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FTIR Spectra of Cyanamide Complexes with Hydrogen Fluoride in Solid Argon

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Cyanamide vapor was condensed at 12 K with HF in excess argon producing a 1:1 complex of the form H_2NCN--HF. The HF submolecule stretching fundamental was observed at 3458 cm^{-1}, and the HF librational modes appeared at 694 and 686 cm^{-1}, which are very similar to the HF modes observed for the CH_3CN--HF complex. Several perturbed submolecule modes of cyanamide in the 1:1 complex were identified; large perturbations for the C≡N stretch at 2306 cm^{-1} and the N–C stretch at 1113 cm^{-1} and a small blue shift for the NH_2 wag at 427 cm^{-1} support bonding of HF to the nitrile nitrogen. Increasing the HF concentration favored a 1:2 complex H_2NCN--$(HF)_2$ with two HF stretching modes appropriate for an open-chain structure.

Introduction

Cyanamide has been the subject of several investigations, which were primarily concerned with its structure.[1] Detailed microwave studies have shown that cyanamide is nonplanar but substantially flatter than ammonia.[2-4] Gas-phase infrared studies[1] were severely hampered by the rapid polymerization of cyanamide even at room temperature. However, the matrix isolation technique is uniquely suited to study the vibrational spectrum of monomeric cyanamide by retarding aggregation in a solid argon medium.[5]

Matrix isolation has also proven to be very useful for the characterization of hydrogen-bonded complexes between hydrogen fluoride and small base molecules. The structure and bonding of complexes, including such base molecules as HCCH,[6] HCN,[7] CH_3CN,[8] XCN,[9] and CH_3NH_2,[10] have been examined by the matrix method. The purpose of this study is to investigate the complexes between hydrogen fluoride and cyanamide and to compare these results with similar complexes in order to examine the competing effects of electron-donating ($-NH_2$) and electron-withdrawing (–CN) functional groups. Infrared spectra of complexes of hydrogen fluoride with cyanamide and cyanamide-d_2 in solid argon will be described.

Experimental Section

The vacuum, cryogenic, and spectroscopic techniques used have been reported previously.[11,12] All spectra were recorded with a Nicolet 7199 Fourier-transform infrared spectrometer between 4000 and 400 cm^{-1} at 1-cm^{-1} resolution. A single-beam spectrum of the CsI window at 10–12 K was recorded and ratioed as a background to a single-beam spectrum of the sample to produce a simulated double-beam spectrum for each experiment. The reported frequency values were rounded to the nearest wavenumber.

TABLE I: Absorptions (cm^{-1}) Produced on Codeposition of Cyanamide and Hydrogen Fluoride with Excess Argon at 12 K

H_2NCN + HF	H_2NCN + DF	D_2NCN + HF	D_2NCN + DF	assignment
3643	2678	3640	2675	2
3505	3505	2619	2619	$\nu_1{}^c$ (3488, 2597)[a]
3458	2554	3457	2556	ν_s
3427	2548	3426		ν_s (site)
3413	3414	2505	2504	$\nu_7{}^c$ (3400, 2493)
3119	2291	3119	2302	2
3090		3090	2287	2
2316	2312	2307		$\nu_2{}^{cc}$ (2)
2306	2307	2298		$\nu_2{}^c$ (2264, 2262)
		1232	1230	$\nu_3{}^{cc}$ (2)
1583	1582	1224	1225	$\nu_3{}^c$ (1589, 1215)
1279, 1276	963	1278	959	$2\nu_l$
1113	1114			$\nu_4{}^c$ (1061, ...)
780	582	780	582	2
694	508	694	508	ν_l
686, 683	498	684, 682	497	ν_l
598	440	596		2
584	436	587	436	2
427	427			$\nu_5{}^c$ (414, 311)

[a] Values for mode of uncomplexed H_2NCN and D_2NCN, respectively.

Hydrogen fluoride (Matheson), deuterium fluoride, cyanamide (Kodak), dimethylcyanamide (Aldrich), and cyanamide-d_2 were each purified by evacuation at 77 K to remove volatile impurities. Deuterium fluoride was produced by the reaction of F_2 (Matheson) with D_2 (Air Products) at low pressures in a passivated stainless steel vacuum system. Cyanamide-d_2 was prepared from cyanamide by five successive exchanges with D_2O and dried under vacuum.

