(dd, H_{4n}, $J_{4n,4x}$ = 16.3 Hz, $J_{4n,5}$ = 2.86 Hz), 2.64 (dt, H_{4x}, $J_{4x,4n}$ = 16.3 Hz, $J_{4x,5}$ = 3.05 Hz), 2.72 (m, H_{2x}, $J_{2x,CH}$ = 6 Hz); ^{13}C NMR δ 213.24 (C_3), 50.72 (C_1), 46.56 (C_4), 45.92 (C_2), 44.46 (C_5), 42.58 (C_8), 28.13 (C_6), 26.38 (C_{10}), 22.87 (C_7), 20.94 (C_9), 12.98 (C_{11}); mass spectrum, *m/z* (rel. intensity) 166 [$M^{\bullet +}$] (38%), 109 (77%), 96 (36%), 95 (100%) amu. The CH_3 groups showed aromatic solvent-induced shifts in the ^{1}H NMR determined in perdeuteriobenzene, $\Delta\delta(CDCl_3-C_6D_6)$ C_9 (+0.30), C_{10} (+0.40), C_{11} (−0.03).

Anal. Calcd for $C_{11}H_{18}O$ (166.26): C, 79.46; H, 10.91. Found: C, 79.58; H, 10.86.

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Spectroscopic Identification of Formyl Cyanide (CHOCN) in the Flash Pyrolysis of Methoxyacetonitrile

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Abstract: The gas-phase infrared spectrum of the short-lived species formyl cyanide has been recorded at low resolution. Four of the nine fundamentals were oserved: ν_2(C≡N stretch) = 2229 cm^{-1}, ν_3(C=O stretch) = 1716 cm^{-1}, ν_5(C—C stretch) = 914 cm^{-1}, and ν_7(C—C≡N bend) = 230 cm^{-1}. Identification of the CHOCN bands among the numerous absorption bands of the pyrolysis products of methoxyacetonitrile was made by stop-flow techniques and by comparison to recent ab initio calculations.

Formyl cyanide is a species of considerable chemical interest for several reasons. It is the simplest combination of the aldehyde and cyano groups and forms the prototype for the acyl cyanides.[1] From the viewpoint of organic synthesis, formyl cyanide has a variety of potential uses as a formylating agent for nucleophilic species. The prevalence of carbonyl and cyano compounds in the interstellar medium[2] suggests the likelihood that acyl cyanides are of astrophysical importance. Finally, HCOCN is a small enough molecule to be attractive for high-resolution spectroscopic studies in the microwave, infrared, and ultraviolet regions of the spectrum.

Formyl cyanide was recently reported by one of us[3] as an unstable product of the flash pyrolysis of methoxyacetonitrile. This was the first laboratory identification of this species although attempts to synthesize it by classical preparative organic techniques have been reported.[4,5] Ultraviolet long path absorption spectroscopy was used to identify CHOCN by the characteristic n → π* absorption bands found in the 350–390-nm region. Comparison of the band frequencies and rotational profiles to the well-known bands of propynal led to the firm conclusion that CHOCN was responsible for the new spectrum. Despite the substantial number of products anticipated from the thermal decomposition of CH_3OCH_2CN, the UV absorption technique provided a clear window for the observation of formyl cyanide in the pyrolysis mixture.

Since the initial discovery, a set of high-level ab initio calculations have been published[6] predicting the vibrational frequencies, rotational constants, and dipole moment of formyl cyanide. These calculations were motivated by an unsuccessful search for the microwave spectrum of CHOCN.[7] The reasons for the failure to observe a microwave spectrum are unclear. A large dipole moment (calculated to be 2.75 D[6]) is expected for the molecule and the pyrolysis conditions appeared well-established from previous experiments which monitored the electronic transition in the ultraviolet.[3] However, a variety of other stable products were identified by microwave and UV absorption techniques, proving that the pyrolysis did not lead solely to the production of CHOCN. Due to these complications, we felt it was necessary to establish the identity and relative abundance of formyl cyanide in the pyrolysis mixtures using independent spectroscopic methods. Gas-phase infrared and mass spectrometric measurements under optimized conditions are reported in this work.

