The Atmospheric Chemistry of Hydrogen Cyanide (HCN)

R. J. CICERONE

National Center for Atmospheric Research

R. ZELLNER

Universität Göttingen, Institut für Physikalische Chemie

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 x 10^14 cm^-2. Assuming that HCN is distributed uniformly with altitude above 12 km, they deduced a stratospheric mixing ratio of 1.55 x 10^-7 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) x 10^-7. 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 x 10^15 cm^-2, yielding an average tropospheric mixing ratio of 1.66 x 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^- and CN^- in precipitation and whether atmospheric HCN can interfere with attempts to measure NO and 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 λ < 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

\[ \text{HCN} + h\nu \rightarrow \text{H}(2S) + \text{CN}(^2\Sigma) \]

the 2\Sigma state of CN is 1.15 eV above the X\Sigma ground state. In Davis and Okabe's [1968] work, they actually excited HCN with much shorter wavelengths and observed fluorescence of CN(B^2Σ), an excited state of CN that is 3.20 eV above ground. There are no available data on photodissociation of HCN for 175 nm < λ < 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 $\Delta H_r$ for Possible Reactions of HCN With 14 Atmospheric Gases

| Reactants $\rightarrow$ Products | $\Delta H_r$, kcal/mol |
|----------------------------------|------------------------|
| HCN + O$_2$ $\rightarrow$ HOCN + O | +14 |
| $\rightarrow$ HNCO + O | +20 |
| HCN + OH $\rightarrow$ HOCN + H | > +2 |
| $\rightarrow$ HNCO + OH | +43 |
| HCN + HNO$_2$ $\rightarrow$ HOCN + CH | +66 |
| $\rightarrow$ HNCO + HNO$_2$ | +35 |
| HCN + H$_2$O$_2$ $\rightarrow$ HNCO + H$_2$O | +102 |
| $\rightarrow$ HOCN + water | +43 |
| HCN + HCl $\rightarrow$ HOCN + HCl | +94 |
| $\rightarrow$ HNCO + HCl | +104 |
| HCN + SO$_2$ $\rightarrow$ NCO + HSO | +101 |
| HCN + O $\rightarrow$ OH + CN | +19 |
| HCN + Cl $\rightarrow$ HCl + CN | +18 |
| HCN + H$_2$O $\rightarrow$ CN + H$_2$O | +17 |
| HCN + CO $\rightarrow$ CHO + CN | +23 |
| HCN + H + H$_2$ + CN | +105 |

Heats of formation for these calculations are taken from Okabe [1978] and apply for 0 K except for H$_2$O$_2$ for which we took Howard's [1980] value of 2.5 $\pm$ 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 Landoldt-Börnstein [1962]. On the basis of this solubility and the fact that HCN is a very weak acid

$$\text{HCN}_a \approx \text{H}^+ + \text{CN}^- \quad (K = 1.3 \times 10^{-9})$$

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 $pH$; 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($^1\Delta$) and in the upper stratosphere, photolysis. First we will examine and dismiss other potential reactions. Table 1 lists enthalpies of reaction, $\Delta H_r$, for potential reactions between HCN and 14 atmospheric gases. The significantly positive values of $\Delta H_r$ 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 reactions 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 Wolfum, 1980].

In other cases from Table 2, for example, HCN + O$_3$ $\rightarrow$ HOCN + O$_2$, while one can imagine reasonable pathways like

$$\text{HCN} + \text{O}_3 \rightarrow \text{HOCN} + \text{O}_2$$

primary attacks on a closed electron shell molecule (HCN) are required. For example, the reaction of CO (isosoelectronic with HCN) and O$_3$ is unmeasurably slow ($k < 10^{-23}$ cm$^3$/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 reactions of significance in the atmospheric chemistry of HCN: O($^1\Delta$) 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 $\Delta H_{298}^o$ for HCN, OH, CN, and H$_2$O lead to the conclusion that HCN + OH $\rightarrow$ CN + H$_2$O 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·OH and HOCN + H. Formation of HNCO + H is less likely than HOCN due to an additional isomerization of the heavy atom moiety.

See Table 1 for definitions and sources of thermodynamic data; a heat of formation, $\Delta H_f$, of 9 kcal/mol has been taken for CHO [Benson, 1976]. We have taken $\Delta H_f \geq -14$ and $\geq -8$ 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($^1\Delta$).
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, $k_0$, for the O$_2$ addition shown at point A in Figure 1. At ambient pressures $k_0$ 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 $\rightarrow$ NO + HO$_2$). This effect was not observed; the experiments placed an upper limit of $5 \times 10^{-13}$ 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$_2$H$_4$OH most closely resembles our candidate reaction both in complexity and exothermicity (for HCNOH + O$_2$ $\rightarrow$ HOCN + HO$_2$, $\Delta H_f = -12.5$ kcal/mol). The reaction rate listed in Table 3, $1.3 \times 10^{-13}$ cm$^3$/molecule s [Peeters et al., 1982] applies for vibrationally excited C$_2$H$_4$OH. Peeters et al. also found that deactivation of C$_2$H$_4$OH$^*$ 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.

