Products of the Chlorine-Atom- and Hydroxyl-Radical-Initiated Oxidation of CH_3CN

G. S. Tyndall*,[†] and J. J. Orlando
Atmospheric Chemistry Division, National Center for Atmospheric Research, P.O. Box 3000,
Boulder, Colorado 80307

T. J. Wallington*,[‡] and M. D. Hurley
Ford Research Laboratory, SRL-3083, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121-2053

Received: November 29, 2000; In Final Form: March 28, 2001

FTIR smog chamber techniques were used in the first investigation of the products following oxidation of $CH_3C{\equiv}N$ initiated by Cl atom or OH radicals in air at 296 ± 2 K. It is shown that reaction of Cl atoms with $CH_3C{\equiv}N$ gives $^{\bullet}CH_2C{\equiv}N$ radicals in essentially 100% yield. These radicals add O_2 to form the peroxy radical $N{\equiv}CCH_2O_2^{\bullet}$. Self-reaction of the peroxy radicals gives the alkoxy radical $N{\equiv}CCH_2O^{\bullet}$ which reacts exclusively with O_2 to give $HC(O)C{\equiv}N$ (formyl cyanide). The reaction of Cl atoms with $HC(O)C{\equiv}N$ proceeds with a rate constant of $(7.0 \pm 1.0) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} via H-abstraction to give $^{\bullet}C(O)C{\equiv}N$ radicals which add O_2 to give $N{\equiv}CC(O)OO^{\bullet}$ radicals. The subsequent chemistry of these radicals leads to the production of $HC{\equiv}N$ and CO_2 or the acyl peroxy nitrate $N{\equiv}CC(O)OONO_2$, the IR spectrum of which is reported here. The reaction of OH radicals with $CH_3C{\equiv}N$ in 700 Torr of air gives $HC(O)C{\equiv}N$ in (40 ± 20)% yield implying that up to half of the OH + $CH_3C{\equiv}N$ reaction could proceed via H-atom abstraction, with the remaining fraction proceeding via addition to the $-C{\equiv}N$ group. These results are discussed in terms of the atmospheric oxidation mechanism of $CH_3C{\equiv}N$.

1. Introduction

Acetonitrile, CH_3CN, is an important trace gas in the atmosphere. It is emitted from a variety of sources including biomass burning and industrial applications.[1] The major tropospheric sinks for acetonitrile are believed to be reaction with hydroxyl radicals[2] (reaction 1)

$$OH + CH_3CN \rightarrow \text{products} \tag{1}$$

and uptake into the ocean.[3]

However, these are slow processes and a large amount of acetonitrile survives transport through the troposphere and enters the stratosphere. The stratospheric lifetime of CH_3CN due to reaction with OH, as calculated by Arijs and Brasseur,[4] ranges from 30 years at the tropopause to 1 month at 45 km altitude. The CH_3CN stratospheric lifetime is controlled by OH chemistry, but reactions with $O(^3P)$ and $O(^1D)$ each contribute up to 10% below 40 km, and $O(^3P)$ can dominate above 50 km. Calculations using present-day rate coefficients and radical concentrations do not differ dramatically from the earlier work. Recent satellite measurements of CH_3CN suggest that previously unaccounted-for sources and sinks may exist in the stratosphere, and also highlight some uncertainties in the background tropospheric mixing ratio.[5] In the stratosphere CH_3CN plays an important role in ion−molecule chemistry. CH_3CN has a high proton affinity and is able to displace water from positively charged ionic clusters to form so-called nonproton hydrates.[6]

$$CH_3CN + H(H_2O)_n^{\ +} \rightarrow H(H_2O)_{n-1}(CH_3CN)^+ + H_2O \tag{2}$$

A quantitative understanding of the distribution of CH_3CN is vital to the interpretation of ion measurements in the stratosphere. There have been suggestions that the chemistry of acetonitrile and HCN may be coupled in the stratosphere,[7] but no definitive link has been found to date.

To our knowledge, no studies of the oxidation of CH_3CN have been conducted in the laboratory. To shed light on the atmospheric chemistry of acetonitrile, we have conducted laboratory studies of the Cl-atom and OH-radical-initiated oxidation of CH_3CN using FTIR−smog chamber techniques. Formyl cyanide, HC(O)CN, was identified as essentially the sole primary product (yield indistinguishable from 100%) of the Cl-initiated oxidation of CH_3CN and as a 40−50% product from OH attack. The rate coefficient for the reaction of Cl atoms with HC(O)CN was measured, and the chemistry after this reaction quantified.

