HCN should decrease if HOCN and HO_2 are produced (due to the fast regeneration of OH through HO_2 + NO → OH + NO_2). This effect was not observed; the experiments placed an upper limit of 5×10^{-13} cm^3/molecule s on k_a. If the reaction does proceed at this upper limit rate, it could represent an important pathway in the oxidation of the HCNOH adduct, if the adduct's structure is as shown in Figure 1. A few other reactions in which O_2 abstracts an H atom from a free radical have been studied. Table 3 lists six such reactions and their thermochemistry. Unfortunately, reaction rates are not available for all these reactions especially at atmospheric temperatures. The reactions of Table 3 are not fast; some are very slow. The reaction of C_2H_4OH most closely resembles our candidate reaction both in complexity and exothermicity (for HCNOH + O_2 → HOCN + HO_2, $\Delta H_R = -12.5$ kcal/mol). The reaction rate listed in Table 3, 1.3×10^{-13} cm^3/molecule s [*Peeters et al.*, 1982] applies for vibrationally excited C_2H_4OH. Peeters et al. also found that deactivation of $C_2H_4OH^*$ by O_2 was faster than reactions with O_2. Hence in air the dominant pathway would be deactivation by N_2 and O_2, and the vibrationally excited states would be unimportant.

The HCNOH adduct could appear either as shown at the top of Figure 1 or at the top of Figure 2. Experimentally, *Fritz et al.* [1983] and R. Zellner and B. Fritz (unpublished manuscript, 1983) saw no dissociation of the HCNOH adduct on a few millisecond time scale, leading them to deduce that the adduct is at least -15 kcal/mol stable with respect to the reactants that form it. The thermochemistry of addition reactions can be used to estimate the heat of formation of the adduct. For example, for

$$\begin{array}{c} HO \\ \diagdown \\ \diagup \\ H \end{array} C = \dot{N}$$

we estimate ΔH_f to be 7 ± 4 kcal/mol. With this value of ΔH_f the adduct would be $35 (\pm 4)$ kcal/mol stable with respect to the reactants. This structure of the adduct might be preferred because C–O bonds generally tend to be more stable than N–O bonds. Nonetheless, following Fritz et al., we consider the possible oxidation chains of both isomers of HCNOH; these are sketched in Figures 1 and 2. These oxidation pathways, beginning with attack either by O_2 or O_3 in Figure 1 and by O_2 in Figure 2, are suggested by analogy with hydrocarbon oxidation pathways. At point G in Figure 1 we indicate the possibility that a bimolecular reaction with O_2 could abstract an H atom from the HCNOH adduct if the adduct is of the structure shown in Figure 1, that is,

$$\begin{array}{c} HO \\ \diagdown \\ \diagup \\ H \end{array} C = \dot{N} + O_2 \xrightarrow{k_a} HOCN + HO_2$$

Fig. 2. Atmospheric oxidation pathway of the HCN·OH adduct assuming that the OH is associated with the nitrogen atom. Processes labeled $\alpha, \beta, \cdots, \varepsilon$ are discussed in the text. See also Figure 1.

TABLE 3. Thermochemistry and Rate Coefficients for Several Radical Reactions With O_2 That Form HO_2

Reaction	Rate, cm^3/molecule s	ΔH_R, kcal/mol
$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$k_i = 2.1 \times 10^{-13}$	-11.5
$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$	$k_{ii}(1000\ K) = 1.5 \times 10^{-12}$	-12.3
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	$k_{iii}(298\ K) = 6 \times 10^{-16}$	-23
	$k_{iii} = 5 \times 10^{-13} \exp(-2000/T)$	
$CHO + O_2 \rightarrow CO + HO_2$	$k_{iv} \approx 5 \times 10^{-12}$	-32
$C_2H_4OH + O_2 \rightarrow C_2H_3OH + HO_2$	$k_v \approx 1.3 \times 10^{-13}$	-13.5
	(for vibrationally excited C_2H_4OH)	
[structure: CH_3 cyclohexadienyl-OH with CH] $+ O_2 \rightarrow$ [structure: CH_3 phenol-OH with O] $+ HO_2$	$k_{vi}/k_{deactivation\ by\ O_2 \approx 0.6}$	
		-26
	$k_{vi} < 10^{-15}(T = 350-400\ K)$	

For comparison, the reaction $\overset{HO}{\underset{H}{>}}C=\dot{N} + O_2 \rightarrow HOCN + O_2$ would be exothermic by 12.5 kcal/mol.