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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

$$\text{HO}_2 + \text{C} = \text{N} \rightarrow \text{HOCN} + \text{HO}_2$$

we estimate $\Delta H_f$ to be $7 \pm 4$ kcal/mol. With this value of $\Delta H_f$ the adduct would be $35$ 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,

$$\text{HO}_2 + \text{C} = \text{N} + \text{O}_2 \rightarrow \text{HOCN} + \text{HO}_2$$

![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].](image1)

![Fig. 2. Atmospheric oxidation pathway of the HCN-OH adduct assuming that the OH is associated with the nitrogen atom. Processes labeled α, β, ..., ε are discussed in the text. See also Figure 1.](image2)
Vibrationally excited HCNOH would probably be quenched similarly. Also, for C\textsubscript{2}H\textsubscript{4} it has been shown that the addition of O\textsubscript{2} proceeds about 20 times faster than the formation of C\textsubscript{2}H\textsubscript{4} + HO\textsubscript{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 s-carbon atom that is double bonded to the N atom with a free-radical position, a situation unlike those for (CH\textsubscript{3})\textsubscript{2}N + O\textsubscript{2} \rightarrow CH\textsubscript{2} - N-CH\textsubscript{3} or (CH\textsubscript{3})\textsubscript{2}N + HO\textsubscript{2} [Lindley et al., 1979] or C\textsubscript{2}H\textsubscript{5} + O\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{4} + HO\textsubscript{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\textsubscript{2} is presented below.

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

\[
\text{HOO} + \text{N} = \text{N-O} + \text{O}_2
\]

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\textsubscript{2} is by analogy with NH\textsubscript{2} + O\textsubscript{2} \rightarrow products, a reaction that is found to be relatively fast [Hack et al., 1982] and whose products are suggested to be NH\textsubscript{2}O + O\textsubscript{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 \( \beta \) (reaction with NO by analogy to hydrocarbon oxidation) might be with HO\textsubscript{2} instead, to yield

\[
\text{HOO} + \text{H} \rightarrow \text{N-OH + O}_2
\]

This might occur in clean tropospheric air where HO\textsubscript{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\textsubscript{2} to yield CO + HO\textsubscript{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]:

\[
k_1(z) = \left[ \frac{k_0[M]}{1 + k_0[M]/k_n} \right] \times 0.8^{(1 + \log(k_0[M]/k_n))^2} \times 10^{-11} (T = 350 - 400 K)
\]

For comparison, the reaction \( \text{HO}_2 + \text{OH} \rightarrow \text{HOCN} + \text{O}_2 \) would be exothermic by 12.5 kcal/mol.

### Table 3: Thermochemistry and Rate Coefficients for Several Radical Reactions With O\textsubscript{2} That Form HO\textsubscript{2}

| Reaction | Rate, cm\textsuperscript{3}/molecule s | \( \Delta H_{\text{R}} \), kcal/mol |
|----------|----------------------------------------|----------------------------------|
| C\textsubscript{2}H\textsubscript{2}O + O\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{2} + HO\textsubscript{2} | \( k_1 = 2.1 \times 10^{-13} \) | -11.5 |
| C\textsubscript{2}H\textsubscript{2}O + O\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{2} + HO\textsubscript{2} | \( k_0(1000 \text{ K}) = 1.5 \times 10^{-12} \) | -12.3 |
| CH\textsubscript{2}O + O\textsubscript{2} \rightarrow CH\textsubscript{2} + HO\textsubscript{2} | \( k_0(298 \text{ K}) = 6 \times 10^{-16} \) | -23 |
| CHO + O\textsubscript{2} \rightarrow CO + HO\textsubscript{2} | \( k_0 \approx 5 \times 10^{-13} \text{ exp} (-2000/T) \) | -32 |
| C\textsubscript{2}H\textsubscript{4}OH + O\textsubscript{2} \rightarrow C\textsubscript{2}H\textsubscript{4}OH + HO\textsubscript{2} | \( k_0 \approx 1.3 \times 10^{-13} \) | -13.5 |
| \text{CHO} + O\textsubscript{2} \rightarrow \text{CO} + HO\textsubscript{2} | \( k_0 \approx 5 \times 10^{-13} \text{ exp} (-2000/T) \) | -26 |