2. Experimental Section

Experiments were performed in the environmental chamber at the Ford Motor Company.[8] The reaction chamber consists of a 140 L Pyrex cell surrounded by 22 blacklamps used to irradiate the gas mixtures. The chamber was equipped with internally mounted gold-coated mirrors in a White-type configuration for FTIR detection. Spectra of reactants and products were taken using a Mattson Sirus FTIR spectrometer with a path length in the chamber of 27 m. Reactions of Cl atoms were initiated by the UV irradiation of mixtures containing 107−300 mTorr Cl_2, 299−619 mTorr CH_3CN, 1.8−3.1 mTorr methyl formate, and 7−700 Torr O_2 in 700 Torr total pressure made up with N_2 diluent at 296 K. Methyl formate was added to reaction mixtures to calibrate the Cl atom production rate. The major product of CH_3CN oxidation, formyl cyanide HC(O)CN, was identified using the ν_5 absorption band centered at 914 cm^{-1} and was quantified using an absorption cross section $\sigma = 3.7 \times 10^{-19}$ cm^2 molecule^{-1} at 931 cm^{-1}.[9] Other products,

---

* Corresponding authors.
[†] Fax: 303-497-1411. E-mail: tyndall@acd.ucar.edu.
[‡] E-mail: twalling@ford.com.

10.1021/jp004318p CCC: $20.00

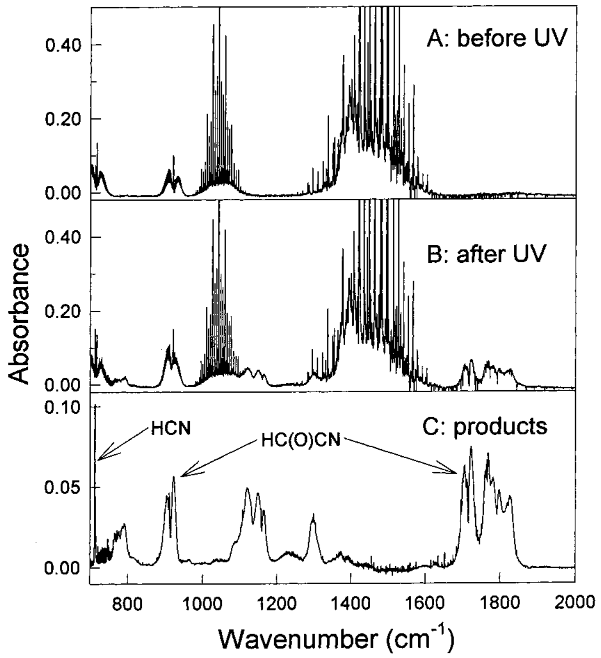

Figure 1. IR spectra acquired before (A) and after (B) a 30 s irradiation of a mixture of 300 mTorr Cl_2, 299 mTorr CH_3CN, in 700 Torr total pressure of air diluent at 296 K. Panel C is the product spectrum obtained by subtracting features attributable to CH_3CN from panel B. The IR features at 914 and 1716 cm^{-1} in panel C match those of HC(O)CN reported by Lewis-Bevan et al.[9]

HCN, CO_2, and CO, were determined using their absorption bands in the 700−3000 cm^{-1} region. A number of experiments were also carried out using hydroxyl radicals to initiate the reaction. Hydroxyl radicals were produced from the photolysis of CH_3ONO (~60 mTorr) in the presence of NO and O_2. The initial concentration of CH_3CN was 1.2 Torr, and 3.0 mTorr ethylene was added to calibrate the OH production.

