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Infrared Spectra of Hydrogen-Bonded π Complexes between Hydrogen Halides and Acetylene

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Abstract: Hydrogen-bonded π complexes C_2H_2--H–X have been formed by codeposition of C_2H_2 and HX in excess argon at 15 K and by vacuum-UV photolysis of vinyl halides. The strength of the hydrogen bond, as measured by the displacement of the H–X vibrational fundamental below the isolated HX value, decreases in the series HF, HCl, and HBr as expected. Similar complexes made from di- and trichloroethylenes give slightly higher H–Cl vibrations which show minimal interaction between the halide and the acetylene substituent. The H–F fundamentals for C_2H_4 and C_2H_2 complexes at 3732 and 3747 cm^{-1}, respectively, show that the π electrons in double and triple bonds are comparable hydrogen-bond acceptors.

Introduction

Hydrogen bonding is of significant interest owing to its physical and biological importance. The traditional view of the hydrogen-bonding interaction has been expanded to include many electron-rich systems as the donor species, and in the past decade some experimental and theoretical work has been done on hydrogen-bonding π-electron complexes.[1-3] The present study focuses on the H bond formed between acetylene and hydrogen halide molecules HX (X = F, Cl, Br) through its effect on the H–X stretching vibration.

Recent matrix isolation work has characterized the neutral hydrogen-bonding complexes CH_3--H–F and CH_3F--H–F by H–F stretching modes at 3764 and 3774 cm^{-1}, respectively,[4,5] and the charged complexes $(F\text{–}H\text{--}CF_2)^-$ and $(F\text{–}H\text{--}CHF)^-$ by H–F fundamentals at 3562 and 3124 cm^{-1}, respectively.[6,7] In contrast, the HF diatomic fundamental is at 3962 cm^{-1} in solid argon.[8] The displacement of the H–F stretching mode to lower frequency is a measure of the strength of the H bond in the complex,[9] and the large shifts observed for the charged complexes may help determine the electron distribution in these anions.

Hydrogen halide–acetylene or olefin complexes of the type studied here are possible intermediates in addition reactions of these materials. Hydrogen chloride infrared laser emission has been observed following vacuum-UV photolysis of dichloroethylenes in the gas phase, and the isomeric form of the precursor was found to influence the population of HCl vibrational levels.[10] Parallel studies of the vacuum-UV photolysis of dihaloethylenes during condensation in solid argon trapped a complex of HX and HC≡CX, which is probably a primary photolysis product. Here follows an experimental study of the synthesis and spectroscopy of π complexes between acetylene and hydrogen halides.

Experimental Section

Acetylene–hydrogen halide complexes were formed by vacuum ultraviolet photolysis of haloethylenes and by codepositing hydrogen halides and acetylene with excess argon at 15 K. The cryogenic apparatus and the vacuum-UV photolysis technique have been described previously.[11,12] The various substituted ethylenes, 1,1-dichloro-, *trans*-dichloro-, trichloro-, tetrachloro-, 1,2-dibromo-, vinyl bromide (Aldrich Chemical Co.), vinyl fluoride, *cis*-difluoro- (Peninsular Chemresearch), and vinyl chloride (Matheson) were purified through fractional distillation on a vacuum line. HF and DF were produced by the reaction of F_2 (Matheson) with H_2 (Air Products) or D_2 (Airco) at very low pressures in a stainless steel vacuum system. Hydrogen bromide, hydrogen chloride, and chlorine (Matheson) and deuterium chloride (Merck Sharpe and Dohme) were used as received. Acetylene (Matheson) and C_2D_2 (Merck Sharpe and Dohme) were frozen and evacuated to remove volatile impurities. *cis*-1,2-Dichloroethylene (Aldrich, 65%) was purified on a preparative gas chromatograph. *cis*- and *trans*-dichlorodideuterioethylene were prepared by reacting C_2D_2 with Cl_2 and separating the isomers on a gas chromatograph. *cis*-$C_2D_2F_2$ was formed by exchange with the hydrogen compound in $NaOD/D_2O$ at 90 °C for 2 days.[13] Argon matrix gas (Air Products) was used without further purification.