The acid samples were diluted between 200/1 and 400/1 mole ratios with argon (Air Products). Cyanamide vapor was sublimed into the matrix from a glass finger heated to 30–45 °C, and dimethylcyanamide was evaporated at room temperature into the matrix through a Teflon needle valve. Reagent samples were codeposited on the CsI window at approximately 13 total mmol/h for 4 h. After deposition the matrix was annealed to between 21 and 28 K for 10 min and recooled to 12 K. Spectra were taken before, during, and after sample preparation and annealing. Blank samples were prepared and annealed for each reagent separately.

Results

Fourier-transform matrix infrared spectra of HF and HF/DF mixtures with cyanamide, cyanamide-d_2, and dimethylcyanamide will be described in turn.

Cyanamide. Three experiments were performed with cyanamide and hydrogen fluoride codeposited at 12 K. In the most dilute experiment the spectrum, displayed in Figure 1a, showed HF monomer, dimer, trimer, and tetramer bands (labeled HF, D, T, and C),[13] absorptions due to water and H_2O–HF complexes (labeled W and W^c),[14] bands due to N_2 complexes (labeled N and

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(1) Fletcher, W. H.; Brown, F. B. *J. Chem. Phys.* **1963**, *39*, 2478 (review).

(2) Lide, D. R., Jr. *J. Mol. Spectrosc.* **1962**, *8*, 142.

(3) Miller, D. J.; Topping, G.; Lide, D. R., Jr. *J. Mol. Spectrosc.* **1962**, *8*, 153.

(4) MacDonald, J. N.; Taylor, D.; Tyler, J. K.; Sheridan, J. *J. Mol. Spectrosc.* **1968**, *26*, 285.

(5) King, S. T.; Strope, J. H. *J. Chem. Phys.* **1971**, *54*, 1289.

(6) Andrews, L.; Johnson, G. L.; Kelsall, B. J. *J. Phys. Chem.* **1982**, *86*, 3375.

(7) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1983**, *105*, 163.

(8) Johnson, G. L.; Andrews, L. *J. Phys. Chem.* **1983**, *87*, 1852.

(9) Hunt, R. D.; Andrews, L., manuscript in preparation.

(10) Andrews, L.; Davis, S. R.; Johnson, G. L. *J. Phys. Chem.* **1986**, *90*, 4273.

(11) Kelsall, B. J.; Andrews, L. *J. Phys. Chem.* **1981**, *85*, 1288.

(12) Andrews, L.; Johnson, G. L. *J. Chem. Phys.* **1982**, *76*, 2875.

(13) Andrews, L.; Johnson, G. L. *J. Phys. Chem.* **1984**, *88*, 425.

(14) Andrews, L.; Johnson, G. L. *J. Chem. Phys.* **1983**, *79*, 3670.

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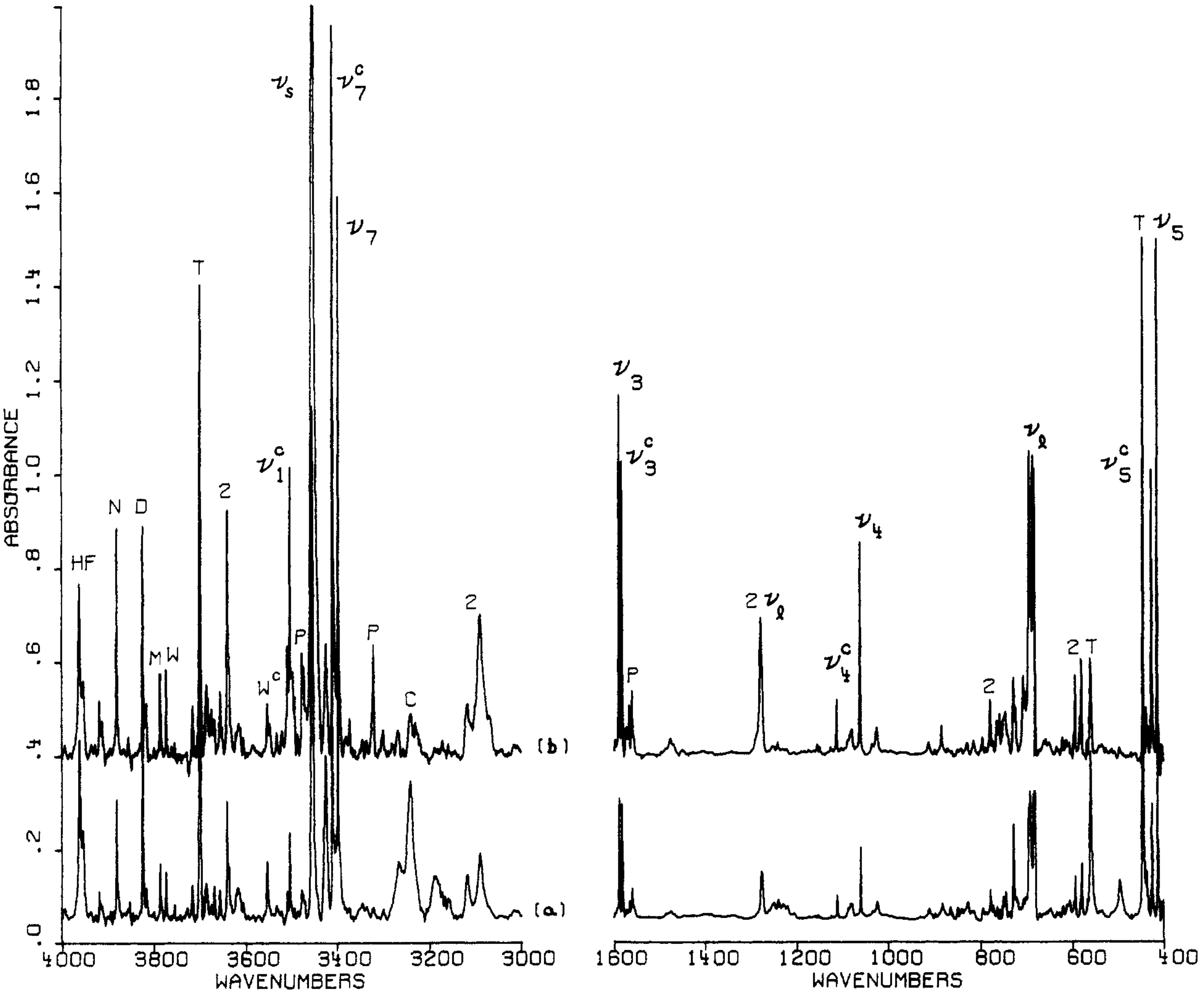

