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Formyl Cyanide: A Stable Species. Experimental and Theoretical Studies

Wyn Lewis-Bevan,* Rick D. Gaston, James Tyrrell, Wilmer D. Stork, and Gary L. Salmon

Contribution from the Department of Chemistry, Southern Illinois University at Carbondale, Carbondale, Illinois 62901-4409. *Received August 28, 1991*

Abstract: Formyl cyanide has been generated by the retro-ene cleavage of cinnamyloxyacetonitrile using flash vacuum pyrolysis. Isolation of pure formyl cyanide in the gas phase has shown that the compound is much more stable than originally reported, with a measured half-life of 45.5 h under our experimental conditions. Formyl cyanide readily reacts with water to form hydrogen cyanide and formic acid. The observed vibrational frequencies are compared with the results of high-level ab initio calculations. Ab initio calculations are also reported for the transition state and the intrinsic reaction pathway of formyl cyanide into the products HCN and CO. The calculations are in agreement with the experimental observation that formyl cyanide does not undergo a unimolecular decomposition to HCN and CO as originally suggested.

Introduction

Recently, some considerable interest has been given to the prototype of the acyl cyanide family of compounds, namely formyl cyanide, HCOCN. Despite its simplicity, formyl cyanide has only recently been successfully synthesized, and even now, no experimental geometry is known. This elusive nature is surprising considering the stability of the methyl-substituted derivative, acetyl cyanide, CH_3COCN, which is a stable but flammable liquid. If formyl cyanide was found to be sufficiently stable, then it is feasible that it could be an interstellar species of significant importance in view of the large abundance of cyano and formyl radical and ion species in the interstellar medium.

The elusive formyl cyanide molecule was finally identified in 1986 by Judge et al.[1] as one of several postulated products from the pyrolysis of methoxyacetonitrile, CH_3OCH_2CN, at 600 °C. It was identified via its ($\pi^* \leftarrow n$) $\tilde{A}A'' \leftarrow \tilde{X}A'$ lowest electronic transition which arises within the carbonyl functional group. As expected, the structure of the electronic band closely resembled that of propynal, CHOCCH, consisting of a series of clearly defined vibrational progressions together with an open rotational structure. Along with a number of excited electronic state vibrational bands, the authors were able to identify the two lowest lying vibrational bands of the ground electronic state: the CCN in- and out-of-plane bending fundamentals (see Table I). Under their experimental conditions, formyl cyanide had a lifetime of about 6 min.

Also in 1986, Goddard[2] reported the first ab initio results on the structure, vibrational frequencies, and dipole moment of formyl cyanide. Even though the estimated dipole moment of formyl cyanide is around 2.0 D, the initial search for the microwave spectrum from the pyrolysis of CH_3OCH_2CN was unsuccessful.[3] It is unclear why this should have been the case, although a large number of stable products were identified.

Following this, an independent spectroscopic observation of the pyrolysis products of CH_3OCH_2CN was reported by Clouthier and Moule.[4] At a pyrolysis temperature of 1000 °C and using low-resolution infrared spectroscopy, several stable byproducts were identified together with formyl cyanide. The stable byproducts included methane, formaldehyde, acetonitrile, and methanol as well as both hydrogen cyanide and carbon monoxide, which were thought to be derived from the decomposition of formyl cyanide itself. In that study, it was concluded that formyl cyanide

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(3) Judge, R. H.; Moule, D. C.; Gerry, M. C. L. Unpublished results.

(4) Clouthier, D. J.; Moule, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 6259–6261.

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Table I. Observed and Previously Calculated Vibrational Frequencies for Formyl Cyanide

			exptl frequencies, cm^{-1}			calcd frequencies, cm^{-1} previous work		
			this work	previous work				
	mode	description	gas phase	gas phase	solid[c]	scaled[d]	scaled[e]	SQM[f]
a′	ν_1	CH str	2892			2955	2894	2996
	ν_2	CN str	2230	2229[a]	2240	2355	2329	2222
	ν_3	CO str	1716	1716[a]	1700	1824	1803	1713
	ν_4	CH rock	1383		1365	1385	1363	1382
	ν_5	CC str[g]	914	914[a]	905	907	896	914
	ν_6	CCO bend[g]	626			614	607	611
	ν_7	CCN bend		230,[a] 227[b]		241	238	230
	$2\nu_5$		1823					
	$2\nu_3$		3405					
a″	ν_8	CH wag				1004	993	1008
	ν_9	CCN bend		278[b]		326	332	306

[a] From ref 4, gas-phase IR. [b] From ref 1, gas-phase UV. [c] From refs 5 and 6, solid phase at 77 K on NaCl. [d] From ref 2, HF/6-31G* scaled frequency. [e] From ref 8, HF/6-31G** scaled frequency. [f] From ref 8, HF/6-31G** SQM frequency. [g] The main character of the vibrational fundamental is given for conciseness.