Samples were diluted with argon (Ar/sample = 400/1) and deposited at 2–3 mM/h for about 12–18 h with 1048–1067-Å photolysis

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of haloethylenes and for 2-8 h when reacting HX with C_2H_2. Spectra were recorded with a Beckman IR-12, calibrated against standard vibration-rotation lines;[14] band positions are reported to the nearest 1 cm^{-1}.

Results

Hydrogen Chloride. Argon/acetylene and argon/hydrogen chloride samples (100/1 concentration) were codeposited at 14 K for 2 h and a sharp, strong new product band appeared at 2764 cm^{-1} (absorbance = A = 0.36, full width at half-maximum = fwhm = 5 cm^{-1}), which is shown in Figure 1a along with HCl monomer bands at 2888 and 2854 cm^{-1}, HCl dimer at 2818 cm^{-1}, and trimer at 2791 cm^{-1} in accord with the assignments of Barnes et al.[15] The sample was subjected to 220-1000-nm photolysis with a high-pressure mercury arc; the 2764-cm^{-1} band was unchanged and vinyl chloride absorptions were not produced. In the next experiment, an Ar/C_2H_2 = 400/1 sample was deposited for 3 h and the acetylene spectrum was observed as a very strong, sharp 737-cm^{-1} band with sharp, weak 745- and 751-cm^{-1} satellites, a moderately intense, sharp peak at 1335 cm^{-1}, and a strong, sharp doublet at 3303, 3290 cm^{-1}, with satellites at 3272 and 3241 cm^{-1}. Upon codeposition of an Ar/HCl = 100/1 sample with the Ar/C_2H_2 = 400/1 mixture for an additional 2 h, the HCl bands, the strong 2764-cm^{-1} product band, and new 752-cm^{-1} absorption appeared. In the reverse process, an Ar/HCl = 100/1 sample was deposited for 5 h, giving the HCl spectrum, and when acetylene was added in further codeposition, the strong 2764-cm^{-1} product band and additional 752-cm^{-1} absorption reappeared.

The cocondensation reaction of HCl and C_2D_2 produced the 2764-cm^{-1} product absorption (A = 0.12) unshifted within experimental error, and a new, weak 555-cm^{-1} band (A = 0.04). Deuterated acetylene alone gave strong bands at 542, 1044, and 2439 cm^{-1}.

Deuterium chloride was repeatedly exchanged with the vacuum system heated to about 50 °C for 1 day. A fresh Ar/DCl = 100/1 sample deposited for 5 h revealed the HCl bands from exchange with the vacuum system and new DCl bands at 2089, 2069, 2039, and 2018 cm^{-1}.[15] The sharp 2764-cm^{-1} product band and its 2004-cm^{-1} deuterium counterpart, shown in the spectrum of Figure 1b, appeared in the spectrum after codeposition of an Ar/C_2H_2 = 400/1 sample for 6 h with more of the HCl/DCl mixture. No intermediate product absorption was observed. A subsequent experiment with HCl/DCl and C_2D_2 producted the same 2764- and 2004-cm^{-1} product bands only after the C_2D_2 reagent was added to the condensing mixture.

The above cocondensation studies were performed in an attempt to synthesize the species that produced a strong 2764-cm^{-1} absorption in argon resonance photolysis (1048-1067 Å) experiments with vinyl chloride. Part of the spectrum recorded from a sample prepared by codepositing an Ar/CH_2CHCl = 400/1 mixture at 15 K with concurrent vacuum-UV photolysis for 18 h is shown in Figure 1c; the strong 2764-cm^{-1} band (A = 0.43, fwhm = 8 cm^{-1}) is dominant. Strong acetylene absorptions, a sharp 752-cm^{-1} band (A = 0.85, fwhm = 3 cm^{-1}), and chloroacetylene[16] absorptions at 607 and 3330 cm^{-1} were also observed.

Similar argon resonance photolysis experiments with the three dichloroethylene isomers produced acetylene, chloroacetylene at 606 and 3320 cm^{-1}, a new band at 618-621 cm^{-1}, and a strong new absorption at 2784 cm^{-1}, in general agreement with an earlier matrix study.[17] The 2784-cm^{-1} band was strongest in the 1,1-dichloroethylene study (A = 0.40, fwhm = 12 cm^{-1}) illustrated in Figure 1; the cis and trans isomers produced A = 0.2 bands with 12- and 18-cm^{-1} fwhm, respectively. Similar photolysis of a *cis*-$C_2D_2Cl_2$ sample gave C_2DCl at 469 and 2596 cm^{-1}, a new 478-cm^{-1} band, and a strong product absorption at 2016 cm^{-1} (A = 0.27, fwhm = 6 cm^{-1}), the latter of which is shown in Figure 1e.