Figure 1. FTIR spectra of cyanamide–hydrogen fluoride samples: (a) matrix formed by codeposition of cyanamide (30 °C) and 47 mmol of Ar/HF = 400/1 at 12 K; (b) matrix formed by codeposition of cyanamide (40 °C) and 54 mmol of Ar/HF = 400/1 at 12 K. P denotes precursor aggregate band.

M),[15] and strong precursor absorptions. New product absorptions included a strong sharp band at 3458 cm^{-1} (A = absorbance = 1.1, labeled ν_s) with a satellite band at 3427 cm^{-1} (A = 0.34), a sharp doublet (labeled ν_l) at 694 (A = 0.25) with one component split at 686 and 683 cm^{-1}, and a weaker split band (labeled $2\nu_l$) at 1279 and 1276 cm^{-1}. Other weaker product absorptions (labeled 2) involving HF are given in Table I. In addition, an unusually large number of new precursor satellites were seen at 3505, 3413, 2306, 1583, 1113, and 427 cm^{-1}. Due to the extensive amount of aggregation that occurred during sample deposition, annealing the matrix to 20 and 28 K failed to produce any significant changes in the spectrum. In the most concentrated experiment (Figure 1b) the *2* bands were considerably stronger.

Three additional experiments were performed with DF/HF mixtures. The absorptions observed in the HF experiments were again present. In the most dilute DF/HF experiment, displayed in Figure 2a, new absorptions specific to the DF system appeared at 2554 cm^{-1} (A= 0.57, labeled ν_s), at 508 and 498 cm^{-1} (labeled ν_l), and at 963 cm^{-1} (labeled $2\nu_l$). Additional DF absorptions (labeled 2) and perturbed base submolecule modes due to DF product complexes are listed in Table I. Again annealing the sample failed to produce any major changes. In the most concentrated experiment (Figure 2b), the 2 absorptions were considerably stronger.

Cyanamide-d_2. Four experiments were performed with D_2NCN and HF. Very little H_2NCN was present in the spectra which appeared very similar to those in Figure 1 with small displacements in the HF submolecule bands as shown in Table I; four perturbed D_2NCN submolecule modes were also observed. The samples deposited in two experiments with DF/HF mixtures are illustrated in Figure 3. Sample annealing to 29 K produced counterparts of the product bands (labeled 2) described previously.

Dimethylcyanamide. Similar experiments were done with dimethylcyanamide vapor at room temperature codeposited with HF. New product bands were observed at 3459 cm^{-1} (ν_s) and 696, 687 cm^{-1} (ν_l) with lower yield than found for cyanamide.

Discussion

The new product bands will be identified, and vibrational assignments will be made. The structures and bonding of the cyanamide complexes will be compared to other similar complexes.