3. Results

3.1. Product Study of Cl-Atom-Initiated Oxidation of CH_3CN. Figure 1 shows typical spectra acquired before (A) and after (B) a 30 s UV irradiation of a mixture containing 300 mTorr Cl_2 and 299 mTorr CH_3CN in 700 Torr of air diluent. Panel C shows the product spectrum obtained by subtracting IR features attributable to CH_3CN from panel B. The product features in panel 1C centered at 913 and 1716 cm^{-1} match both the shape and relative intensity of those reported previously for HC(O)CN.[9,10] The sharp feature at 712 cm^{-1} is attributable to HCN. As discussed later, the broad features at 790, 1121, 1298, 1764, and 1827 cm^{-1} are assigned to the peroxynitrate NCC(O)OONO$_2$. We have shown previously that the reaction of Cl atoms with acetonitrile proceeds predominantly, if not exclusively, by abstraction of an H atom.[11] Addition of O_2 to the resulting CH_2CN radical gives a peroxy radical which will undergo self-reaction to give the corresponding alkoxy radical, $NCCH_2O$, or molecular products.

$$Cl + CH_3CN \rightarrow HCl + CH_2CN \tag{3}$$

$$CH_2CN + O_2 + M \rightarrow NCCH_2O_2 + M \tag{4}$$

$$NCCH_2O_2 + NCCH_2O_2 \rightarrow NCCH_2O + NCCH_2O + O_2 \tag{5a}$$

$$NCCH_2O_2 + NCCH_2O_2 \rightarrow NCCH_2OH + HC(O)CN + O_2 \tag{5b}$$

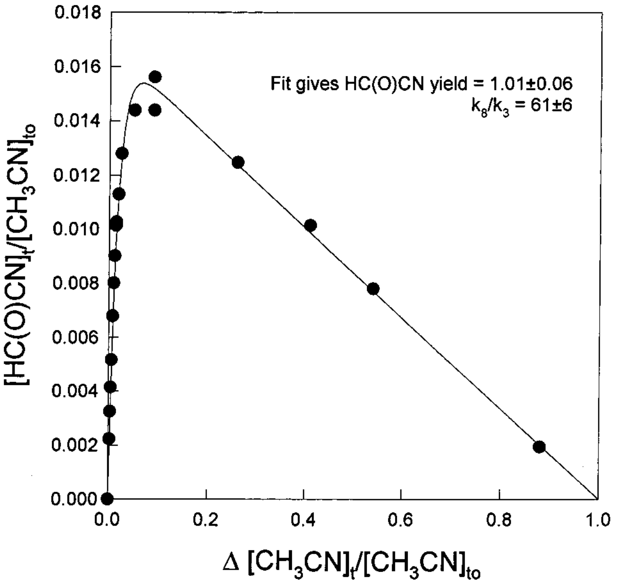

Figure 2. Formation of HC(O)CN, normalized to the initial concentration of CH_3CN, plotted against the fractional loss of CH_3CN for experiments employing UV irradiation of $Cl_2/CH_3CN/O_2/N_2$ mixtures.

It is expected that the alcohol formed in reaction 5b will react with Cl atoms, which will rapidly lead to HC(O)CN formation. By analogy to the very strong C−C bond in CH_3CN,[12] the strength of the C−C bond in the $NCCH_2O$ alkoxy radical can be estimated to be greater than 40 kcal mol^{-1}, and so reaction with O_2 (6) rather than decomposition to CH_2O + CN radicals (7) is expected to dominate its atmospheric fate.

$$NCCH_2O + O_2 \rightarrow HC(O)CN + HO_2 \tag{6}$$

$$NCCH_2O \rightarrow CH_2O + CN \tag{7}$$

When post-reaction mixtures were allowed to stand in the dark, no loss of HC(O)CN was observed, suggesting that its heterogeneous hydrolysis was unimportant on the time scale of an experiment.

Upon successive UV irradiations of the same reaction mixture it was observed that the concentration of HC(O)CN increased, passed through a maximum which was <2% of the initial CH_3CN, and then decreased; such behavior is indicative of loss via reaction with Cl atoms.

$$Cl + HC(O)CN \rightarrow HCl + COCN \tag{8}$$

To obtain the yield of HC(O)CN and the rate coefficient k_8, the concentration of HC(O)CN was plotted against the fractional loss of CH_3CN following irradiation of CH_3CN-Cl_2-air mixtures. Methyl formate ($HC(O)OCH_3$) was included in the reaction mixture to estimate the loss of CH_3CN at low conversion. Methyl formate reacts with Cl atoms with a rate coefficient 120 times larger than that of CH_3CN;[11,13] thus its loss could be measured accurately and that of CH_3CN calculated from the relative rate coefficients. Figure 2 shows the observed HC(O)CN concentration, normalized to the initial concentration of CH_3CN, plotted against the fractional loss of CH_3CN. The line through the data is a fit to the function described by Meagher et al.,[14] which gives a rate coefficient ratio $k_8/k_3 = 61 \pm 6$, and a yield of HC(O)CN of 1.01 ± 0.06, where the errors are 2 σ uncertainties from the fit.