accounted for no more than about 10% of the total pressure in the cell. Their static sample (P = 5 Torr) gradually lost HCOCN with an increase in the quantity of HCN, CO, and CH_4. In addition, strong absorption bands that grew in with time near 1755 cm^{-1} and the 1250–1080-cm^{-1} region could not be identified, adding a further complication to the decomposition mechanism. However, Clouthier and Moule were able to identify four absorption bands of formyl cyanide including the CN, CO, and CC stretching fundamental bands and the previously identified CCN in-plane bend (see Table I). All four bands were found to decay at the same rate, with a half-life of approximately 30 min. The assignments and locations of the bands were in good agreement with the previously reported ab initio calculations of Goddard[2] as well as the first experimental results of Judge et al.[1]

The millimeter-wave spectrum of formyl cyanide was reported by Bogey et al.[5] in 1988. To possibly reduce the number of byproducts, Bogey et al. produced the molecule via the flash vacuum thermolysis of a new precursor: allyloxyacetonitrile, $CH_2{=}CHCH_2OCH_2CN$. At 850 °C and a pressure of 2 Pa (15 mTorr), their proposed retro-ene cleavage mechanism led to two products, formyl cyanide and propene. The presence of HCOCN was confirmed by its low-temperature, 77 K (−196 °C), IR spectrum (see Table I), which vanished on warming to 198 K (−75 °C). Longer interaction times in the pyrolysis region led to the production of HCN and CO. They reported a consistent $1/e$ lifetime of 29 min, which was measured at a pressure of 2 Pa.

In 1990, a more extensive characterization was reported by Vallée et al.[6] They observed the photoelectron, IR, and UV spectra of formyl cyanide formed by the retro-ene thermolysis of $CH_2{=}CHCH_2OCH_2CN$ at 1270 K (997 °C). The only byproducts were propene, hydrogen cyanide, and carbon monoxide. The infrared spectrum was recorded in the solid phase at 77 K on NaCl. Again, four vibrational bands were identified (see Table I). On warming to 200 K, all absorptions due to formyl cyanide disappeared and a polymeric material was recovered.

Recently the $\tilde{A}A'' \leftarrow \tilde{X}A'$ electronic transition of formyl cyanide has been revisited and studied at high resolution by Karolczak et al.[7] using both CH_3OCH_2CN and $CH_2{=}CHCH_2OCH_2CN$ as precursors. They used spectrographic absorption and pyrolysis jet spectroscopy to study the origin (0,0) band near 26 283 cm^{-1}.

Besides the earlier paper of Goddard,[2] Csaszar[8] recently reported a new theoretical prediction of the vibrational and rotational spectra of formyl cyanide and thioformyl cyanide. Goddard determined the geometry and vibrational frequencies at the SCF level using either 3-21G or 6-31G* basis sets. The geometry was also determined at the MP3 level using a 6-31G* basis set. Csaszar, on the other hand, used larger basis sets including polarization of all atoms (6-31G** and 6-311G**) at the MP2 level to determine the molecular geometry. In addition to this, Csaszar also reports the results of scaled quantum mechanical (SQM) force fields, used in the prediction of vibrational frequencies. Unfortunately, the SQM results were based upon a Hartree–Fock SCF treatment rather than at the MP2 or higher level. The SQM results are in good agreement with the previously reported gas-phase results of refs 1 and 4. Centrifugal distortion constants derived from the SQM force field[8] are in very good agreement with those measured experimentally.

The motivation for our study was threefold: There was, until now, no clean synthetic route to the formyl cyanide. Even though $CH_2{=}CHCH_2OCH_2CN$ looked like a promising precursor, there was still the problem of separating the major byproduct, propene, which interferes strongly in the assignment of the infrared spectrum of formyl cyanide. A severe disadvantage of $CH_2{=}CHCH_2OCH_2CN$ is its short shelf life, with the necessity to prepare fresh batches every few days.

The stability of formyl cyanide was also a puzzle since we had calculated the activation energy, E_A, for the unimolecular decomposition to HCN and CO and found it to be consistent with a stable molecule. Hence, it seemed unlikely that the major gas-phase decomposition mechanism was a simple unimolecular decomposition. The yellow polymeric material reported in the literature was also curious, since we had not observed this in our previous experiments.

Finally, there was no complete or clean infrared gas-phase infrared spectrum of such a simple molecule; this prompted us to investigate both the chemistry and spectroscopy of formyl cyanide in more detail, both experimentally and theoretically. In this paper, we report the first successful attempt at observing pure formyl cyanide in the gas phase, the assignment of the strongest vibrational bands above 400 cm^{-1}, its stability, and its reaction with water. We also report our ab initio results on the geometries, vibrational frequencies, and intensities of both the ground state and transition state (to HCN and CO) together with the intrinsic reaction pathway from the ground state to the products.

Experimental Section

Rationale. To study the infrared spectroscopy of this molecule successfully, as many interfering vibrational bands from byproducts had to be removed from the spectrum as possible. In particular, our attempts to study the fine structure of the C—C stretch of HCOCN near 930 cm^{-1}, produced via the flash pyrolysis of $CH_2{=}CHCH_2OCH_2CN$, were severely hindered due to the predominance of the fine structure of the C—C stretching fundamental of propene which lies in the same region. We had previously attempted to study HCOCN via the flash vacuum pyrolysis (FVP) of CH_3OCH_2CN but were puzzled by its long lifetime (more than 16 h) under the conditions of our experiment. The lifetime measurement was inconsistent with the observations reported in the literature at that time.[1,4] This, together with the uncertainty as to whether the molecule was in fact formyl cyanide and the presence of ethene as a dominant impurity in this spectral region (not previously identified in ref 4), forced us to abandon further high-resolution studies with the diode

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laser and CH_3OCH_2CN as the precursor molecule.