Identification. The product absorptions listed in Table I were not seen in argon matrix samples of cyanamide or hydrogen fluoride. However, these bands were seen in high yields when the reagents were mixed during condensation. Two groups of HF product absorptions can be identified based on sample concentration. Bands of the first group were strong after sample deposition even in the most dilute experiment, and they increased by over a factor of 3 in the most concentrated experiment. Absorptions of the second group were weak following reagent condensation, and they increased by a factor of almost 2 in the more concentrated experiments.

The first group of absorptions with labels ν_s and ν_l were very strong after sample deposition indicating that the bands belong to the major product species. This group of bands maintained constant relative intensities over a wide range of sample concentrations. These observations indicate that the first group of

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(15) Andrews, L.; Kelsall, B. J.; Arlinghaus, R. T. *J. Chem. Phys.* **1983**, *79*, 2488.

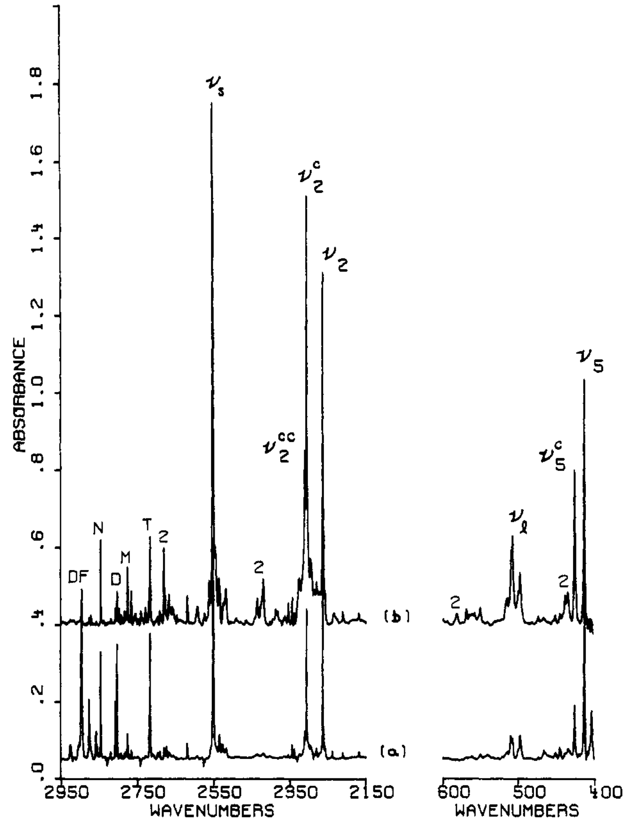

Figure 2. FTIR spectra of cyanamide–deuterium fluoride samples: (a) matrix formed by codeposition of cyanamide (32 °C) and 34 mmol of Ar/(DF + HF) = 300/1 at 12 K; (b) matrix formed by the codeposition of cyanamide (30 °C) and 54 mmol of Ar/(DF + HF) = 200/1 at 12 K.

absorptions can be assigned to the 1:1 complex **1** between cyanamide and HF. The second group of HF product absorptions exhibited a higher order concentration dependence on HF which is characteristic of 1:2 complexes, **2**.

$H_2N{-}C{\equiv}N{:}{-}{-}H{-}F$

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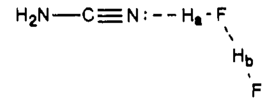

$H_2N{-}C{\equiv}N{:}{-}{-}H_a{-}F{-}{-}H_b{-}F$

2

In addition to the HF submolecule absorptions, six product bands can be identified for perturbed submolecule modes of cyanamide. The two groups of cyanamide product absorptions can be separated by sample concentration in the same way that the HF product bands were identified. The bands (labeled ν^c) exhibited the same HF concentration dependence as the HF product bands for the 1:1 complex while the cyanamide absorptions (labeled ν^{cc}) have the HF concentration pattern of the 1:2 complex.

Assignments. The strong, sharp primary product absorptions labeled ν_s have similar DF counterparts with HF/DF ratios of 1.345 to 1.354 which is characteristic of the fundamental vibration of the H–F ligand in the primary complex **1**. The very small shift in the ν_s bands when NH_2 was replaced by ND_2 indicates that a cyanamide–HF complex is formed and provides further evidence of the H–F nature of this vibration. These absorptions are appropriately red shifted from the 3919-cm^{-1} HF fundamental in solid argon[13] due to the hydrogen-bonding interaction. The ν_l doublet at 694 and 686 cm^{-1} is assigned to the two librational motions of the HF submolecule in the 1:1 complex arising from the two rotational degrees of freedom from the diatomic. The sharp doublet is resolved for the two libration directions and the components have almost identical HF/DF ratios (1.366, 1.378). The small (8 cm^{-1}) splitting and similar isotopic ratios indicate that the potential surfaces for the two libration directions are nearly identical. The smaller subsplitting (3 cm^{-1}) is presumably due to a steric effect for one of the librational mode directions.