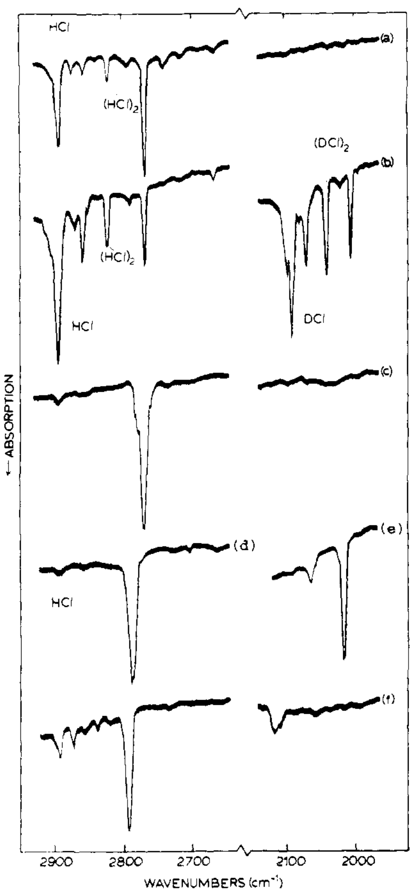


Figure 1. Infrared spectra of complexes between HCl and acetylenes: (a) Ar/C_2H_2 = 100/1 and Ar/HCl = 100/1 samples codeposited for 2 h; (b) Ar/(HCl + DCl) = 100/1 mixture deposited for 5 h followed by codeposition with Ar/C_2H_2 = 400/1 sample for 6 h more; (c), (d), (e), and (f) Ar/reagent = 400/1 samples subjected to concurrent vacuum-UV photolysis for 18 h, reagents (c) C_2H_3Cl, (d) 1,1-$C_2H_2Cl_2$, (e) *cis*-$C_2D_2Cl_2$, (f) C_2HCl_3.

Vacuum ultraviolet photolysis experiments with trichloroethylene produced the dichloroacetylene triplet at 995, 992, 989 cm^{-1}, chloroacetylene at 606, 756, and 3320 cm^{-1}, a new 616-cm^{-1} shoulder, and a strong 2790-cm^{-1} band and HCl absorptions, the latter of which are illustrated in Figure 1f. A similar C_2Cl_4 study produced the dichloroacetylene triplet and weak HCl absorptions with water impurity serving as a hydrogen atom source; no absorption was observed in the 2700-2850-cm^{-1} region.

Laser-Raman experiments were performed on the C_2H_2/HCl reagent mixture using techniques described previously.[18] Raman spectra revealed the strong C≡C fundamental at 1965 cm^{-1} and the symmetric C—H stretching mode at 3350 cm^{-1} without evidence of a new nearby signal. A weak Raman band near 633 cm^{-1} in an Ar/C_2H_2 blank experiment is probably due to C_2H_2. A similar C_2H_2/Cl_2 sample gave the Raman spectrum of C_2H_2 and a strong chlorine fundamental[19] at 550 cm^{-1} without any new product signal.

Hydrogen Fluoride. The infrared spectrum of HF codeposited with acetylene revealed a strong new product absorption at 3747 cm^{-1} (A = 0.20, fwhm = 6 cm^{-1}) which is shown in Figure 2a along with the HF doublet at 3962 and 3954 cm^{-1} and an impurity-perturbed (HF) absorption at 3882 cm^{-1} [8] A new 758-cm^{-1} absorption (A = 0.15, fwhm = 3 cm^{-1}) was observed on the side of the strong acetylene absorption at 737 cm^{-1}, which is also shown in the figure. Experiments were performed depositing the Ar/C_2H_2 gas mixture first and then