In light of the previous reports on the inability to revaporize HCOCN after being trapped at 77 K[4,5] and the difficulties involved in the separation of formyl cyanide from the many gas-phase byproducts of the CH_3OCH_2CN FVP or propene from the FVP of $CH_2{=}CHCH_2OCH_2CN$, it was decided to approach the synthesis via a different route. Our initial attempts to synthesize HCOCN via the reaction of formyl chloride with metal salts failed. It is interesting to note that the gas–solid reaction of HCOCl(g) with AgCN(s) led directly to the products CO and HCN. An alternate method was to replace the terminal H that lies trans with respect to the remainder of the molecule in allyloxyacetonitrile with a large substituent, such that the byproduct would have a low vapor pressure at or near room temperature. This led to the synthesis of cinnamyloxyacetonitrile, $C_6H_5CH{=}CHCH_2OCH_2CN$.

Cinnamyloxyacetonitrile. Cinnamyloxyacetonitrile was generated via the method of Magnus.[9] Cinnamyl alcohol was treated with dimethyl sulfoxide (46 equiv), acetic anhydride (23 equiv), and acetic acid (11.5 equiv) at ambient temperature, producing the methyl thiomethyl ether[10] in 68% yield after hydrolysis of acetate byproducts with lithium hydroxide in aqueous methanolic tetrahydrofuran (**warning**: extreme stench, an efficient fume hood required). The sulfide was oxidized to the corresponding sulfoxide in 77% yield with *m*-chloroperbenzoic acid (1.05 equiv) in dichloromethane at −78 °C. Finally, treatment of the sulfoxide with fresh trimethylsilyl cyanide (TMSCN, 2.5 equiv) at ambient temperature catalyzed by zinc iodide (0.08 equiv) resulted in the formation of cinnamyloxyacetonitrile[11] in 26% yield. It is imperative that fresh TMSCN is used since older reagent results in considerably decreased yields.

Cinnamyloxyacetonitrile is readily obtained in a pure form by flash chromatography.[12] The compound is a stable albeit somewhat light-sensitive, pale yellow oil at room temperature and can be stored for at least 2 months in a −20 °C freezer without showing any signs of decomposition.

Infrared. Formyl cyanide has been generated by the controlled retro-ene cleavage of cinnamyloxyacetonitrile, $C_6H_5CH{=}CHCH_2OCH_2CN$, using flash vacuum pyrolysis (FVP) in a flow system. Due to its very low vapor pressure, less than 3 mTorr at 298 K, the liquid sample of cinnamyloxyacetonitrile was preheated to between 70 and 80 °C in a narrow quartz tube by means of a heating tape. This produced a 10–15-mTorr pressure of $C_6H_5CH{=}CHCH_2OCH_2CN$. The resulting vapor was pumped slowly along the quartz tube, also maintained at 70 °C, and through a short and narrow flash pyrolysis region (4 mm i.d. × 25–30 mm), where it was decomposed at temperatures ranging from 450 to 800 °C. Allylbenzene, the only byproduct of the pyrolysis, was removed with either an ice water bath or in later experiments a methanol/CO_2 cold trap, allowing pure formyl cyanide to be observed in a 2-m optical cell using a tunable infrared diode laser (Spectra-Physics SP5000 series) in the frequency region around 928 cm^{-1}. The cell was constructed of 30 mm o.d. standard wall Pyrex tube. KBr windows were used to seal the tube at either end. Teflon valves were used throughout the apparatus to control the flow rates and in the stop flow experiment. The cell pressure was maintained at 15 mTorr under slow flow conditions. To establish that formyl cyanide was the major product being observed in the laser spectrum, the products from the FVP of CH_3OCH_2CN and $CH_2{=}CHCH_2OCH_2CN$ were studied with the diode laser in the same frequency region. Absorption lines from the FVP products of both compounds matched exactly those recorded from the FVP of $C_6H_5CH{=}CHCH_2OCH_2CN$. A sample of the products from the FVP of cinnamyloxyacetonitrile was trapped in a side arm of the 2-m cell at 77 K after the cell was isolated from the vacuum pump. After several hours had elapsed, the trap was isolated and the contents were transferred to an 18-cm-long, 2-cm-diameter, Pyrex cell fitted with KBr windows. The initial cell pressure was 1.8 Torr. The 2-cm^{-1} resolution IR spectrum of this gas-phase sample was recorded on a Nicolet DX-20 FT-IR instrument. Limitations of the beam splitter did not allow the observation of the two lowest lying fundamentals (below 400 cm^{-1}). One hundred scans were co-added and transformed into the IR spectrum shown in Figure 1. These data, together with the laser data, confirm that pure formyl cyanide was being observed in the gas phase.