TABLE II: Comparison of H–F Stretching and Librational Modes (cm^{-1}) for Cyanamide and Similar Complexes

complex	ν_s (argon)	ν_l (argon)
C_2H_2- -HF	3745	426, 382
C_2H_4- -HF	3730	424, 396
HCN- -HF	3626	586
CH_3CN- -HF	3483	680
$(CH_3)_2NCN$- -HF	3459	696, 687
H_2NCN- -HF	3458	694, 686
H_3N- -HF	3041	916
$(CH_3)H_2N$- -HF	2816	1036, 869

One overtone band, which appeared as a singlet or doublet depending on the deuteriation of the reagent, was observed for the split ν_l mode with an overtone/fundamental ratio of 1.866 for HF and 1.934 for DF showing more anharmonicity for the HF librational motion.

The six perturbed cyanamide submolecule modes in the complex are compared in Table I with cyanamide itself; assignments are based on band position and isotopic data. Although moderate blue shifts (13–17 cm^{-1}) were observed for the N–H stretching modes, large blue shifts were observed for the C≡N stretching mode (42 cm^{-1}) and the N–C stretching mode (52 cm^{-1}) and a small blue shift was observed for the NH_2 wag (13 cm^{-1}). The vibrational modes in the complex reveal the structure of the complex.

Comparisons, Bonding and Structure. Even though cyanamide is a relatively simple molecule, it has three potential bonding sites for HF in the 1:1 complex. The sites are the lone pair on the amine nitrogen (i.e. NH_3 and CH_3NH_2 complexes),[10,16] the lone pair on the nitrile nitrogen (i.e. HCN and CH_3CN complexes),[7,8] and the π system (i.e. C_2H_2 complex).[6] On the basis of the positions of ν_s and ν_l, the ν_l splitting, and the perturbations of cyanamide submolecule modes, the structure of the 1:1 complex is similar to the HCN–HF[7] and CH_3CN–HF[8] complexes. The ν_s and ν_l modes, which are most indicative of bonding and structure, are compared in Table II for cyanamide and other potentially similar bases. The ν_s and ν_l modes for H_2NCN- -HF are very close to those of CH_3CN- -HF. In fact, the major difference between the H_2NCN and CH_3CN complexes is the small ν_l splitting (8 cm^{-1}) in the cyanamide complex. For the proposed complex structure this splitting in ν_l is caused by the lowering of symmetry owing to the NH_2 substituent. If HF were bonded to the lone pair on the amine nitrogen or the π system, the asymmetry and splitting would be larger, based on C_2H_2 and CH_3NH_2 complexes as examples.[6,10] The observed ν_s and ν_l modes require bonding of HF to the nitrile lone pair in the H_2NCN- -HF complex.

Experiments were performed with dimethylcyanamide to compare the effect of methyl substitution with the large effect found for methylamine complexes.[10] The ν_s (3459 cm^{-1}) and ν_l (696, 687 cm^{-1}) values for $(CH_3)_2NCN$- -HF are essentially unchanged from the H_2NCN- -HF values. The absence of a methyl effect indicates nitrile attachment for the HF ligand in the cyanamide complexes. In this case, dimethyl substitution did not increase the basicity of the amine lone pair enough to exceed the basicity of the nitrile lone pair, which led to hydrogen bonding at the nitrile site.

Perturbed submolecule modes of cyanamide are also valuable sources of information about the site of attachment of HF in the complex. One expects the greatest perturbation to occur for the submolecule mode(s) that include atoms involved in the hydrogen bond. The NH_2 stretching and bending modes are blue shifted by 13 cm^{-1} at most while the C≡N stretch, ν_2, and the N–C stretch, ν_4, were blue shifted by 42 and 52 cm^{-1}, respectively. A similar shift in the C≡N stretch (+39 cm^{-1}) was observed for the CD_3CN- -HF complex[8] while the perturbation of the C≡C stretch in the C_2H_2 complex was considerably less (±2 cm^{-1}).[6]

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(16) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1982**, *104*, 3043.