We have included in the model at all altitudes, z, from zero to 80 km. The three loss processes for HCN were

\[
k_1(z) \approx \frac{k_0[M]}{1 + k_0[M]/k_n}
\]

where \( [M] \) is total atmospheric density (cm\textsuperscript{-3}) as a function of altitude, z, and \( k_0 = 1.5 \times 10^{-31} \text{ cm}^6/\text{molecule}^2 \text{ s} \) and \( k_n = 1.16 \times 10^{-13} \text{ exp} (-875/T) \text{ cm}^3/\text{molecule} \text{ s} \) 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 \( z = 0 \text{ km} \) equivalent to a volume mixing ratio of 1.7 \times 10^{-16}. At the model upper boundary (80 km) we employed the condition that the upward flux, \( \phi_{80}(z) \) of HCN equals the steady state loss above that altitude. This flux was calculated from

\[
\phi = fM(H_1 + k_1[\text{OH}] + k_2[O(1D)])
\]

where the term in parentheses is the sum of the first-order loss processes for HCN (in s\textsuperscript{-1}) due to photolysis, \( J \), reaction with OH (\( k_1[\text{OH}] \)) and with O\textsuperscript{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\textsuperscript{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
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$_2$H$_2$ (isoelectronic with HCN), but we could find no suitable C$_2$H$_2$ 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 $2.6 \times 10^{-10}$ 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 $4.5 \times 10^{17}$/cm$^2$ s when column-integrated. If HCN is distributed uniformly over the globe (see below) this is $1.7 \times 10^{11}$ g NO/yr or $3.6 \times 10^{11}$ g NO/yr. This NO$_x$ source is only about one quarter as large as the production rate of NO$_x$ (due to N$_2$O + O(1D) + 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

cardinal direction, you may have missed the table.
of NO) essentially doubles. OH densities half those of Table 4 lead to about half as much HCN loss (NO production). The residence time, \( \tau_{\text{HCN}} \), for HCN can be obtained from

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

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 \([\text{HCN}]\) is the density \( \text{(cm}^{-3}\text{)} \) 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_{\text{HCN}} = 2.5, 1.3, \text{and} 5.0 \text{ 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 by 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 when \( \tau_{\text{HCN}} = 2.5 \text{ years}. \) Accordingly, if there is a NH mixing ratio of 1.65 \( \times 10^{-10} \) \( \text{cm}^-3 \) (in the planetary boundary layer), then there would be 1.37 \( \times 10^{-10} \) in the SH. For \( \tau_{\text{HCN}} = 1.3 \text{ 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\(_2\) 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:

\[
\text{HCN} + hv \rightarrow \text{H} + \text{CN} \\
O(1D) + \text{HCN} \rightarrow \text{OH} + \text{CN}
\]

It is also possible that the exothermic reaction \( O(1D) + \text{HCN} + M \rightarrow \text{HOCN} + M \) or the bimolecular abstraction of H from the HCONOH adduct by O\(_2\) (discussed above) followed by HOCN + \( hv \rightarrow \text{H} + \text{OCN} + \text{CN} \) 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\(_3\)CN could be gained. First, it must be noted that

\[
\text{CN} + \text{O}_2 \rightarrow \text{NCO} + \text{O}
\]

is a very fast reaction. At room temperature, its reaction rate, \( k_3 \), is \( \sim 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) [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

\[
\text{CN} + \text{CH}_4 \rightarrow \text{HCN} + \text{CH}_3
\]

\[
\text{CN} + \text{C}_2\text{H}_4 \rightarrow \text{HCN} + \text{C}_2\text{H}_3
\]

\[
\text{CN} + \text{C}_2\text{H}_6 \rightarrow \text{HCN} + \text{C}_3\text{H}_4
\]

can occur, but reaction rates for each of these reactions is lower than \( k_3 \) [Bullock and Cooper, 1972k], so nearly all 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 [Hersberg, 1966]. An apparent consequence of these facts is that decomposition of atmospheric C\(_2\)N\(_2\) (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\(_3\)CN and HCN. CN radicals are formed in one of the two photochemistry pathways for CH\(_3\)CN at 184.9 nm [McClellan et al., 1958]. Can this represent a stratospheric source of HCN? Because \( k_3 \text{[O}_2\text{]/k}_4 \text{[CH}_3\text{CN]} \) is between 10\(^5\) and 10\(^6\) throughout the atmosphere, only 10\(^{-5}\) or 10\(^{-6}\) of the CN radicals from CH\(_3\)CN (or any other source) can become HCN. Further, if there is only about 10\(^{-12}\) by volume of CH\(_3\)CN 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\(_3\)CN 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 \( (1-3) \times 10^{-11} \text{g} \text{N} \) 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\(_3\)CN) are very unlikely as discussed above. Also, in situ injections by jet aircraft are apparently insignificant [Robertson et al., 1979] as discussed above. Sources of CN radicals are observed occasionally from lightning-disturbed air [Wallace, 1960; Salana 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 Hutchison, 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 CN radicals. 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; Salana 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.

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

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R. J. Cicerone, National Center for Atmospheric Research, P. O. Box 3000, Boulder, CO 80307.

R. Zellner, Universität Göttingen, Institut für Physikalische Chemie, Göttingen, Federal Republic of Germany.

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