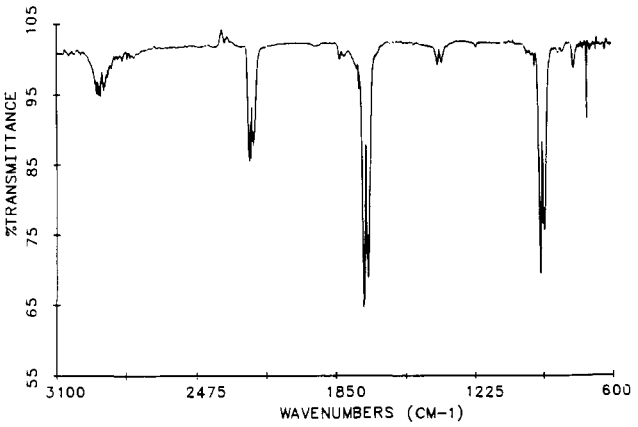

Figure 1. Infrared spectrum of formyl cyanide between 600 and 3100 cm^{-1} taken 5 min after the sample expanded into the 18-cm cell. The initial cell pressure was 1.8 Torr. HCOOH and HCN peaks are seen at 1746 and 713 cm^{-1}, respectively. A small peak at 773 cm^{-1} results from a trace of $CHCl_3$, an impurity from the preparation of the precursor. The peaks near 2300 cm^{-1} (of opposite phase) are due to the continual purge of CO_2 from the spectrometer.

Further confirmation of the existence of formyl cyanide was realized upon addition of water to the sample. Characteristic bands of formic acid and hydrogen cyanide appeared as the formyl cyanide bands diminished. Figure 2 shows part (1960–832 cm^{-1}) of the infrared spectrum of formyl cyanide 25 h after small traces of water on the walls of the cell reacted with the formyl cyanide. Clearly defined bands of formic acid can be seen throughout the spectrum at 1778, 1748, and 1105 cm^{-1}. A strong band due to HCN near 738 cm^{-1} was also detected.

Ab Initio Calculations

To better understand the decomposition of formyl cyanide to the suspected products HCN and CO, a series of high-level ab initio calculations were performed to determine both the ground-state and transition-state geometries and energies. Vibrational frequencies and intensities were also determined in these states. All calculations were performed using the Gaussian 88[13] suite of programs. The geometry optimizations and the calculation of vibrational frequencies and intensities were carried out at the MP2 level using the D95**, 6-31G**, and 6-311G** basis sets. In addition, the reaction pathway from the transition state to the products, HCN and CO, was followed. Both a step-by-step gradient method (MP2/D95**) and an intrinsic reaction coordinate method (IRC) were used to follow the reaction coordinate to the products. The IRC[14] method was also used to follow the reaction coordinate from the transition state back to the reactant. The IRC calculations were carried out at the HF/SCF level using a 3-21G basis set.

Results and Discussion

Formyl cyanide has nine vibrational degrees of freedom, which transform under the symmetry operations of the C_s point group as

$$\Gamma(\text{vib}) = 7A' + 2A'' \quad (1)$$

All of these vibrational bands are infrared active, with the added complication that the in-plane vibrational motions will result in type a,b-hybrid bands due to the asymmetry of the molecule. The two out-of-plane vibrational bands will have pure c-type character. A low-resolution (2 cm^{-1}) spectrum of HCOCN, between 650 and 3050 cm^{-1}, is shown in Figure 1.

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(11) The characteristics of the compound are as follows: R_f 0.47 1:3 ethyl acetate hexanes; ^1H NMR (300 MHz) δ 7.43–7.23 (m, 5 H), 6.68 (br d, 1 H, J = 15.9 Hz), 6.21 (dt, 1 H, J = 15.9, 6.5 Hz), 4.28 (br d, 2 H, J = 6.5 Hz), 4.26 (s, 2 H); ^{13}C NMR (75 MHz) δ 135.86, 135.29, 128.65, 128.28, 126.65, 122.99, 115.95, 71.66, 54.63; IR (neat) 3060 (m), 3029 (s), 2912 (s), 2861 (s), 1677 (s), 1598 (m), 1578 (m), 1495 (s), 1431 (vs), 1435 (s), 1392 (s), 1354 (vs), 1295 (m), 1281 (m), 1267 (m), 1239 (m), 1206 (m), 1189 (m), 1134–1065 (br vvs), 1032 (m), 968 (vvs), 933 (s), 913 (s), 885 (s), 830 (m), 749 (vvs), 693 (vvs) cm^{-1}; MS (EI, 70 eV) 173, 133, 117, 105, 77, 40 m/z. Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 75.88; H, 6.34; N, 7.93.