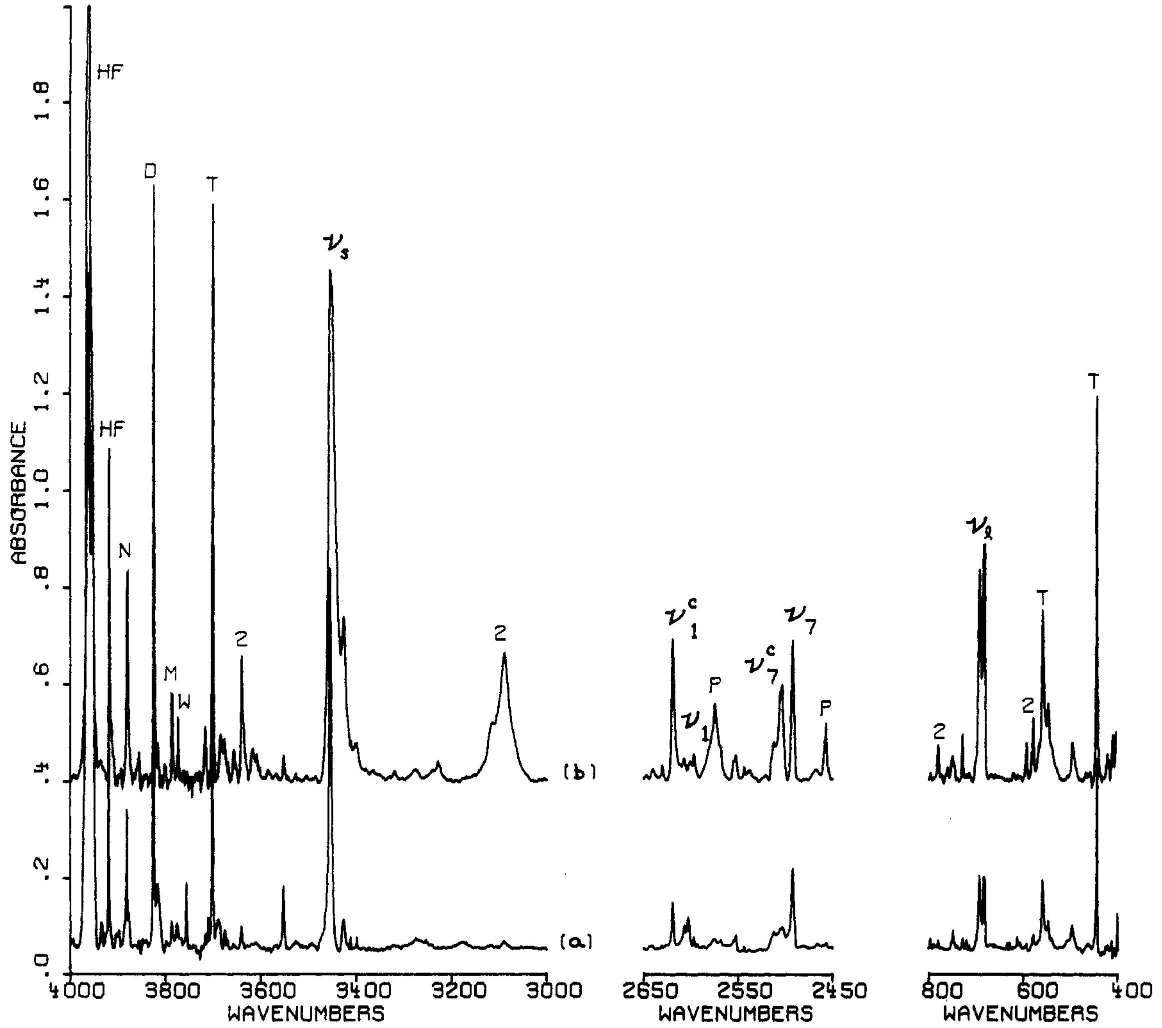

Figure 3. FTIR spectra of cyanamide-d_2-hydrogen fluoride samples: (a) matrix formed by codeposition of cyanamide-d_2 (39 °C) and 56 mmol of Ar/HF = 400/1 at 12 K; (b) matrix formed by codeposition of cyanamide-d_2 (45 °C) and 29 mmol of Ar/HF = 200/1 at 12 K.

On the other hand, the large blue shift in the NH_2 wag found in the CH_3NH_2--HF complex (+137 cm^{-1}) is not matched by the small blue shift (+13 cm^{-1}) in this mode (ν_5) for cyanamide in the HF complex. This evidence strongly indicates that HF does not bond to the lone pair on the amine nitrogen but does in fact bond to the nitrile lone pair. On the basis of the perturbed base submolecule modes, as well as ν_s and ν_l, the structure of the cyanamide complex must be $H_2NC{\equiv}N$--HF.