Vibrationally excited HCNOH would probably be quenched similarly. Also, for C_2H_5 it has been shown that the addition of O_2 proceeds about 20 times faster than the formation of $C_2H_4 + HO_2$, at least at tropospheric pressures [*Plumb and Ryan*, 1981]. Finally, note that our candidate reaction requires that an H atom be abstracted from an α-carbon atom that is double bonded to the N atom with a free-radical position, a situation unlike those for $(CH_3)_2N + O_2 \rightarrow CH_2 = N\text{-}CH_3 + HO_2$ [*Lindley et al.*, 1979] or $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$. We will proceed now to discuss the other, possible dominant paths of HCNOH oxidation; further discussion of the consequences of a rapid bimolecular reaction with O_2 is presented below.

At point B in Figure 1 a rate constant of 10^{-11} cm^3/molecule s and 10 ppt of NO would lead to a lifetime of 1000 s for

$$\overset{HO}{\underset{H}{>}}C = N\text{-}O\dot{O}$$
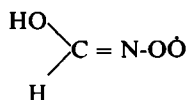
One can also imagine that OH or CO could compete with NO at this point. At point C in Figure 1, the proposed attack by O_3 is by analogy with $NH_2 + O_3 \rightarrow$ products, a reaction that is found to be relatively fast [*Hack et al*, 1982] and whose products are suggested to be $NH_2O + O_2$. Also, at point F in Figure 1 the decay of nitrosoformaldehyde to NO + CHO would occur in about 0.1 s [*Napier and Norrish*, 1967].

If the structure of the HCNOH adduct is as shown at the top of Figure 2, one might imagine that the reaction at point β (reaction with NO by analogy to hydrocarbon oxidation) might be with HO_2 instead, to yield

$$\overset{HOO}{\underset{H}{>}}C = N\text{-}OH + O_2$$
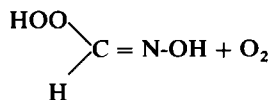
This might occur in clean tropospheric air where HO_2 mixing ratios might be comparable to those of NO [*Thompson and Cicerone*, 1982]. Note that nitrosoformaldehyde would be formed in the scheme of Figure 2 as in Figure 1. Thus, whatever the structure of HCNOH, these oxidation pathways suggest that NO and CHO are formed within minutes. Of course, the CHO reacts quickly with O_2 to yield $CO + HO_2$. Probably the slowest reactions in Figures 1 and 2 are those that require NO.

On the basis of the laboratory experiments of *Fritz et al.*

[1983] of the decay rate of OH and the general behavior of recombination reactions, we have adopted the following expression for the effective altitude-dependent rate constant, $k_1(z)$, for the reaction of HCN and OH [*Zellner*, 1978; *Troe*, 1979]:

$$k_1(z) = \left[\frac{k_0[M]}{1 + k_0[M]/k_\infty}\right] \times 0.8^{\{1 + (\log(k_0[M]/k_\infty))^2\}^{-1}} \quad (1)$$

where $[M]$ is total atmospheric density (cm^{-3}) as a function of altitude, z, and $k_0 = 1.5 \times 10^{-31} \exp(-875/T)$ cm^6/molecule^2 s, and $k_\infty = 1.16 \times 10^{-13} \exp(-400/T)$ cm^3/molecule s, are the experimentally determined rate coefficients in the limit of low and high pressure, respectively.

3. ATMOSPHERIC MODEL CALCULATIONS AND DISCUSSION

By performing calculations with an atmospheric photochemical/transport model, we can learn several things about atmospheric HCN. For example, by assuming steady states for its atmospheric vertical profile and for its ground level sources, we can deduce its atmospheric residence time. Further, we can estimate the total size of its sources by summing the loss rates for HCN at all altitudes. Individual HCN sources (discussed below) should, of course, sum to the total source estimate.