Table I. Observed and Calculated Vibrational Frequencies for Formyl Cyanide (cm^{-1})

mode	description	3-21G scaled[a]	experiment
$\nu_1(a')$	CH stretch	2917	
$\nu_2(a')$	C≡N stretch	2309	2229
$\nu_3(a')$	C=O stretch	1691	1716
$\nu_4(a')$	CH rock	1385	
$\nu_5(a')$	C—C stretch	894	914
$\nu_6(a')$	C—C=O bend	637	
$\nu_7(a')$	C—C≡N bend	258	230, 227[b]
$\nu_8(a'')$	CH wag	1026	
$\nu_9(a'')$	C—C≡N bend	417	278[b]

[a] From ref 6. [b] From ref 3.

Experimental Section

Low-pressure gas-phase infrared spectra of methoxyacetonitrile pyrolysis streams were recorded on a Bomem DA3.02 FTIR. The modulated infrared beam was transferred from the evacuated interferometer into an external, 3 m long, 85 mm i.d. Pyrex absorption cell which it traversed twice before reentering the instrument and impinging on a liquid nitrogen cooled MCT detector (450–5000 cm^{-1}). Two CsI windows separated the cell from the interferometer and homebuilt, gold-coated beam steering optics were employed. For the mid-infrared a KBr beamsplitter was used. Far-infrared experiments, limited to the 200-cm^{-1} cutoff of the CsI windows, were done with use of a 3-μm Mylar beamsplitter and a DTGS detector.

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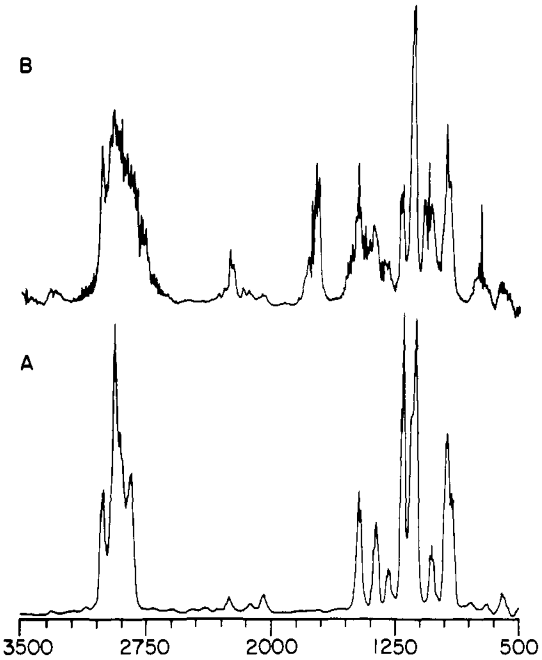

Figure 1. Gas-phase FTIR absorption spectra (4 cm^{-1} resolution) of (A) 2 Torr of methoxyacetonitrile vapor at 25 °C (peak absorbance 1.85) and (B) 3 Torr of the products of the pyrolysis of methoxyacetonitrile at 1000 °C (peak absorbance 0.75). The frequency scale is in cm^{-1}.

Mass spectrometric samples were taken by directly sampling the IR cell with use of a 5-L Pyrex bulb and by monitoring the residual gas in the long path cell over the course of obtaining the mass spectrum. Mass spectra were run on a Hitachi RMU-7 instrument with an all-glass batch inlet system which was heated to 200 °C.

Formyl cyanide was prepared by the pyrolysis of methoxyacetonitrile (Aldrich, used as received). The vapor (0.5–5 Torr) was flowed rapidly through a dimpled quartz tube heated over 20 cm of its length and through a large bore stopcock into the absorption cell. The pyrolysis temperatures in these experiments were varied from 400 to 1000 °C. Both continuous and stop-flow conditions were used in the course of the work.

Results

Mid-infrared spectra of pure methoxyacetonitrile at 25 °C and the products of its pyrolysis at 1000 °C under stop-flow conditions are shown in Figure 1, A and B, respectively. After pyrolysis at the optimized temperature of 1000 °C there is no evidence for residual substrate. Instead a complex spectrum appears, consisting of a large number of bands, many with sharper rotational structure than that of the starting material, even at low resolution. By closing stopcocks to isolate the sample in the cell from the pyrolysis oven and the vacuum pump, spectra could be taken to monitor changes in the pyrolysis mixture as a function of time. In this way, three absorption bands in the mid-infrared at 914, 1716, and 2229 cm^{-1} were found to decay slowly with time, as shown in Figure 2, A–C. Clearly a transient species is present. Furthermore, the three bands all decay at the same rate, implying they belong to a single species. The assignments of the 1716-cm^{-1} band as a C=O stretch and the 2229-cm^{-1} band as a C≡N stretch are in good agreement with the ab initio results shown in Table I for the vibrational frequencies of CHOCN, and we conclude that the transient species is formyl cyanide. The 915-cm^{-1} band is readily assigned as the C–C stretch, which, by analogy to the infrared spectrum of propynal, is expected to be a strong feature. In the far-infrared, a weak band at ~230 cm^{-1} was found to decay at the same rate as the 915-cm^{-1} band, which could be recorded simultaneously due to the secondary transmission maximum of the Mylar beamsplitter in this region. This band can be assigned as ν_7 and correlates well with a value determined from hot bands in the UV spectrum. Comparable decay times and the same vibrational frequency found in the IR and earlier UV experiments confirm that the same species, namely CHOCN, is being detected in both cases.