$$Cl + HC(O)CN \rightarrow HCl + COCN \tag{8}$$

$$Cl + CH_3CN \rightarrow CH_2CN + HCl \tag{3}$$

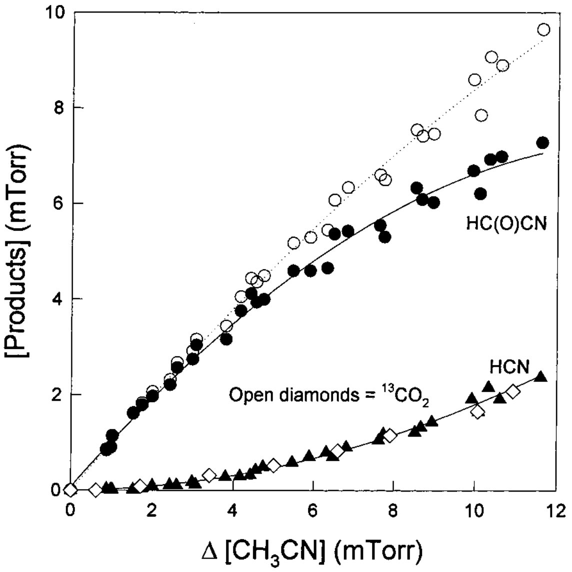

Figure 3. Formation of HC(O)CN (filled circles), HCN (filled triangles), and CO_2 (open diamonds) versus loss of CH_3CN observed in experiments using the UV irradiation of mixtures of 582−614 mTorr CH_3CN, 1.4−3.1 mTorr CH_3OCHO, 107−133 mTorr Cl_2, 7−700 Torr O_2, in 700 Torr total pressure made up with N_2 diluent at 296 K. The CO_2 yields were obtained from experiments using $^{13}CH_3{}^{13}CN$. The open circles show the total of HC(O)CN + HCN. The lines are quadratic least-squares fits through the data points.

Using the rate coefficient for Cl + CH_3CN measured previously,[11] we obtain $k_8 = (7.0 \pm 0.7) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Propagating an additional 10% uncertainty associated with the rate coefficient k_3 leads to $k_8 = (7.0 \pm 1.0) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. This rate coefficient is similar to that for the reaction of Cl atoms with HC(O)Cl, $k = 7.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.[15] Within experimental uncertainties, the observed formation of HC(O)CN accounts for 100% of the initial loss of CH_3CN, which is consistent with our previous finding that essentially 100% of the reaction of Cl atoms with CH_3CN proceeds via H atom abstraction.[11] No dependence on $[O_2]$ of the yield of HC(O)CN was discernible when the partial pressure of O_2 in the system was varied from 7.2 Torr to 700 Torr. Thermal decomposition of the $NCCH_2O$ radical thus appears to be of little, or no, importance at room temperature.

The experiments performed at small conversions of CH_3CN, using methyl formate as described above, could also be used to determine the secondary products arising from the loss of HC(O)CN. The major products, HCN and CO_2, were both formed with yields ~50% of the loss of HC(O)CN. Figure 3 shows the observed formation of HC(O)CN and HCN as a function of the loss of CH_3CN for a series of mixtures using an initial CH_3CN concentration of 600 mTorr. Experiments were performed using isotopically labeled $^{13}CH_3{}^{13}CN$ to allow the CO_2 to be distinguished from atmospheric levels present in the spectrometer light path. As seen from Figure 3, the yields of HCN and CO_2 are indistinguishable, suggesting that they are formed by the same mechanism. Variation of the O_2 partial pressure over the range stated above did not affect the HCN or CO_2 yields. The dotted line through the open circles in Figure 3 shows that the observed products still do not account for all the loss of CH_3CN at longer times and that other minor products must also be formed from HC(O)CN oxidation.

The possible formation of CO as a product in the Cl-atom-initiated oxidation of CH_3CN and HC(O)CN was investigated in experiments employing isotopically labeled $^{13}CH_3{}^{13}CN$. There was little ^{13}CO product (<5% molar yield relative to loss of CH_3CN) in such experiments. CO could be formed directly from radical reactions, or via the intermediate CH_2O, which reacts rapidly with Cl atoms under the conditions described, and hence remains below the detection limit.