The numerical model we used for these calculations is very similar to that described by *Cicerone* [1979]. For HCN, we adopted a fixed-density lower boundary condition at ($z = 0$ km) equivalent to a volume mixing ratio of 1.7×10^{-10}. At the model upper boundary (80 km) we employed the condition that the upward flux, $\phi(80)$ of HCN equals the steady state loss above that altitude. This flux was calculated from

$$\phi = fMH(J + k_1[OH] + k_2[O(^1D)]) \quad (2)$$

where the term in parentheses is the sum of the first-order loss processes for HCN (in s^{-1}) due to photolysis (J), reaction with OH ($k_1[OH]$) and with $O(^1D)$ ($k_2[O^1D]$). H and f are the vertical scale height and the volume mixing ratio of HCN at 80 km, respectively. The three loss processes for HCN were included in the model at all altitudes, z, from zero to 80 km. Values for the altitude-dependent steady state concentrations of [OH(z)] and [O(^1D)(z)] are shown in Table 4; these are from *Cicerone et al.* [1983] and *Thompson and Cicerone* [1982] and represent 24-hour averages. The vertical profile of eddy diffusion coefficient was taken from these same references. The rate coefficient $k_1(z)$ is calculated from (1); k_2 has

TABLE 4. Input Data for Atmospheric Model Calculations: OH and $O(^1D)$ Densities From Cicerone et al. [1983] and Thompson and Cicerone [1982]

Altitude, km	OH, cm^{-3}	$O(^1D)$, cm^{-3}	J s^{-1}	$k_1(z)$, cm^3/molecule s
80	4.81 (6)	17	1.2 (−6)	6.9 (−19)
78	4.70 (6)	13	9.2 (−7)	1.0 (−18)
76	4.66 (6)	10	6.6 (−7)	1.5 (−18)
74	4.72 (6)	11	4.5 (−7)	2.3 (−18)
72	4.80 (6)	14	2.9 (−7)	3.4 (−18)
70	4.78 (6)	20	1.9 (−7)	5.0 (−18)
68	4.74 (6)	27	1.2 (−7)	7.4 (−18)
66	4.74 (6)	37	8.4 (−8)	1.1 (−17)
64	4.86 (6)	49	6.0 (−8)	1.6 (−17)
62	5.09 (6)	63	4.4 (−8)	2.2 (−17)
60	5.48 (6)	81	3.3 (−8)	3.0 (−17)
58	6.04 (6)	102	2.4 (−8)	4.1 (−17)
56	6.73 (6)	124	1.8 (−8)	5.5 (−17)
54	7.65 (6)	148	1.3 (−8)	7.2 (−17)
52	8.77 (6)	172	9.6 (−9)	9.4 (−17)
50	1.01 (7)	195	7.0 (−9)	1.2 (−16)
48	1.16 (7)	216	5.2 (−9)	1.5 (−16)
46	1.30 (7)	229	3.8 (−9)	1.9 (−16)
44	1.41 (7)	226	2.8 (−9)	2.4 (−16)
42	1.42 (7)	197	2.0 (−9)	2.9 (−16)
40	1.29 (7)	152	1.4 (−9)	3.5 (−16)
38	1.07 (7)	108	9.6 (−10)	4.3 (−16)
36	8.28 (6)	74	6.1 (−10)	5.3 (−16)
34	5.96 (6)	47	3.5 (−10)	6.6 (−16)
32	3.92 (6)	28	1.8 (−10)	8.3 (−16)
30	2.35 (6)	15	8.0 (−11)	1.0 (−15)
28	1.33 (6)	8	3.0 (−11)	1.3 (−15)
26	7.52 (5)	4	9.4 (−12)	1.7 (−15)
24	4.42 (5)	2	2.5 (−12)	2.1 (−15)
22	2.78 (5)	1	5.3 (−13)	2.6 (−15)
20	1.95 (5)	0.6	9.0 (−14)	3.3 (−15)
18	1.55 (5)	0.3	1.1 (−14)	4.0 (−15)
16	1.47 (5)	0.14	0	5.0 (−15)
14	3.08 (5)	0.03	0	6.0 (−15)
12	3.20 (5)	0.008	0	7.3 (−15)
10	2.13 (5)	0.004	0	8.8 (−15)
8	7.30 (5)	0	0	1.1 (−14)
6	8.60 (5)	0	0	1.4 (−14)
4	8.10 (5)	0	0	1.7 (−14)
2	7.30 (5)	0	0	1.9 (−14)
0	3.20 (6)	0	0	2.2 (−14)