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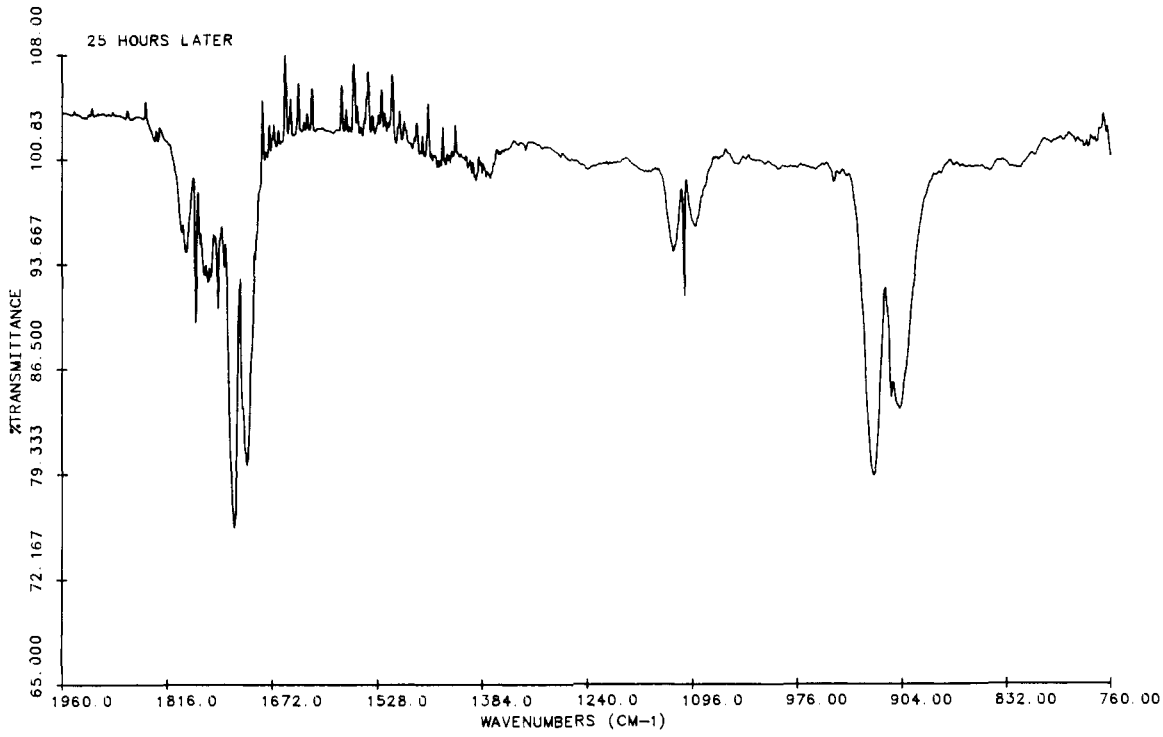

Figure 2. Infrared spectrum of formyl cyanide between 760 and 1960 cm^{-1} taken 25 h after the beginning of the reaction with water. Note the strong absorptions due to formic acid near 1105 and 1740 cm^{-1}. The sharp peaks between ~1400 and ~1700 cm^{-1} (of opposite phase) are due to the continual purge of water vapor from the spectrometer.

The strong band near 1716 cm^{-1} indicates very clearly that the molecule contains the CO functional group. Likewise, the medium-intensity band near 2230 cm^{-1} clearly demonstrates the presence of a CN functional group. The medium-strong band near 914 cm^{-1} can be attributed to a CC single bond stretch, while the medium-strength vibrational band near 2892 cm^{-1} can be attributed to the CH stretching fundamental. The CH rock is located near 1383 cm^{-1} and is surprisingly weak compared to the 77 K spectra.[6] The two remaining weak bands can be attributed to the overtone of the CC stretching fundamental (1823 $cm^{-1} \approx 2 \times 914$ cm^{-1}) and the in-plane CCO bend (626 cm^{-1}) which manifests itself as an extremely weak feature in our spectrum. Not shown in Figure 1 is a very weak band near 3405 cm^{-1}. This can be attributed to the overtone of the CO stretching fundamental (3405 $cm^{-1} \approx 2 \times 1716$ cm^{-1}). All of the observed vibrational bands are of a' symmetry and have characteristic structures which, at 2-cm^{-1} resolution, reflect predominantly either a- or b-type band contours rather than a,b-type hybrid structure, which will be discussed below. The two lowest lying fundamental bands were not observable with the present configuration of the FT-IR instrument. Only one fundamental now remains to be observed; the CH wag of a'' symmetry which should be present in the 1000-cm^{-1} region. At 2-cm^{-1} resolution there is no evidence of the characteristic strong central Q-branch spike expected in the central portion of a c-type band; this is consistent with the vibrational intensities calculated using ab initio methods discussed below.

Because the relative amounts of ^{13}C and ^{15}N in natural abundance (~1% and ~0.3%, respectively) are insignificant, there are no isotopic effects to complicate the spectrum. Upon closer examination, it can be seen that the majority of the bands have a full width at half-maximum, fwhm, of less than 50 cm^{-1}. The one exception is the CH stretching fundamental near 2892 cm^{-1}, which boasts a fwhm of ~80 cm^{-1}. The larger fwhm of this band suggests a strong b-type component in the spectrum $(\partial\mu_b/\partial Q_1)_0 \gg (\partial\mu_a/\partial Q_1)_0$. Observation of this band at higher dispersion shows clearly the b-type Q-branch structure of a near prolate asymmetric rotor. Both the CC and the CN stretches show some evidence of a-type Q-branches, suggesting that the change in $(\partial\mu_a/\partial Q_n)_0 \gg (\partial\mu_b/\partial Q_n)_0$. The lack of the strong a-type Q-branch in the CO stretching fundamental, together with the narrow fwhm, suggests either that the Q-branch is strongly degraded or that the structure is perturbed by one or more dark states due to either overtones or combinations of lower lying fundamentals. Higher resolution studies, either with the diode laser or with high-resolution FT-IR, will be required to determine the relative magnitudes of the dipole derivatives. Perturbations in the higher vibrational bands may also lead to the location and assignment of the missing out-of-plane CH wag.