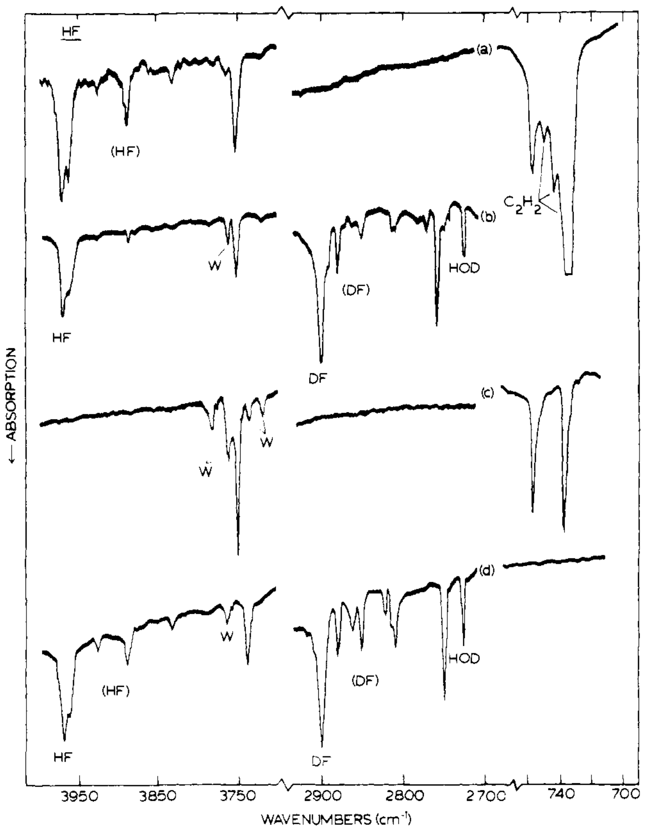


Figure 2. Infrared spectra of HF-acetylene complexes: (a) Ar/C_2H_2 = 400/1 and Ar/HF = 100/1 samples codeposited for 5 h; (b) Ar/C_2H_2 = 400/1 and Ar/(HF + DF) = 100/1, HF/DF ≈ 1/2, codeposited for 5 h; (c) Ar/C_2H_3F = 400/1 sample subjected to vacuum-UV radiation for 12 h during deposition; (d) Ar/C_2H_4 = 400/1 and Ar/(HF + DF) = 100/1, HF/DF ≈ 1/2, codeposited for 6 hr.

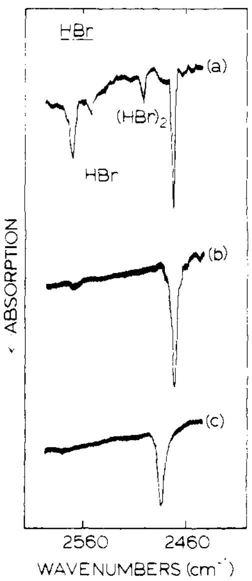


Figure 3. Infrared spectra of acetylene complexes with HBr: (a) Ar/C_2H_2 = 400/1 sample deposited with Ar/HBr = 100/1 sample for 8 h; (b) and (c) Ar/reagent = 400/1 samples photolysed by simultaneous vacuum-UV radiation for 18 h using C_2H_3Br reagent in (b) and a *cis*- and *trans*-$C_2H_2Br_2$ mixture in (c).

adding the Ar/HF reagent to the condensing mixture and condensing Ar/HF first, then adding C_2H_2 to the mixture; in each case the 3747- and 758-cm^{-1} product absorptions required both HF and C_2H_2.

An Ar/HF/DF mixture was deposited at 15 K, and the infrared spectrum contained strong HF and (HF) bands and the DF and (DF) counterparts at 2896 and 2875 cm^{-1}. In the following experiment with greater deuterium enrichment, the Ar/HF/DF mixture (HF/DF ≈ 1/2) was codeposited with an Ar/C_2H_2 sample for 5 h; the spectrum, illustrated in Figure 2b, contained strong new 3747- and 2755-cm^{-1} product bands without an intermediate feature, an HOD impurity at 2719 cm^{-1}, and the 758-cm^{-1} absorption.