The reaction rate $k_1(z)$, for $HCN + OH$ is from equation (1). Photodissociation frequencies, $J(s^{-1})$ were calculated as described in the text. All quantities represent 24-hour averages. Further calculations were performed with OH densities equal to 50% and 200% those listed here.

been assumed to be 10^{-10} cm^3/molecule s, independent of pressure and temperature and hence altitude. By evaluating all terms in (2) at 80 km and iterating numerically, a suitable upper boundary condition obtains. In additional calculations, OH densities were varied from those shown in Table 4. Because we are not aware of any data on the photoabsorption cross section of HCN as a function of wavelength (except for $\lambda < 155$ nm [Lee, 1980]), we have had to estimate this quantity. Specifically, we have assumed that HCN photoabsorption and photolysis should be similar to that for HCl. A better analogy might be with C_2H_2 (isoelectronic with HCN), but we could find no suitable C_2H_2 data for wavelengths longer than 200 nm. The J values shown in Table 4 for HCN are those for HCl; they are taken from Cicerone et al. [1983].

Figure 3 shows our calculated vertical profile of HCN along with all available HCN measurements. In the troposphere the Rinsland et al. [1982] data were reported as the average

mixing ratio between 2.1 and 12 km, assuming a nearly constant mixing ratio with altitude. Our calculation shows that this is a good assumption, that is, the mixing ratio of HCN should decrease only about 5% between 0 and 12 km. With OH densities twice those of Table 4 we calculate that the HCN mixing ratio decreases by 8% between 0 and 12 km. In Figure 3 the Coffey et al. [1981] data are shown as a uniform mixing ratio $(1.55 \pm 0.19) \times 10^{-10}$ between 12 and 40 km. Actually, Coffey et al. reported a total column amount at all altitudes above 12 km; we have indicated that their deduced mixing ratio applies to altitudes below 40 km because only about 1% of the measured absorption could arise from over 40 km even if HCN were distributed uniformly. In other words, their data contain virtually no information on the HCN above 40 km, so comparison with our calculated profile is meaningless for altitudes above, say, 40 km. Our model does predict a slow but significant decrease of HCN above 20 km. The Carli et al. [1982] data were reported as HCN mixing ratios of 1.3 to 2.6×10^{-10} at all altitudes between 20 and 40 km. With OH densities 50% those of Table 4, HCN decreases more slowly with altitude; at 40 km it is 1.13 times that shown in Figure 3.

Attack by OH (with subsequent rapid oxidation to $CO + NO$, as shown in Figures 1 and 2) is the dominant HCN loss process throughout the troposphere. With the OH and $O(^1D)$ densities of Table 4, the rate of attack by $O(^1D)$ dominates in the stratosphere above 34 km, and photolysis matches the $O(^1D)$ rate at 54 km. Only about 2% of the HCN (from presumed ground level sources) reaches the stratosphere; the remaining 98% is oxidized in the troposphere by OH addition followed by the reactions shown in Figures 1 and 2. This tropospheric oxidation of HCN represents a source of NO_x for the troposphere; it amounts to 4.5 $\times 10^7/cm^2$ s when column-integrated. If HCN is distributed uniformly over the globe (see below) this is 1.7×10^{11} g N/yr or 3.6×10^{11} g NO/yr. This NO_x source is only about one quarter as large as the production rate of NO_x (due to $N_2O + O(^1D) \rightarrow 2$ NO) in the stratosphere [Liu et al., 1980], most of which flows downward into the troposphere. About half of this NO would be produced between 0 and 2 km altitude. When OH densities twice those of Table 4 are used in the calculations, the column-integrated loss of HCN (production
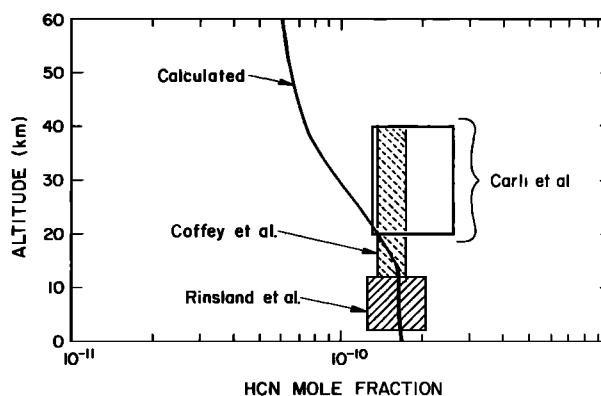