The decomposition mechanism of formyl cyanide is not clearly understood. To compare our results with those previously reported,[4-6] we attempted to trap the products from the FVP of both CH_3OCH_2CN and $CH_2{=}CHCH_2OCH_2CN$. The inability to trap and revaporize formyl cyanide at 77 K from these precursors is mysterious. Using exactly the same technique that had been successful for products from the FVP of $C_6H_5CH{=}CHCH_2OCH_2CN$, were were unable to trap and revaporize any formyl cyanide. Also, we failed to observe any yellow film or deposit on the walls of the cold trap after warming to room temperature.

Careful attention was taken to observe and identify the decomposition products of the formyl cyanide that had been trapped and transferred to the 18-cm IR cell. There was no evidence of decomposition to form either a polymeric material or hydrogen cyanide and carbon monoxide, although small amounts of both HCN and CO are evident in the initial preparation. The amounts of HCN and CO vary depending upon the residence time and temperature within the FVP region, suggesting that high-temperature decomposition to these products may indeed take place. The direct decomposition of the precursor should, of course, not be ruled out either. Depending upon the conditions of our experiment, and especially on how dry the apparatus was, various values of $t_{1/2}$ were measured. Under the driest conditions a value of $t_{1/2}$ of 45.5 h was measured ($P_{initial}$ = 1.8 Torr). However, the reaction is predominantly with water on the surfaces of the sample cell rather than either a polymerization or decomposition to HCN and CO. The only identifiable products of the reaction were HCN and HCOOH.

Ab initio calculations were performed at a variety of levels to study the unimolecular gas-phase decomposition of formyl cyanide into the products HCN and CO. The most extensive calculations involving large basis sets and correlation are reported here. Table II lists the geometries and energies for both the equilibrium ground

Table II. Optimized Geometries[a] and Energies[b] of Formyl Cyanide

	ground state			transition state		
	MP2/D95**	MP2/6-31G**	MP2/6-311G**	MP2/D95**	MP2/6-31G**	MP2/6-311G**
R_{C-C}	1.4811	1.4689	1.4733	2.2277	2.2178	2.2438
R_{C-O}	1.2230	1.2202	1.2092	1.1577	1.1541	1.1411
R_{C-H}	1.0980	1.0952	1.1003	1.0997	1.0954	1.0979
R_{C-N}	1.1892	1.1817	1.1756	1.2004	1.1920	1.1858
∠CCO	122.2238	121.8594	122.1330	117.3890	116.9249	117.846
∠CCN	180.9331	180.4309	180.515	166.046	161.6197	163.8337
∠CCH	114.4584	115.0117	114.4918	52.6071	52.9717	52.7689
E_{HCOCN}	−206.265739	−206.195201	−206.336167	−206.152924	−206.077993	−206.226623
E_{CO}	−113.068770	−113.028180	−113.111416			
E_{HCN}	−93.204097	−93.174366	−93.242684			

[a] Bond lengths (R) are in angstroms; angles (∠) are in degrees. [b] Energies are in hartrees.

state and the transition state. Three basis sets were used at the MP2 level: D95**, 6-31G**, and 6-311G**. To obtain $\Delta E_{HCOCN-(HCN+CO)}$, the ground-state equilibrium energies of HCN and CO were also determined at the same level. These are listed in Table II also. While no experimental data are available on the bond lengths and angles, a set of rotational constants have been obtained (A = 67.47354 GHz, B = 5.01019 GHz, C = 4.65660 GHz),[5] and these can be compared with those obtained theoretically as, for example, with the MP2/6-311G** calculation (A = 65.19989 GHz, B = 4.96889 GHz, C = 4.61703 GHz), although it should be remembered that the theoretical constants are for an equilibrium structure and the experimental values are for the effective structure. However, all three basis sets lead to geometries in close agreement with each other both for the ground state and for the transition state. The transition state is characterized by a planar structure in which the C—C bond is lengthened by about 0.8 Å, a substantial reduction in the CCH angle, bringing the hydrogen much closer to the C≡N group but without significant change in the C—H bond length, and a bending of the CCN angle such that the carbon of the C≡N group is properly oriented for attack by the hydrogen. On the basis of Mulliken populations the transition state exhibits a significant transfer of electron density from the HCO fragment to the CN fragment relative to the ground state, and it would seem that the hydrogen would effectively transfer as a proton. From the total energies of formyl cyanide, its transition state, and its decomposition products (HCN + CO), it is possible to determine the activation energy for the unimolecular decomposition as well as the overall energy change for the process. Using the values obtained in the MP2/6-311G** calculation, we obtain an activation energy of 68.74 kcal mol^{-1} and an energy difference between reactant and products of −11.25 kcal mol^{-1}. These values suggest that the unimolecular decomposition of formyl cyanide, if it occurred, would be slightly exothermic but that such a process is quite unlikely. This is in agreement with the experimentally observed stability of formyl cyanide and the absence of any detectable amount of carbon monoxide once the formyl cyanide has been prepared and isolated.