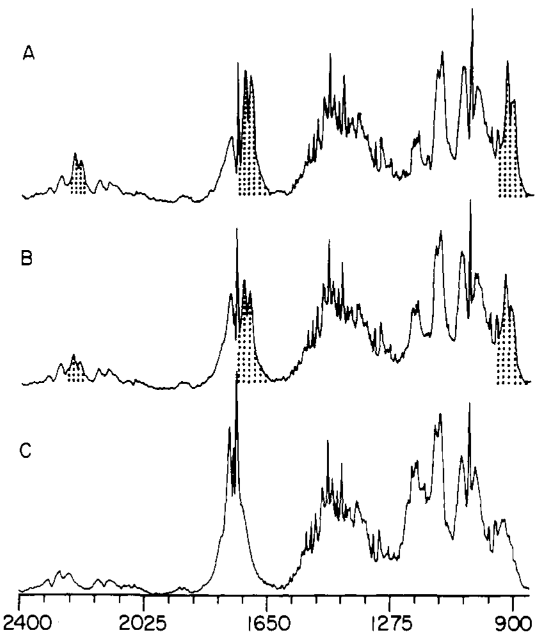

Figure 2. Time evolution of the spectrum of a 5-Torr sample of the products of the pyrolysis of methoxyacetonitrile at 1000 °C: (A) spectrum taken within 1 min after pyrolysis, (B) after 15 min and (C) after 2 h. The bands assigned to CHOCN are shaded. The frequency scale is in cm^{-1}.

Further confirmation of the assignment of the bands to CHOCN comes from a consideration of the unresolved rotational structure. Formyl cyanide is of C_s symmetry with nine normal modes which have the representations 7a′ + 2a″. The a″ modes, ν_8 and ν_9, should give typical type C bands with strong Q-branches while the a′ modes should give type AB hybrids, with or without a Q-branch, having well-defined P- and R-branch maxima. Hybrid bands of mainly type A should exhibit a Q-branch and little resolved K structure at the resolution employed in this work. The bands at 914, 1716, and 2229 cm^{-1} show the latter characteristics indicative of predominantly parallel transitions. Calculations of the P–R separations, using the formulae of Paul and Dijkstra[8] and the rotational constants calculated by Goddard,[6] gave values of 17–18 cm^{-1}, in good agreement with the measured intervals of 18.5, 18, and 17 cm^{-1} for the ν_2, ν_3, and ν_5 fundamentals.

It is obvious from an examination of Figure 2 that formyl cyanide accounts for only a small fraction of the observed infrared absorption bands. In their original paper, Judge et al.[3] suggested two possible routes for the pyrolytic degradation of methoxyacetonitrile:

$$CH_3OCH_2C{\equiv}N \rightarrow CHOC{\equiv}N + CH_4$$

$$CH_3OCH_2C{\equiv}N \rightarrow CH_2O + CH_3C{\equiv}N$$

From the UV spectrum they concluded that substantial quantities of formaldehyde were present in the pyrolysis mixture. From an analysis of our infrared spectra and comparisons with spectra of pure samples taken under the same instrumental conditions, we have positively identified seven stable species in the mixture, as shown in Table II. Methane, formaldehyde, acetonitrile, and methanol comprise about 80% of the gas mixture. Although HCN and CO were not determined directly, estimates lead to the conclusion that formyl cyanide contributes not more than 10% of the total gas pressure. A 5 Torr static sample of the pyrolysis mixture gradually loses CHOCN while HCN, CO, and CH_4 increase by about 25% of the initial quantity. It is tempting to ascribe the HCN and CO increase to the decomposition of formyl cyanide, but the increase in methane pressure is then unexplained. A further complication is evident from the growth of strong bands at 1755 cm^{-1} (C=O stretch?) and 1250–1080 cm^{-1} with time.