Fig. 3. Vertical profile of HCN calculated with the atmospheric model described in the text and the data of Table 4. Also shown are the tropospheric observations of Rinsland et al. [1982] and the stratospheric observations of Coffey et al. [1981] and Carli et al. [1982]. Lower tropospheric concentrations are likely in the southern hemisphere's troposphere (see text) and no appreciable diurnal variations are expected below about 40 km.

of NO) essentially doubles. OH densities half those of Table 4 lead to about half as much HCN loss (NO production). The residence time, τ_R, for HCN can be obtained from

$$\tau_R^{-1} = \int_0^\infty L(z)[\text{HCN}(z)] \, dz \bigg/ \int_0^\infty [\text{HCN}(z)] \, dz$$

where $L(z)$ is the total loss rate for HCN due to attack by OH, by $O(^1D)$ and photolysis at each altitude, z, and [HCN] is the density (cm^{-3}) of HCN. For OH densities equal to those of Table 4, twice those of Table 4, and half those of Table 4 we find $\tau_R = 2.5$, 1.3, and 5.0 years, respectively.

From this estimate of atmospheric residence time, we may proceed to predict southern hemispheric (SH) tropospheric mixing ratios of HCN which are as yet unmeasured. By assuming that the sources of HCN are primarily in the NH (see below) and applying the analysis that *Khalil and Rasmussen* [1983] used for CH_4 (whose principal sink is also OH) we estimate that the ratio of northern hemispheric HCN mixing ratio to that in the SH is 1.21 if $\tau_R = 2.5$ years. Accordingly, if there is a NH mixing ratio of 1.66×10^{-10} (in the planetary boundary layer), then there would be 1.37×10^{-10} in the SH. For $\tau_R = 1.3$ and 5.0 years, the N/S ratio would be 1.36 and 1.11, respectively. All of these values are approximate, of course.

Based on our calculations and the measurements summarized in Figure 3, HCN might be as abundant as any other odd-nitrogen compound in the middle and upper troposphere; see *Kley et al.* [1981] for NO_x data and *Singh and Salas* [1983] for peroxyacetyl nitrate data. Owing to its relatively low water solubility and weak acidity and to its relative photochemical inertness, there should be no significant diurnal variation in HCN concentrations, and there are no obvious and major roles for HCN in tropospheric chemistry. Further, due to overlaps with other major infrared absorbers there is no significant role for HCN in climate (V. Ramanathan and J. Kiehl, private communication, 1982).

In the stratosphere there are two potentially interesting paths for HCN oxidation that produce CN radicals:

$$\text{HCN} + h\nu \rightarrow \text{H} + \text{CN}$$

$$O(^1D) + \text{HCN} \rightarrow \text{OH} + \text{CN}$$
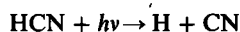
It is also possible that the exothermic reaction $O(^3P) + \text{HCN} + M \rightarrow \text{HOCN} + M$, or the bimolecular abstraction of H from the HCNOH adduct by O_2 (discussed above) followed by $\text{HOCN} + h\nu \rightarrow \text{HO} + \text{CN}$ could be important in the stratosphere. The fate of the CN radical needs explored; it is conceivable that insights into the origin of stratospheric CH_3CN could be gained. First, it must be noted that

$$\text{CN} + O_2 \rightarrow \text{NCO} + O \tag{3}$$
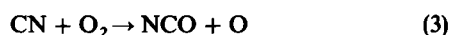
is a very fast reaction. At room temperature, its reaction rate, k_3, is $10^{-11} \text{ cm}^3/\text{molecule s}$ [see, e.g., *Boden and Thrush*, 1968; *Bullock and Cooper*, 1972a; *Albers et al.*, 1975]. No required activation energy (or perhaps a slight negative activation energy) was observed by *Bullock and Cooper* [1972a]. Clearly, it would be difficult for any hydrogen donor, R-H, to compete with O_2 for any available CN radicals. Formation of HCN through