It is interesting to compare the proton affinities of ammonia (203 ± 2 kcal/mol)[17] and acetonitrile (188 ± 2 kcal/mol)[18] with cyanamide (220 kcal/mol value calculated for the optimized NH_3^+CN structure, which is estimated by comparison to NH_3 to be 50 kcal/mol too high; this predicts an experimental value of 170 ± 5 kcal/mol for the amine proton affinity of cyanamide).[19] The ν_s fundamentals of CH_3CN--HF and NH_2CN--HF are close enough to suggest similar nitrile proton affinities for these two bases. Since the $-NH_2$ substituent is electron donating and activating for electrophilic aromatic substitution, as is the $-CH_3$ substituent, NH_2CN should have a higher nitrile proton affinity than HCN, as does CH_3CN.[18] In fact the greater electron-donating ability of $-NH_2$ as compared to $-CH_3$ suggests an even higher nitrile basicity for NH_2CN relative to CH_3CN, and the larger displacement in ν_s and the higher ν_l modes for NH_2CN--HF support a slightly stronger cyanamide complex. Accordingly, a higher nitrile proton affinity is predicted for cyanamide (190 ± 5 kcal/mol estimate), and the gaseous conjugated acid structure is proposed to be NH_2CNH^+.

While the intermolecular interactions that cause a red-shift of the H–F fundamental in a 1:1 complex are complicated,[20] the larger displacement of ν_s from the isolated molecule value generally indicates a stronger interaction and results from a stronger hydrogen bond and a more stable complex. On the basis of the ν_s values from Table II, it appears that the cyanamide complex might be more stable if HF were bonded to the lone pair on the amine nitrogen, since ν_s values for the NH_3 and NH_2CH_3 complexes[10,16] are 600 cm^{-1} lower than the corresponding nitrile complexes. However, cyanamide is different from ammonia; conjugation, which causes cyanamide to be nearly planar,[2-4] delocalizes the lone pair on the amine nitrogen and decreases its basicity, which allows the σ lone pair on the nitrile nitrogen to become a more basic site than the lone pair on the amine nitrogen. Ab initio calculations show that cyanamide has an unusually low amine proton affinity.[19]

Note Added in Proof: Ab initio Hartree–Fock SCF calculations of amine and nitrile proton affinities for cyanamide were performed using the program HONDO5 with the 6-31G basis set and STO-3G geometry optimization. Theoretical proton affinities for the amine and nitrile sites were found to be 222 and 226 kcal/mol, respectively. The former agrees with a previous report.[19] In an effort to calibrate these theoretical proton affinities to experimental values, theoretical proton affinities of NH_3 and CH_3CN were also obtained by using the same program. The theoretical values for NH_3 and CH_3CN were 56 and 33 kcal/mol, respectively, higher than their experimental values.[17,18] This predicts an experimental

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(17) Collyer, S. M.; McMahon, T. B. *J. Phys. Chem.* **1983**, *87*, 909.

(18) Wolf, J. F.; Staley, R. H.; Koppell, I.; Taagepera, M.; McIver, Jr., R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.

(19) Hopkinson, A. C.; Csizmadia, I. G. *Theoret. Chim. Acta* **1974**, *34*, 93.

(20) Liu, S-Y., Dykstra, C. E. *J. Phys. Chem.* **1986**, *90*, 3097.

value of 166 ± 5 kcal/mol for the amine proton affinity of cyanamide while a higher (193 ± 5 kcal/mol) nitrile proton affinity is predicted for cyanamide. These theoretical calculations provide further evidence that the structure of the gaseous conjugated acid is NH_2CNH^+.

The structure of the 1:2 cyanamide $(HF)_2$ complex is probably open chain based on the position of the two H–F stretching fundamentals. The H_a–F vibration at 3090 cm^{-1} in **2** is displaced more than ν_s of **1** (3458 cm^{-1}) owing to interaction with H_b–F, and the H_b–F mode at 3643 cm^{-1} in **2** is likewise displaced more than the 3826-cm^{-1} value[13] for the H_b–F mode in $(HF)_2$ due to the effect of the base. The 2 bands for the cyanamide complex are very similar to the 2 bands of the 1:2 acetonitrile complex of the same structure.[8,21] The only perturbed submolecule mode assigned to the 1:2 complex is the C≡N stretch. There is no evidence that the second HF bonds to the amine nitrogen or the π system.