Vacuum-ultraviolet photolysis of an Ar/CH_2CHF = 400/1 sample produced the strong, sharp 3747-cm^{-1} absorption (A = 0.36, fwhm = 4 cm^{-1}) and a sharp 758-cm^{-1} band (A = 0.22, fwhm = 3 cm^{-1}), which are shown in Figure 2c. Weak water absorptions at 3784, 3757, 3728, and 3713 cm^{-1},[20] strong acetylene bands at 738 and 3282 cm^{-1}, fluoroacetylene absorptions[16] at 585, 1058, 2240, and 3335 cm^{-1}, and other product absorptions were observed in general agreement with the 1400-1800-Å photolysis study of Guillory and Andrews.[21] Argon resonance photolysis experiments with *cis*-difluoroethylene produced strong fluoroacetylene absorptions at 584, 1058, 2235, and 3335 cm^{-1} and new absorptions at 3778 and 3902 cm^{-1} of particular interest here. The present difluoroethyelene observations are in excellent agreement with previous work.[21] Matrix photolysis of *cis*-$C_2D_2F_2$ yielded strong C_2DF bands[16] at 444, 1044, 2054, and 2632 cm^{-1}, a strong new 2775-cm^{-1} absorption, and a medium-intensity product at 2864 cm^{-1} with a weaker counterpart at 2875 cm^{-1}.

In order to contrast the effect of a different π system on the product spectrum, an Ar/HF/DF sample was codeposited with ethylene. The initial Ar/C_2H_4 = 400/1 deposit exhibited ethylene absorptions at 949, 1439, 2996, and 3114 cm^{-1}. After the reagent mixtures were codeposited for 6 h, strong new product absorptions appeared at 3732 and 2742 cm^{-1} (A = 0.12 and 0.25, respectively, fwhm = 4 cm^{-1}), as shown in Figure 2d, which may be contrasted with the spectrum in Figure 2b from the analogous C_2H_2 experiment performed on the previous day. An additional new band was observed at 974 cm^{-1} (A = 0.13, fwhm = 3 cm^{-1}) near the strong 949-cm^{-1} ethylene absorption; no new feature was observed near the 1439-cm^{-1} ethylene band.

Similar hydrogen fluoride codeposition experiments were performed with vinyl fluoride and *cis*-difluoroethylene. After Ar/CH_2CHF = 400/1 and Ar/HF = 100/1 samples were codeposited for 5 h, a strong 3805-cm^{-1} product (A = 0.30) with 3802-cm^{-1} shoulder and a sharp 3827-cm^{-1} satellite (A = 0.10) appeared in the hydrogen fluoride stretching region and strong new absorptions (A = 0.30) were found at 876, 909, and 1126 cm^{-1}, near completely absorbing CH_2CHF bands at 865, 923, and 1149 cm^{-1}. In the CHFCHF study, a sharp 3865-cm^{-1} band (A = 0.15, fwhm = 4 cm^{-1}) was observed without absorption in the 3900-cm^{-1} region, a sharp new 1710-cm^{-1} band appeared near the intense 1716-cm^{-1} parent absorption, and a strong new 1112-cm^{-1} band was observed adjacent to the completely absorbing 1127-1118-cm^{-1} CHFCHF band.

Hydrogen Bromide. The codeposition of hydrogen bromide with acetylene produced the spectrum shown in Figure 3a. In addition to HBr monomer absorptions at 2569 and 2550 cm^{-1} and the $(HBr)_2$ dimer band at 2497 cm^{-1},[15] a sharp, strong product band was observed at 2467 cm^{-1} (A = 0.22, fwhm = 3 cm^{-1}), and additional absorption was observed at 750 cm^{-1} on top of the weak 751-cm^{-1} site for acetylene. A similar study with C_2D_2 produced the same 2467-cm^{-1} absorption.

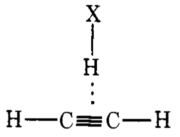
Argon resonance photolysis of an Ar/CH_2CHBr = 400/1 sample for 14 h with a 1-mm diameter orifice discharge tube gave acetylene at 737 cm^{-1} (A = 0.21), bromoacetylene[16] at 617 cm^{-1} (A = 0.01), and new bands at 750 (A = 0.24) and 2467 cm^{-1} (A = 0.17); mercury arc photolysis (220-1000 nm) of this sample for 30 min slightly decreased all CH_2CHBr precursor absorptions and increased the above product bands, 737 (to A = 0.42), 617 (to A = 0.10), 750 (to A = 0.54), and 2467 cm^{-1} (to A = 0.45). A similar irradiation for 18 h with a 3-mm diameter orifice discharge tube gave increased yields of the product bands; the 750- (A = 0.55, fwhm = 3 cm^{-1}) and 2467-cm^{-1} (A = 0.36, fwhm = 6 cm^{-1}) absorptions are of particular interest, the latter of which is shown in Figure 3b. A mixture of *cis*- and *trans*-1,2-dibromoethylene subjected to a similar treatment produced strong acetylene bands, 616- and 3324-cm^{-1} bromoacetylene absorptions, and the 2479-cm^{-1} band (A = 0.12, fwhm = 7 cm^{-1}) shown in Figure 3c.