The vibrational frequencies for both ground- and transition-state optimized geometries, calculated at the MP2 level, are given in Table III and have not been scaled. These calculated values are based on a harmonic force field and can be expected to show deviations from the experimentally observed values. There is good agreement between the calculated intensities for the ground-state fundamentals and the observed spectrum (Figure 1). The only fundamental not yet observed by us or other workers is the out-of-plane CH wag, which is predicted from our calculations to be about 50 times weaker than the next weakest fundamental, the CCO in-plane rock. In the transition state the imaginary frequency correlates with the in-plane CH rock corresponding to the large change in the CCH angle as the molecule passes through that state. The CN and the CO stretching vibrations are coupled in the transition state with the higher of the two frequencies representing a CO stretch and a CN contraction while the lower frequency corresponds to both bonds stretching.

The pathway for the unimolecular decomposition of formyl cyanide is summarized in the data presented in Table IV. These

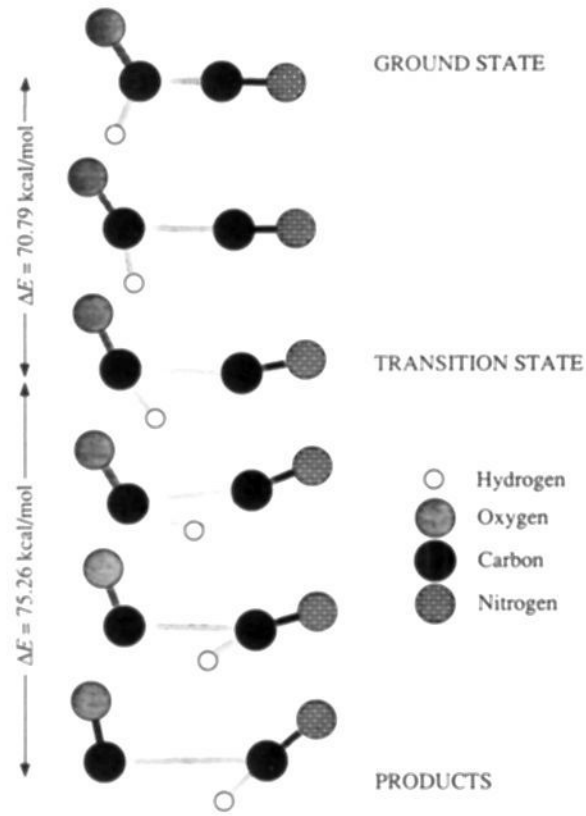

Figure 3. Change in geometry of formyl cyanide from its ground state through the transition state toward the products, HCN and CO, at arbitrary points along the reaction coordinate. The values of ΔE are taken from the results of MP2/D95** ab initio calculations. The increase in the CC bond length from the ground up until the transition state is clearly evident, as well as the decrease in the CCH angle up and until the hydrogen is equidistant from the two carbons.

data were obtained by following the intrinsic reaction coordinate from the transition state back to the reactant and forward to the products. The data presented here were determined at the HF/SCF level using a 3-21G basis set to reduce the computational effort but do present a good qualitative picture of the energetic and geometric changes occurring during the unimolecular decomposition. We have also used a gradient method to follow the decomposition from the transition state to the products at the MP2 level using the D95** basis set, and these results confirm the pattern we observe with the less rigorous calculation. As shown in Figure 3, the dominant changes as the molecule proceeds from the ground state to its transition state are represented by a lengthening of the C–C bond in conjunction with a decrease in the CCH angle. These two changes are well under way before the CCN angle shows any significant departure from its ground-state value. Simultaneously, the CO bond shortens somewhat, the CN bond lengthens, and the CH bond first shortens and then recovers its ground-state length. Only after the molecule

Table III. Vibrational Frequencies[a] and Intensities[b] of Formyl Cyanide

	mode	description	ground state			transition state		
			MP2/D95**	MP2/6-31G**	MP2/6-311G**	MP2/D95**	MP2/6-31G**	MP2/6-311G**
a'	ν_1	CH str[c]	3138 (40)	3123 (42)	3072 (46)	3155 (92)	3181 (89)	3151 (89)
	ν_2	CN str	2144 (53)	2190 (51)	2170 (54)	2000 (45)	2041 (22)	2028 (32)
	ν_3	CO str	1719 (107)	1732 (79)	1735 (91)	1967 (604)	1984 (571)	1992 (588)
	ν_4	CH rock	1430 (8.4)	1446 (9.0)	1429 (10.3)	1542i	1562i	1496i
	ν_5	CC str	930 (90)	950 (87)	933 (89)	577 (223)	581 (228)	577 (228)
	ν_6	CCO bend	608 (2.4)	619 (1.7)	620 (1.6)	312 (112)	330 (97)	315 (109)
	ν_7	CCN bend	213 (10.9)	215 (11.7)	220 (11.2)	85 (1.2)	84 (1.8)	67 (0.9)
a''	ν_8	CH wag	990 (0.07)	1009 (0.03)	1009 (0.04)	893 (20)	923 (17)	924 (15)
	ν_9	CCN bend	297 (0.6)	316 (1.7)	317 (1.2)	135 (9.2)	144 (9.4)	124 (11)

[a] Frequencies are in units of cm^{-1}. [b] Intensities are given in parentheses in units of km mol^{-1}. [c] str, stretch.