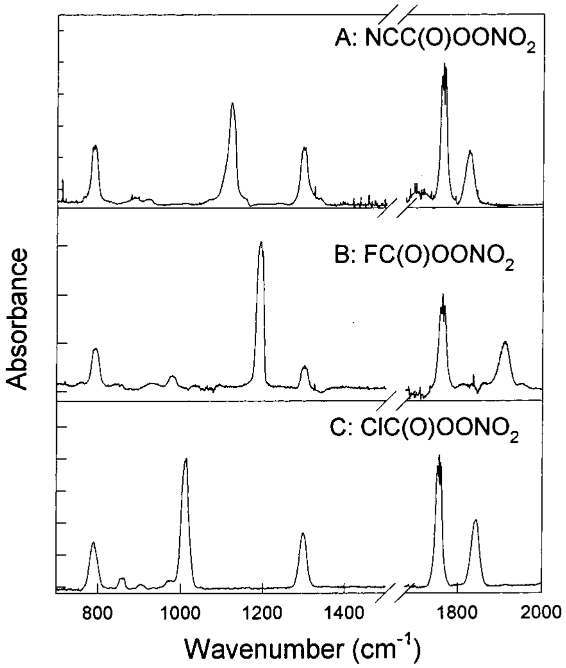

Figure 4. IR spectra of (A) $NCC(O)O_2NO_2$, (B) $FC(O)O_2NO_2$ [ref 17], and (C) $ClC(O)O_2NO_2$ [ref 16]; see text for details (abscissa scales are arbitrary).

$$Cl + CH_2O \rightarrow HCl + HCO \tag{9}$$

$$HCO + O_2 \rightarrow HO_2 + CO \tag{10}$$

The low yield of CO provides further evidence that decomposition of $NCCH_2O$ radicals (reaction 7) is not important at room temperature.

To investigate the mechanism of the reaction of Cl with HC(O)CN, and the stability of the COCN radical, experiments were performed in the presence of NO_2. On photolysis of $CH_3CN/Cl_2/NO_2$/air mixtures a product was obtained displaying the characteristic bands of a peroxyacyl nitrate. Figure 4A shows the spectrum observed, after the absorptions due to known products have been subtracted. The prominent bands, at 790, 1121, 1298, 1764, and 1827 cm^{-1} are typical for $RC(O)O_2NO_2$ type molecules and are assigned to $N{\equiv}CC(O)O_2NO_2$.

$$COCN + O_2 + M \rightarrow NCC(O)O_2 + M \tag{11}$$

$$NCC(O)O_2 + NO_2 \rightarrow NCC(O)O_2NO_2 \tag{12}$$

The peroxy nitrate resulting from the cyanomethyl radical is expected to be thermally unstable and is not expected to build up under the experimental conditions employed.

$$NCCH_2O_2 + NO_2 + M \rightarrow NCCH_2O_2NO_2 + M \tag{13}$$

$$NCCH_2O_2NO_2 + M \rightarrow NCCH_2O_2 + NO_2 + M \tag{14}$$

As shown in Figure 4, the $N{\equiv}CC(O)O_2NO_2$ frequencies can be compared with those of $ClC(O)O_2NO_2$, at 790, 1300, 1755, and 1843 cm^{-1} observed by Niki,[16] and those of $FC(O)O_2NO_2$ at 790, 1190, 1300, 1760, and 1911 cm^{-1} reported by Wallington et al.[17] All three spectra exhibit two bands in the 1700−2000