Conclusions

In summary, cyanamide and HF reacted to form a strong, well-defined, 1:1 hydrogen-bonded complex of the form H_2NCN--HF in solid argon. The matrix ν_s and ν_l modes compare favorably with CH_3CN--HF observations,[8] providing spectral identification of the 1:1 product as a σ cyanide complex with a linear CN--HF structure. The interaction of HF with the base submolecule perturbed the C≡N stretch, ν_2, much more than the NH_2 submolecule modes. The effect of the –CN substituent on the amine is to withdraw electron density from the lone pair and thereby reduce the basicity of the amine site *and* increase the basicity of the cyanide group; these effects ultimately result in HF attachment to the cyanide substituent. In the more concentrated experiments, an additional HF reaction product was observed. This product was identified as a 1:2 cyanamide–$(HF)_2$ complex with an open chain structure and characterized by considering the perturbation of the second HF submolecule upon the 1:1 complex.

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Registry No. HF, 7664-39-3; DF, 14333-26-7; Ar, 7440-37-1; cyanamide, 420-04-2; cyanamide-d_2, 4850-53-7; dimethylcyanamide, 1467-79-4.

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[21] Davis, S. R.; Andrews, L. *J. Mol. Spectrosc.* **1985**, *111*, 219.

The ΔH for Thermal *trans*-Stilbene/*cis*-Stilbene Isomerization. Do S_0 and T_1 Potential Energy Curves Cross?

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Equilibrium compositions of *trans*- and *cis*-stilbene, attained with atomic iodine as a catalyst in benzene or *tert*-butylbenzene solutions, were measured in the 303.2–461.2 K range. Significant differences from literature values (Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968** 156) are traced to probable interference in earlier analyses by bibenzyl, present as a contaminant in stilbene samples. The temperature dependence of the equilibrium constant *K* for the trans ⇄ cis reaction gives $\Delta H = 4.59 \pm 0.09$ kcal/mol and $\Delta S = 1.05 \pm 0.24$ eu. The ΔH value is sufficiently large to require intersection of S_0 and T_1 potential energy curves close to the perpendicular geometry.

Introduction

The interpretation of the photophysical and photochemical behavior of electronically excited stilbene molecules has been based on the proposed shapes of the potential energy curves for twisting about the central bond.[1] These curves have therefore been the subject of intense theoretical interest.[2] An evaluation of the various proposals has been hampered by uncertainty in the ground-state energy of the cis, ${}^1c$, relative to that of the trans isomer, ${}^1t$. Values for the enthalpy difference range from 5.7 kcal/mol (liquid trans ⇄ liquid cis), obtained from heats of hydrogenation in glacial acetic acid,[3] to 3.8 kcal/mol, obtained from the heats of combustion,[4] and 2.3 kcal/mol, based on the temperature dependence of *K* for the iodine

$$ {}^1t \overset{K}{\rightleftharpoons} {}^1c \tag{1} $$

atom catalyzed equilibration of the two isomers.[5] The 3.4 kcal/mol uncertainty in the energy of ${}^1c$ is transferred to all points on the potential energy curves which are based on ${}^1c$ through spectroscopic or kinetic observations. Obscured, for example, is the important question of whether or not the ground state and lowest triplet state potential energy curves cross near the perpendicular configuration, p.

Aside from being the most recent, the 2.3 kcal/mol value appeared most attractive because it was based on *K* for toluene solutions under conditions approximating those used in photochemical studies.[5] However, the validity of this value was brought to question by an analysis of activation enthalpies and entropies for endothermic triplet excitation transfer from anthracene and from 9,10-dichloroanthracene to the stilbenes which led to the conclusion that the energy of ${}^1c$ must be at least 3 kcal/mol above that of ${}^1t$.[6] A further concern was that, at the high stilbene/I_2 concentrations employed,[5] stilbene/I_2 complexes might absorb some of the radiation intended for iodine atom generation and through their participation[7] shift $[{}^1c]/[{}^1t]$ ratios away from those reflecting true thermodynamic equilibria. This paper describes a reinvestigation of the iodine atom (thermally and photochemically generated) catalyzed equilibration of the stilbenes which

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[1] For reviews see (a) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1. (b) Saltiel, J.; Charlton, J. L. *Rearrangements in Ground and Excited States*, Vol. 3, de Mayo, P., Ed.; Academic: New York, 1980; p 25.

[2] (a) Gregory, R. A.; Williams, D. F. *J. Phys. Chem.* **1979**, *83*, 2652 (includes a review of earlier work). (b) Orlandi, G.; Palmery, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492.

[3] Williams, R. B. *J. Am. Chem. Soc.* **1942**, *64*, 1395.

[4] Stegemeyer, H. Ph.D. Dissertation, Hannover, 1961, as quoted in ref 5.

[5] Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968**, 156.

[6] Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144.

[7] Yamashita, S. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 972.

0022-3654/87/2091-2755$01.50/0