Table IV. Results of ab Initio Calculations for the Intrinsic Reaction Coordinate of Formyl Cyanide to the Products, HCN and CO[a]

reaction coordinate	energy, kcal mol^{-1}	R_{CC}[b]	R_{CO}	R_{CN}	R_{CH}	∠CCO	∠CCN	∠CCH
–[c]	−80.075	1.4514	1.2040	1.1382	1.0775	123.6462	181.2224	113.5011
−1.792	−78.941	1.5076	1.1965	1.1387	1.0924	124.1641	181.3603	111.5752
−1.595	−73.186	1.6068	1.1845	1.1400	1.0881	125.2700	180.8932	106.1304
−1.397	−63.937	1.7103	1.1733	1.1418	1.0740	125.8796	180.3259	100.3036
−1.197	−52.548	1.8114	1.1628	1.1438	1.0568	126.2254	179.4690	93.4611
−0.999	−40.481	1.9112	1.1531	1.1459	1.0452	126.1121	178.6848	86.7317
−0.700	−22.226	2.0483	1.1402	1.1490	1.0342	125.1377	176.8545	75.4871
−0.600	−16.786	2.0907	1.1364	1.1499	1.0340	124.6621	176.1266	17.9689
−0.500	−11.904	2.1341	1.1328	1.1507	1.0374	124.0676	175.4919	67.9763
−0.400	−7.731	2.1735	1.1296	1.1514	1.0423	123.4667	174.6309	64.2250
−0.300	−4.386	2.2110	1.1267	1.1519	1.0499	122.8813	173.7266	60.5237
−0.200	−1.952	2.2469	1.1243	1.1523	1.0603	122.3174	172.7516	56.8868
−1.100	−0.489	2.2812	1.1223	1.1525	1.0739	121.7964	171.7213	53.3155
0.000[d]	0.000	2.3138	1.1207	1.1524	1.0908	121.3495	170.6532	49.8367
0.100	−0.483	2.3451	1.1196	1.1522	1.1122	120.9920	169.5631	46.4804
0.200	−1.901	2.3750	1.1189	1.1518	1.1379	120.7138	168.4653	43.2590
0.300	−4.223	2.4033	1.1186	1.1512	1.1673	120.5124	167.3815	40.1973
0.400	−7.423	2.4304	1.1186	1.1505	1.2011	120.3821	166.3319	37.3208
0.500	−11.496	2.4564	1.1189	1.1496	1.2391	120.3077	165.3322	34.6385
0.600	−16.409	2.4814	1.1194	1.1487	1.2809	120.2763	164.3905	32.1545
1.000	−42.614	2.5735	1.1225	1.1446	1.4719	120.3090	161.2095	24.0692
1.496	−76.481	2.6889	1.1256	1.1399	1.7516	121.2516	157.2891	16.9105
1.932	−86.640	2.8718	1.1263	1.1377	2.0108	126.3570	152.3920	13.9484
2.421	−90.418	3.1019	1.1259	1.1376	2.2267	138.3443	150.6599	12.6385

[a] Calculations are carried out at HF/3-21G level. [b] Bond lengths are in angstroms; angles are in degrees. [c] Ground state. [d] Transition state.

has passed through its transition state do we observe a significant lengthening of the CH bond along with a further decrease in the CCH angle leading to the transfer of the hydrogen from the CO fragment to the CN fragment. Once the hydrogen passes from primarily being attached to the CO to being linked to the CN, the CO and the CN bonds reverse somewhat their respective shortening and lengthening and there is a substantial increase in the CCO angle. The product molecules, HCN and CO, end up being oriented at approximately 90° to each other with the hydrogen of the HCN oriented toward the carbon of the CO.

Concluding Remarks

In this paper we have described a new technique for the production of pure formyl cyanide. We have also demonstrated that the molecule is far more stable than had previously been realized and that it readily reacts with water to form HCOOH and HCN. We have also shown that the molecule may be trapped at low temperatures and revaporized to room temperature without forming a polymer as described elsewhere. The intrinsic reaction coordinate was followed for the unimolecular decomposition of HCOCN into the products HCN and CO. The high activation energy calculated concurs with the experimental observation that formyl cyanide should be stable in isolation from other (reactive) molecular species.

The next step in our study of this interesting molecule is the spectroscopic characterization of the fundamentals at high resolution using both the diode laser and high-resolution FT-IR techniques. These studies are underway at the present time.