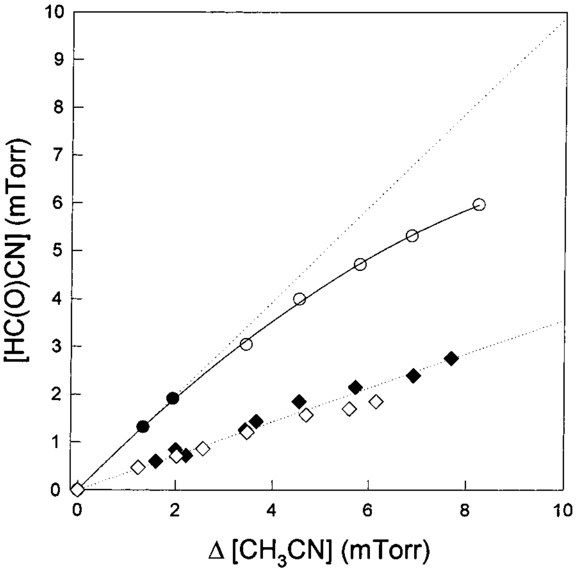

Figure 5. Formation of HC(O)CN relative to the calculated loss of CH_3CN for experiments in synthetic air initiated by OH radicals. The closed and open diamonds are from experiments using normal or doubly isotopically labeled CH_3CN, respectively (see section 3.2). The circles and curved line show data for Cl-initiated oxidation of CH_3CN in air for comparison. The dotted lines are a linear fit to the OH data set (diamonds) and the initial slope of the Cl data set (circles).

cm^{-1} region and one at approximately 1300 cm^{-1} attributable to C=O, and NO_2 asymmetric, and NO_2 symmetric stretching modes, respectively. The shifts in features in the 1000−1200 cm^{-1} region are consistent with those expected for the N≡C−, F−, and Cl− groups attached to the carbonyl group. Thus the COCN radical appears to react with O_2 rather than decomposing under atmospheric conditions.

3.2. Product Study of OH-Radical-Initiated Oxidation of CH_3CN. The reaction of OH radicals with acetonitrile was also observed to lead to the production of HC(O)CN. Figure 5 shows the formation of HC(O)CN plotted against the depletion of CH_3CN, as calculated from the measured loss of ethylene (using rate coefficients for reaction of OH with CH_3CN and C_2H_4 of 2.6×10^{-14} and 8.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively[2,12]). The initial yield of HC(O)CN was (40 ± 10)% (2σ statistical error only). However, since the rate coefficient for OH + CH_3CN is not well determined, we quote a 50% uncertainty on the HC(O)CN yield, i.e., (40 ± 20)%. Results from an experiment using Cl atoms under similar conditions are also shown for comparison. The plot of HC(O)CN against the loss of CH_3CN exhibits less curvature using OH than in the case of chlorine atoms, indicating that the relative rate coefficients are much closer for the OH reactions. Experiments were conducted using isotopically labeled CH_3CN to try to observe other carbon-bearing products (CO, CO_2, CH_2O); however, none could be unambiguously identified.

4. Discussion

The atmospheric oxidation of CH_3CN is initiated by reaction with OH radicals.[2] Approximately 50% of this reaction is believed to proceed via H-atom abstraction to give CH_2CN radicals.[2] We present here a substantial body of data concerning the Cl-atom-initiated oxidation of CH_3CN which provides insight into the atmospheric fate of CH_2CN radicals. The reaction of Cl atoms with CH_3CN gives essentially 100% yield of CH_2CN radicals, which then add O_2 to form the peroxy radical $NCCH_2O_2$. Self-reaction of the peroxy radicals gives the alkoxy radical $NCCH_2O$, which reacts exclusively with O_2 to give HC(O)CN (formyl cyanide).

It is noteworthy that no evidence for cyanomethyl hydroperoxide, $NCCH_2OOH$, was found. Hydroperoxy radicals will undoubtedly be present in the system following the reaction of CH_3CN and methyl formate (added as a tracer for CH_3CN loss, see section 3.1) with Cl atoms, and so formation of cyanomethyl hydroperoxide might be expected.

$$NCCH_2O_2 + HO_2 \rightarrow NCCH_2OOH + O_2 \qquad (15)$$

The absence of the hydroperoxide could be caused by three factors. First, the hydroperoxide could be lost heterogeneously on the walls of the chamber, and HC(O)CN product released into the gas phase. However, the observation of an essentially 100% yield of HC(O)CN immediately after the cessation of photolysis suggests that this is not the case. Second, the reaction between peroxy radical and HO_2 could proceed through the direct channel to give HC(O)CN. Such a mechanism is known to occur for other simple alkylperoxy radicals substituted with electronegative atoms such as F or Cl.[18,19]

$$NCCH_2O_2 + HO_2 \rightarrow HC(O)CN + H_2O + O_2 \qquad (16)$$

Third, and most likely, it is possible that attack of Cl atoms on the hydroperoxide is very rapid, so that any $NCCH_2OOH$ formed in the system is rapidly consumed by chlorine atoms, leading to the production of HC(O)CN.