Discussion

The 3747-, 2764-, and 2467-cm^{-1} absorptions are due to a molecular species formed by the reaction of HF, HCl, and HBr, respectively, with C_2H_2. These product absorptions are displaced 215,124,102 cm^{-1} below the corresponding HX monomer absorptions in solid argon; this displacement is appropriate for a perturbed H–X vibration in a molecular complex. The HX/DX ratios for the complexes are essentially the same as for the monomer: HF/DF = 3962/2896 = 1.368, complex ratio = 1.362; HCl/DCl = 2888/2089 = 1.382, complex ratio = 1.379. The isotopic ratios for the complexes further characterize the new product absorptions as H–X fundamental vibrations. Deuterium-substituted acetylene did not affect the π complex band position. The observation of sharp product bands (fwhm = 3-6 cm^{-1}), which are quite sharp for a hydrogen-bonded species, shows that the molecular complex has a unique, well-defined structure. It is proposed that the cocondensation reaction of hydrogen halides with acetylene produces a "T-shaped" complex, **1**, with hydrogen bonding between the acid hydrogen and the acetylene π electron cloud.

The present π complexes of C_2H_2 with HF, HCl, and HBr combined with the Barnes et al. data[2] assigned here to the analogous HI complex (observed at 2187 cm^{-1}, below HI monomer at 2255 cm^{-1}) show the expected spectroscopic trend with decreasing hydrogen bond strength. The displacements below the isolated HX fundamental value decrease by 215, 124, 102, and 68 cm^{-1} for the HF, HCl, HBr, and HI series which represent 5.4, 4.3, 4.0, and 3.0% decreases in the HX fundamental.

The vacuum ultraviolet photolysis studies of haloethylenes also provide data on these complexes. The vinyl fluoride, chloride, and bromide work produced identical absorptions with slightly increased fwhm as the corresponding HF, HCl, and HBr–acetylene complexes. This shows that photoelimination of HX from the CH_2CHX precursors followed by trapping of the C_2H_2 and HX products as the hydrogen-bonded complex **1** occurs. The observation of C_2H_2 in the vinyl halide experiments also shows that HX elimination is a major photochemical process, as demonstrated by earlier work.[21]



$$\begin{array}{c} X \\ | \\ H \\ \vdots \\ H-C\equiv C-H \end{array}$$

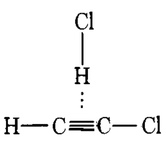
1

An additional strong, sharp absorption was observed at 758 cm^{-1} in the vinyl fluoride experiments, 752 cm^{-1} with vinyl chloride, and 750 cm^{-1} with vinyl bromide. These bands exhibited constant relative intensities with the 3747-, 2764-, and 2467-cm^{-1} H–X vibrations in the complexes in different experiments, on sample warming and photolysis. In particular, photolysis of CH_2CHBr produced a marked *increase* in the 2467- and 750-cm^{-1} bands. The 758-, 752-, and 750-cm^{-1} absorptions were also observed in the HX + C_2H_2 studies, but, owing to the large excess of unreacted acetylene and the presence of weak 751- and 745-cm^{-1} C_2H_2 satellite absorptions, their identification is less definitive in C_2H_2 experiments. A possible counterpart for C_2D_2 in the $C_2D_2\cdots$HCl complex was found at 555 cm^{-1}.

The 758-, 752-, and 750-cm^{-1} absorptions are probably due to the strongly absorbing bending mode of acetylene in the complex. The bending mode is the strongest infrared absorption for C_2H_2, and its observation in the complex is reasonable. Since the hydrogen bond in the HF complex is stronger, a larger perturbation on the 737-cm^{-1} bending mode of C_2H_2 is expected by HF; this perturbation decreases with HCl and HBr, as indicated by the decrease in displacement of the complex bending mode from the acetylene value.