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Table II. Stable Products of the Pyrolysis of Methoxyacetonitrile

product[a,e]	characteristic[b] absorption (cm^{-1})	Percentage	time evolution[d]
CH_3CN	strong, sharp lines 1550–1400	15	constant
CH_2O	Q branch 3471.3	30	constant
CH_4	sharp lines 3050–3150	30	increase about 25%
CH_3OH	Q branch 3681.3	5	constant
HCN	sharp lines 3400–3220	n.d.	increase about 25%
CO_2	sharp lines 2380–2320	>1	constant
CO	sharp band 2200–2050	n.d.	increase about 25%
?	broad band 1250–1080	n.d.	these bands initially very weak but quite strong after CHOCN disappears
?	Q branch 1755	n.d.	

[a] Determined from a 0.5 cm^{-1} resolution spectrum of the pyrolysis mixture, $P = 5$ Torr, pyrolysis temperature 1000 °C. [b] These absorption features were the least overlapped and were used to determine the percent of the component in the mixture. [c] From direct comparison with pure samples at known pressures under the same experimental conditions, n.d. = not determined. [d] The relative change in the characteristic absorption feature of the same pyrolysis mixture after 2.5 h. [e] A small amount of acrylonitrile was also found mass spectroscopically and identified by comparison with the IR spectrum of a pure sample.

These bands may be due to reactions depleting formyl cyanide although no definite assignment can be made.

In an attempt to improve the yield of formyl cyanide, we pyrolyzed a sample of *tert*-butoxyacetonitrile at a variety of temperatures and pressures. Although CO, CO_2, H_2CO, CH_4, and HCN were readily observed, formyl cyanide was not detected. The *tert*-butyl leaving group did not promote the formation of formyl cyanide, contrary to our initial expectations.

Mass spectroscopic measurements were used to confirm the presence of formyl cyanide. The parent ion at m/e 55 and an intense M - 1 peak at m/e 54 were observed at low electron beam energies (15 eV). At even lower energies, the parent ion was accentuated and the M - 1 peak intensity decreased as expected. The stable products formaldehyde, methanol, and acetonitrile dominated the rest of the mass spectrum. A weak peak at m/e 53 suggested the presence of a small amount of acrylonitrile ($CH_2{=}CHCN$) which was confirmed by infrared comparisons with a pure sample.

Discussion

It is clear from the infrared and mass spectroscopic evidence that formyl cyanide is formed from the pyrolysis of methoxyacetonitrile. Under our experimental conditions, at an optimum temperature of 1000 °C, the yield is 10% or less. The half-life of CHOCN in a 5-Torr pyrolysis mixture was found to be about 30 min. Thus, formyl cyanide, in this context, can be classified as a short-lived rather than transient species.

The complexity of the pyrolysis mixture will make high-resolution infrared studies difficult. The ν_3 band is badly overlapped by the P-wing of the ν_2 band of formaldehyde. The ν_2 band is also overlapped by CO and CH_3CN bands. The ν_5 band at 914 cm^{-1} is comparatively free of interfering features although there appears to be an underlying absorption which may be troublesome.

The failure to observe the microwave spectrum[7] continues to be puzzling. Although the yield of formyl cyanide is low, it should be readily detectable. It is possible that the metal waveguide cell used in the experiments reacted with or promoted the decomposition of CHOCN. Observation of the microwave spectrum would, of course, be invaluable to further high-resolution IR and UV absorption studies.

The present results, when combined with the UV data, provide 5 of the 9 ground-state fundamentals. The agreement between the theoretically calculated frequencies and those observed here is good and it attests to the strength of the predictions which can be made from ab initio theory. It should be recognized that the present measurements are taken at the band center and not the band origin. The error in the vibrational frequency could be several wavenumbers. This is particularly true for the UV data where the vibrational intervals are taken between the heads of bands of different polarization and therefore of different band contour.

It is interesting to note that most of the stable products of the pyrolysis of methoxyacetonitrile are also molecules that have been identified in the interstellar medium. Combined with the relatively large hydrogen, oxygen, carbon, and nitrogen fractional abundances in the interstellar gas, these facts suggest that formyl cyanide is a good candidate for radioastronomical searches once the ground-state constants are accurately determined. The major obstacle to further detailed laboratory studies at present is the unfavorable precursor. Discovery of a clean source of CHOCN would open up a wide variety of avenues for further studies on this novel and fascinating molecule.

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