$$Cl + NCCH_2OOH \rightarrow HCl + NCCHOOH \qquad (17)$$

$$NCCHOOH \rightarrow HC(O)CN + OH \qquad (18)$$

Following abstraction of a hydrogen atom from HC(O)CN by Cl atoms, COCN radicals are removed by rapid addition of O_2.

$$Cl + HC(O)CN \rightarrow HCl + COCN \qquad (8)$$

$$COCN + O_2 + M \rightarrow NCC(O)O_2 + M \qquad (11)$$

In the absence of NO_x the most likely fate of the acyl peroxy radical $NCC(O)O_2$ is self-reaction or reaction with HO_2.

$$NCC(O)O_2 + NCC(O)O_2 \rightarrow NCC(O)O + NCC(O)O + O_2 \qquad (19)$$

$$NCC(O)O_2 + HO_2 \rightarrow NCC(O)O_2H + O_2 \qquad (20a)$$

$$\rightarrow NCC(O)OH + O_3 \qquad (20b)$$

By analogy to FC(O)O, thermal dissociation of the NC−C bond in NCC(O)O is not expected to be rapid.[20] The dissociation reaction is probably slightly endothermic (~7 kcal mol^{-1}) and a large barrier is expected due to the electronegativity of the −CN leaving group. Instead, NCC(O)O may abstract a labile hydrogen atom from HO_2, for example, to give a cyano-substituted acid, which is expected to decompose rapidly to give the observed equal yields of HCN and CO_2, by analogy to chloroformic acid, ClC(O)OH.[21]

$$NCC(O)O + HO_2 \rightarrow NCC(O)OH + O_2 \qquad (21)$$

$$NCC(O)OH \rightarrow HCN + CO_2 \qquad (22)$$

Thermal decomposition of either the COCN or NCC(O)O radicals would lead to formation of the CN radical. However, CN is known to react very rapidly with O_2 to form NCO + O

(70−80%) or CO + NO (20−30%),[22] and should not lead to HCN formation in the presence of O_2. The low CO yields and observation of the peroxyacyl nitrate $NCC(O)O_2NO_2$ are further evidence of the stability of COCN and NCC(O)O. A small yield of the peroxyacyl nitrate (estimated at <5% from its infrared absorption) was detected even in the absence of added NO_2, suggesting that some NO_x is produced in the system. This may be related to the formation of CO, and may indicate a common source from CN chemistry.

The thermochemistry of HC(O)CN has been the subject of some dispute. Lewis-Bevan et al.[9] measured the first gas-phase infrared spectrum of pure HC(O)CN and performed semi-empirical calculations to obtain an enthalpy of formation of 17.2 kcal mol^{-1}. In 1996 Born et al.[23] carried out mass spectrometric measurements and obtained a heat of formation of 6.2 kcal mol^{-1}. However, this measurement relied on the thermochemistry of reference compounds which was not well established. More recently, Horwitz et al.[24] and Nguyen and Nguyen[25] calculated heats of formation for HC(O)CN of 11.2 and 13.2 kcal mol^{-1}, respectively. We have taken a value of 12 ± 3 kcal mol^{-1} to estimate bond strengths based on the two later studies.

Francisco and Liu[26] derived a heat of formation of 50 ± 3 kcal mol^{-1} for the COCN radical, leading to a calculated H−C bond strength in HC(O)CN of 90 ± 5 kcal mol^{-1}, similar to that of HC(O)Cl, 91 kcal mol^{-1}.[13,25] The calculated dissociation energy of the HCO−CN bond is then 102 kcal mol^{-1}, identical to that in $CH_3C(O)CN$.[24,27] Dissociation of the COCN radical into CO + CN is calculated to be endothermic by 25−30 kcal mol^{-1}. For comparison, decomposition of the ClCO and FCO radicals are 8 and 34 kcal mol^{-1} endothermic, respectively. Thus, it appears that the NC−C bond is intermediate in strength between Cl−C and F−C bonds, which can be partly attributed to the conjugation between the multiple bonds which leads to some double bond character in the C−C bond.