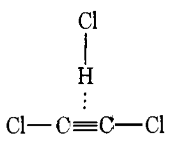
The HF complex with ethylene also exhibited a perturbed bending mode for ethylene in the complex. The sharp 974-cm^{-1} product band, 25 cm^{-1} above the strong out-of-plane bending mode for ethylene at 949 cm^{-1}, is appropriate for the ethylene complex and supports the identification of the bending mode in the acetylene complexes. This observation of a perturbed out-of-plane bending mode for C_2H_4 in the H–F complex, and the lack of a perturbed in-plane bending mode, shows that the hydrogen-bonded H–F molecule is perpendicular to the molecular plane, as expected owing to the π electron density in the double bond.

The data on complexes produced from dichloroethylene photolysis demonstrate the absence of bonding interaction between the hydrogens on C_2H_2 and the chlorine in HCl. Any interaction between the chlorine in HCl and the acetylene hydrogens would be substantially affected by chlorine substitution in the acetylene positions. The complexes produced from dichloroethylene photolysis, **2**, absorb at 2784 cm^{-1}, just 20 cm^{-1} higher than the $C_2H_2\cdots$HCl complex, and the complex produced from trichloroethylene, **3**, exhibits an H–Cl stretch at 2790 cm^{-1}. Hence, chlorine substitution at the carbon position to give **2** and **3** from **1** has little effect on the hydrogen-bond strength as measured by the H–Cl vibrational frequency. The small differences among **1**, **2**, and **3** may be due to an inductive effect of the chlorine substituents on the π bond which contract and strengthen the C≡C bond and render it less basic. The increase in C≡C stretching fundamentals from 1974 cm^{-1} for C_2H_2 to 2110 cm^{-1} for C_2HCl[16] and 2234 cm^{-1} for C_2Cl_2[22] supports this trend. The 618-621 cm^{-1} band observed just above the 606-cm^{-1} C_2HCl absorption in dichloroethylene experiments is probably due to the bending mode of C_2HCl in **2**, analogous to the 752-cm^{-1} bending mode in **1**.



$$\begin{array}{c} Cl \\ | \\ H \\ \vdots \\ H-C\equiv C-Cl \end{array}$$

2



$$\begin{array}{c} Cl \\ | \\ H \\ \vdots \\ Cl-C\equiv C-Cl \end{array}$$

3

The complex formed from dibromoethylene photolysis exhibits an H–Br fundamental at 2479 cm^{-1}, just 12 cm^{-1} above the $C_2H_2\cdots$HBr complex and consistent with a small shift due to the weaker inductive effect of a bromine substituent. On the other hand, the complex formed from difluoroethylene at 3778 cm^{-1} absorbs 31 cm^{-1} above the $C_2H_2\cdots$HF complex, a larger shift owing to the stronger inductive effect of fluorine. These new absorptions are assigned to the bromine and fluorine counterparts of **2**, respectively. Observation of the monohaloacetylenes in all three dihaloethylene vacuum-UV photolysis studies further verifies HX photoelimination in these experiments.

The 3902-cm^{-1} product absorption was favored over the 3778-cm^{-1} complex in difluoroethylene experiments with the 1-mm orifice discharge tube, whereas the 3778-cm^{-1} band was favored with larger orifice tubes and in the earlier studies.[21] The 3902-cm^{-1} band exhibits a deuterium counterpart at 2864 cm^{-1} and approximately the same HF/DF ratio as the hy-

Table I. Hydrogen-Halide Stretching Fundamentals (cm^{-1}) in π Complexes with Acetylene, Substituted Acetylenes, and Ethylene

X	HX	C_2H_2—H-X	C_2HX—H-X	C_2X_2—H-X	C_2H_4—H-X	DX	C_2H_2—D-X	C_2HX—D-X	C_2H_4—D-X
F	3962	3747	3778		3732	2896	2752	2775	2742
Cl	2888	2764	2784	2790	2753[a]	2089	2004	2016	
Br	2569	2467	2479		2455[a]				
I	2255	2187[a]			2177[a]				

[a] Data from ref 1.

drogen-bonded complexes, and it is tentatively associated with a $C_2HF \cdots HF$ complex having a different structural arrangement, perhaps a σ complex such as $H—C\equiv C—F \cdots HF$.