$$\text{CN} + CH_4 \rightarrow \text{HCN} + CH_3 \tag{4}$$

$$\text{CN} + C_2H_6 \rightarrow \text{HCN} + C_2H_5 \tag{5}$$

$$\text{CN} + C_3H_8 \rightarrow \text{HCN} + C_3H_8 \tag{6}$$
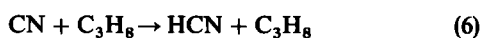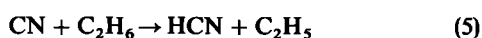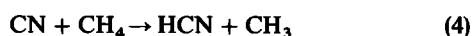
can occur, but reaction rates for each of these reactions is lower than k_3 [*Bullock and Cooper*, 1972b], so nearly all $\text{CN} \rightarrow \text{NCO}$. Due to its strong absorption bands between 360 and 450 nm [*Holland et al.*, 1958], NCO must decompose rapidly (minutes) in daylight to N + CO [*Herzberg*, 1966]. An apparent consequence of these facts is that decomposition of atmospheric C_2N_2 (if any) would not yield HCN.

The high rate of the reaction between CN and O_2 can also serve to partially decouple the atmospheric chemistry of CH_3CN and HCN. CN radicals are formed in one of the two photolysis pathways for CH_3CN at 184.9 nm [*McElcheran et al.*, 1958]. Can this represent a stratospheric source of HCN? Because $k_3[O_2]/k_4[CH_4]$ is between 10^5 and 10^6 throughout the atmosphere, only 10^{-5} or 10^{-6} of the CN radicals from CH_3CN (or any other source) can become HCN. Further, if there is only about 10^{-12} by volume of CH_3CN in the middle stratosphere [*Henschen and Arnold*, 1981], the magnitude of this source of CN radicals is very small. Recent reports of much higher concentrations of CH_3CN near ground level [*Becker and Ionescu*, 1982] require further consideration.

What is the origin of atmospheric HCN? According to our calculations, an annual source of $(1-3) \times 10^{11}$ g(N) as HCN is required to maintain the measured atmospheric HCN burden. This annual source of HCN to the atmosphere is less than 1% of the estimated global annual amount of N in NO_x [*Logan*, 1983] from all sources. Significant indirect sources such as the atmospheric decomposition of R-CN species (e.g., CH_3CN) are very unlikely as discussed above. Also, in situ injections by jet aircraft are apparently insignificant [*Robertson et al.*, 1979] because with adequate O_2, turbine engines produce very little HCN. Some catalytic converters that reduce automotive emissions of NO_x, when in ill repair, are known to produce high concentrations (500 ppm) of HCN.

The possibility that HCN is produced by lightning has been considered by *Chameides and Walker* [1981] and J. T. Kasting (private communication, 1981). With present epoch oxygen levels, this HCN source appears negligible, although it should be noted that emissions from CN radicals are observed occasionally from lightning-disturbed air [*Wallace*, 1960; *Salanave et al.*, 1962]. Similarly, thermodynamic equilibrium calculations indicate that volcanoes can emit HCN, especially in high-temperature, low-oxygen zones (R. Prinn, private communication, 1982), but this source is difficult to quantify, and it is probably relatively small.

Direct evident does exist for the release of HCN from several biological sources and from several industrial practices such as the production of coke. The production and release of HCN from higher plants and from bacteria and fungi is well documented [*Conn*, 1980; *Bach*, 1948; *Robbins et al.*, 1950; *Marshall and Hutchinson*, 1970], although no estimates of global release rates into the atmosphere are available. These biogenic HCN sources clearly need further investigation. Returning to nonbiogenic sources, large amounts of HCN appear in coke oven gas when coke is produced [*Grosick and Kovacic*, 1981] and in other coal carbonization processes. Generally, high-temperature, low-oxygen processes are likely to produce HCN; an example might be the process of steel degassing when Argon is used in place of oxygen as a purge gas [*Cottrell*, 1967]. Many other hydrocarbon-rich flames are throught to produce HCN, but little if any HCN escapes oxidation to NO in general [*Glassman*, 1977]. Smoldering biomass might produce HCN and CH_3CN; this should be explored. Thus, in principle, several likely sources exist for atmospheric HCN. Biological sources would be of great interest to

quantify to determine if atmospheric HCN is mostly natural or anthropogenic.

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