In the present work it is observed that OH-initiated oxidation of acetonitrile leads to the formation of HC(O)CN with a yield of 40 ± 20%. Hynes and Wine[2] observed regeneration of OH in the presence of O_2 in time-resolved experiments, and suggested that H-atom abstraction occurs about 50% of the time, and adduct formation about 50%. This conclusion is in overall agreement with the products observed here. On the basis of the results of OH isotopic scrambling experiments Hynes and Wine suggested that CH_2O may be formed following reaction of the OH adduct.

$$OH + CH_3CN + O_2 \rightarrow OH + CH_2O + HOCN \quad (23)$$

However, we saw no evidence for $^{13}CH_2O$ (or its byproduct ^{13}CO) in experiments in which $^{13}CH_3{}^{13}CN$ was oxidized by OH. The mechanism of OH regeneration and hence of acetonitrile oxidation by OH thus remain unexplained at present. Further experiments to elucidate the mechanism of OH attack on acetonitrile are needed.

Acknowledgment. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation. This work was partly supported by NASA's Upper Atmosphere Research Program. We thank Roc Carter (Ford) for helpful discussion regarding IR spectra, and Prof. J. Tyrrell for supplying details of the HC(O)CN infrared spectrum.

References and Notes

(1) Hamm, S.; Warneck, P. *J. Geophys. Res.* **1990**, *95*, 20593.
(2) Hynes, A. J.; Wine, P. H. *J. Phys. Chem.* **1991**, *95*, 1232.
(3) Hamm, S.; Hahn, J.; Helas, G.; Warneck, P. *Geophys. Res. Lett.* **1984**, *11*, 1207.
(4) Arijs, E.; Brasseur, G. *J. Geophys. Res.* **1986**, *91*, 4003.
(5) Livesey, N. J.; Waters, J. W.; Khosravi, R.; Brasseur, G. P.; Tyndall, G. S.; Read, W. G. *Geophys. Res. Lett.* **2001**, *28*, 779.
(6) Beig, G.; Walters, S.; Brasseur, G. *J. Geophys. Res.* **1993**, *98*, 12767.
(7) Murad, E.; Swider, W.; Moss, R.; Toby, S. *Geophys. Res. Lett.* **1984**, *11*, 147.
(8) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.
(9) Lewis-Bevan, W.; Gaston, R. D.; Tyrrell, J.; Stork, W. D.; Salmon, G. L. *J. Am. Chem. Soc.* **1992**, *114*, 1933.
(10) Hashimoto, S.; Bandow, H.; Akimoto, H.; Weng, J.-H.; Tang, X.-Y. *Int. J. Chem. Kinet*. **1984**, *16*, 1385.
(11) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Sehested, J.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 660.
(12) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. JPL Publication 97-4, NASA Jet Propulsion Laboratory, Pasadena, CA, 1997.
(13) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Jenkin, M. *Chem. Phys. Lett*. **1993**, *211*, 41.
(14) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet*. **1997**, *29*, 619.
(15) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *Int. J. Chem. Kinet.* **1980**, *12*, 915.
(16) Niki, H. Unpublished data in IR reference library at Ford Motor Company.
(17) Wallington, T. J.; Schneider, W. F.; Møgelberg, T. E.; Nielsen, O. J.; Sehested, J. *Int. J. Chem. Kinet.* **1995**, *27*, 391.
(18) Wallington, T. J.; Hurley, M. D.; Schneider, W. F.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *218*, 34.
(19) Wallington, T. J.; Hurley, M. D.; Schneider, W. F. *Chem. Phys. Lett.* **1996**, *251*, 164.
(20) Wallington, T. J.; Hurley, M. D.; Maricq, M. M. *Chem. Phys. Lett.* **1993**, *205*, 62.
(21) Tyndall, G. S.; Wallington, T. J.; Potts, A. R. *Chem. Phys. Lett.* **1991**, *186*, 149.
(22) Rim, K. T.; Hershberger, J. F. *J. Phys. Chem. A* **1999**, *103*, 3721.
(23) Born, M.; Ingemann, S.; Nibbering, N. M. M. *J. Phys. Chem.* **1996**, *100*, 17662.
(24) Horwitz, R. J.; Francisco, J. S.; Guest, J. A. *J. Phys. Chem. A* **1997**, *101*, 1231.
(25) Nguyen, T. L.; Nguyen, M. T. *J. Chem. Phys.* **1999**, *110*, 684.
(26) Francisco, J. S.; Liu, R. *J. Chem. Phys.* **1997**, *107*, 3840.
(27) Sumathi, R.; Nguyen, M. T. *J. Phys. Chem. A* **1998**, *102*, 412.