Hydrogen fluoride was codeposited with CH_2CHF and *cis*-CHFCHF to test for a possible fluorine substituent effect on the resulting π complex with HF. The dominant new absorptions at 3805 and 3865 cm^{-1} in these experiments are probably due to the corresponding π complexes. The decrease in displacement of the HF stretching fundamental below the isolated 3962-cm^{-1} value follows an increase in the C═C stretching fundamental from 1623 cm^{-2} for C_2H_4, 1652 cm^{-1} for CH_2CHF, and 1716 cm^{-1} for CHFCHF which should parallel a decrease in basicity of the π bond. The fluorine in vinyl fluoride may be involved to some degree in the bonding interaction with HF as suggested by the observation of a possible C-F stretching mode in the complex at 1126 cm^{-1} below the parent band at 1149 cm^{-1}. A possible C-F mode in the difluoroethylene complex at 1112 cm^{-1} exhibits a smaller 6- or 15-cm^{-1} displacement suggesting that the two C-F bonds in the symmetrical complex may not be involved in the bonding with HF. The 1710-cm^{-1} product band may be due to the C═C stretching mode in the complex, which is displaced just 6 cm^{-1} below the isolated precursor absorption. This shows that the complex has little effect on the π bond itself, which may rationalize the failure to observe a distinct Raman signal for the C≡C stretching mode in the $C_2H_2 \cdots HCl$ complex.

Table I collects the data for the hydrogen halide π complexes reported here and the previous hydrogen iodide observations.[1,2]

Berry and Pimentel have obtained HCl vibration-rotation laser emission from vacuum-UV photolysis of dichloroethylenes.[10] The different dichloroethylene isomers expelled HCl with differing amounts of vibrational energy. The trans isomer was found to have the least overall vibrational excitation and presumably the most translational energy. The 1,1-dichloroethylene isomer gave the highest vibrational excitation. Although the photolysis radiation from the microwave discharge through argon is more energetic, the results mesh nicely with the laser observations. The 1,1-dichloroethylene photolysis produced a very strong 2784-cm^{-1} band, almost twice the absorbance of the cis and trans isomer bands. A possible explanation is that the HCl expelled from the cis and trans compounds has lower vibrational energy but higher translational energy (assuming the same energy in the photofragments from each isomer) making the escape of HCl from C_2HCl more likely. The 1,1 isomer, with more vibrational and correspondingly less translational energy, may form the complex more easily leading to a more intense product band.

The C_2H_2--H-F complex reported here has an H-F fundamental at 3747 cm^{-1} near the H-F modes in the neutral complexes CH_3--H-F at 3764 cm^{-1} and CH_3F--H-F at 3774 cm^{-1}.[4,5] These values are substantially higher than H-F fundamentals for the charged complexes $(F\text{-}H\text{--}CF_2)^-$ and $(F\text{-}H\text{--}CHF)^-$ at 3562 and 3124 cm^{-1}, respectively.[6,7] This is consistent with the suggestion that the charge distribution is $F\text{-}H\text{--}(CF_2)^-$ and that a stronger hydrogen bond is formed to the more basic anion giving a greater reduction in the H-F vibration. A similar comparison may be made for H-Cl vibrations in C_2H_2--H-Cl at 2764 cm^{-1} and $Cl\text{-}H\text{--}(CF_2)^-$ at 2688 cm^{-1} and for the H-Br vibrations in C_2H_2--H-Br at 2467 cm^{-1} and $Br\text{-}H\text{--}(CF_2)^-$ at 2408 cm^{-1}.[16]

Conclusions

The hydrogen-bonded π complexes C_2H_2--H-X have been formed by condensation of C_2H_2 and HX with excess argon and by vacuum-UV photolysis of vinyl halides. These complexes were characterized through a strong H-X fundamental vibration shifted below the isolated HX value by hydrogen bonding and by a slightly perturbed bending mode for C_2H_2 in the complex. The HX/DX fundamental ratios for the complexes were essentially identical with the HX monomer value. The data are consistent with a "T-shaped" complex with a moderately strong hydrogen bond between the acid hydrogen and the π electron cloud of acetylene, in agreement with CNDO/2 calculations. Similar complexes made by photolysis of dihalo- and trichloroethylenes give slightly higher H-X vibrations which show minimal interaction between the halide and the acetylene substituents. Small differences between the H-X vibrations in C_2H_2 and C_2H_4 complexes show that the π electrons in double and triple bonds are comparable acceptors of hydrogen bonds.

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