Photochemistry and Dynamics of Vinyl Bromide and Vinyl Iodide in Rare Gas Matrices

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Dilute solid solutions of vinyl bromide in krypton and vinyl iodide in argon were photolyzed at 10 K with a medium pressure mercury lamp. When the vinyl bromide is photolyzed, both hydrogen bromide–acetylene complexes and bromoacetylene are observed as photolysis products. Kinetic analysis shows that the hydrogen bromide–acetylene complexes are the only *primary* photolysis products and that the bromoacetylene is formed by secondary photolysis of the hydrogen bromide–acetylene complexes. Similar results are observed for the photolysis of vinyl iodide, with hydrogen iodide–acetylene complexes the only primary products and iodoacetylene observed as a secondary photolysis product of the hydrogen iodide–acetylene complex. We present the first reported vibrational frequencies for the HI-acetylene complex.

Introduction

The gas phase photochemistry of vinyl halides has been extensively studied. For vinyl bromide two major reaction channels are reported on UV photolysis. Wodtke et al.,[1] using 193 nm excimer laser photolysis, report that the major decomposition channel is C–Br bond scission,

$$H_2C{=}CHBr + h\nu\ (193\ \text{nm}) \rightarrow Br + C_2H_3 \qquad (1)$$

Molecular elimination of HBr,

$$H_2C{=}CHBr + h\nu\ (193\ \text{nm}) \rightarrow HBr + C_2H_2 \qquad (2)$$

is a secondary reaction. Johnson and Price,[2] photolyzing with a broad-band source emitting between 150 and 200 nm, observe the same products, but with the HBr elimination the major channel.

Gas phase photolysis studies of vinyl iodide, while somewhat rarer, give analogous results. Yamashita et al.[3] on photolysis at either 313 or 254 nm observe both vinyl radical production by C–I bond scission,

$$H_2C{=}CHI + h\nu \rightarrow C_2H_3 + I \qquad (3)$$

and elimination of molecular hydrogen iodide,

$$H_2C{=}CHI + h\nu \rightarrow C_2H_2 + HI \qquad (4)$$

In neither experiment was elimination of molecular hydrogen observed. In fact, at these energies, molecular hydrogen elimination has not been observed on photolysis of any vinyl halide.[4]

We are interested in investigating the photochemistry of these molecules in rare gas matrices for several reasons. First, in previous experiments on the medium pressure mercury lamp photolysis of hydrogen bonded complexes of HBr or HI with acetylene,[5–7] bromoacetylene or iodoacetylene was observed as a primary photolysis products. Both gas phase spectroscopic studies[8] and infrared spectroscopic studies in rare gas matrices[9,10] have shown that complexes of hydrogen halides with acetylene have T-shaped geometries, with the hydrogen pointing toward the acetylene triple bond. Since this geometry is favorable for HX addition to a double bond, it is possible that the haloacetylenes are formed from secondary photolysis of vinyl halides formed in an initial photolysis step. This concern is strengthened by the observation of McDonald[9] and Andrews[10] that bromoacetylene is a minor product on UV photolysis of vinyl bromide in an argon matrix. However, these authors did not study the growth behavior of the products, so they could not conclude whether the bromoacetylene was a primary or secondary product.

A second reason that we are interested in studying the photochemistry of these molecules is that in our earlier study[5] the growth kinetics of iodoacetylene arising from photolysis of HI–acetylene complexes showed slightly different kinetics than that of bromoacetylene arising from photolysis of HBr–acetylene complexes. In the case of the HBr–acetylene photolysis[7] the bromoacetylene showed first order growth kinetics. However, in comparison, the iodoacetylene shows a sigmoidal growth in intensity as a function of photolysis time, but with a finite initial slope. Such a growth pattern suggests that there are two processes which result in iodoacetylene formation. Since substantial amounts of vinyl iodide are stabilized in the experiment as well, it is possible that one of the processes which results in formation of the iodoacetylene is secondary photolysis of vinyl iodide. Thus, a comparative study of the matrix photochemistry of vinyl iodide and vinyl bromide would be of interest.

Finally, in a matrix study, it is sometimes possible to detect the presence of photochemical processes which would be minor processes in the gas phase, because the presence of the cage effect can quench channels involving dissociation into radicals.[11] In the case of vinyl halide photochemistry, one of the major reaction channels is bond scission, as represented by reactions 1 and 3. In a matrix, this channel would be almost completely closed due to cage recombination. Thus in a matrix we could conceivably be able to observe minor channels such as H_2 elimination which may be masked under conditions where competition from the C–X bond scission is present.

Experimental Section

For the vinyl bromide experiments, the cryostat was an Air Products CS202 closed cycle helium refrigerator capable of

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cooling our substrate, cesium iodide, to 12 K. The cryostat was equipped with a hydrogen bulb thermometer and an Au (0.07% Fe) vs chromel thermocouple for temperature determinations as well as a resistance heater for annealing or high-temperature depositions. Matrix temperatures were measured to ±0.5 K using the thermocouple and the hydrogen bulb.

The cryostat was place in the beam path of an IBM Instruments IR97 FTIR for sample analysis following depositions and photolyses. It was fitted with CsI windows in the IR ports and a quartz window in the photolysis port. The cryostat could be rotated 90° from the IR beam path in either direction for photolysis or deposition. The FTIR was run at 0.5 cm^{-1} resolution and has a wavelength accuracy of better than 0.1 cm^{-1} as determined by calibration of the spectrometer against the spectrum of HCl(g) taken at high (0.035 cm^{-1}) resolution.

The vacuum lines used for preparation of the mixtures and deposition of the samples were standard glass high vacuum lines capable of vacuums as low as 10^{-6} Torr. Vinyl bromide/Kr mixtures were prepared by placing a desired quantity of vinyl bromide into our vacuum line and freezing it into our sample bulb at 77 K. The bulb was then closed, and the desired quantity of Kr was introduced into the line and frozen in turn into the sample bulb. Finally the bulb was reclosed, and the mixture was allowed to thaw and then mix diffusively for a minimum of 6 hours. Vinyl bromide (Matheson, 99.5%) and Kr (Pacific Oxygen Co., 99.995%) were used without further purification. All matrices for these experiments were deposited at 12 K at rates varying from 0.5 to 2 mmol/h, with the amounts deposited varying from 1 to 4 mmol.

The photolysis source for these experiments was a medium pressure mercury lamp with its pyrex housing cut off. The photolysis procedure was as follows. With the cryostat rotated so that the radiation shield blocked the photolysis beam, the lamp was turned on and allowed to warm for a minimum of 10 minutes. At the end of this period, the cryostat was rotated so that the matrix sample was exposed to the output of the lamp. All photolyses were performed on the front face of the CsI substrate, i.e., the light from the photolysis source did not pass through the substrate before encountering the sample. After each photolysis, a new IR spectrum was recorded in order to determine product growth kinetics.

The apparatus and procedure for the vinyl iodide photolysis experiments were the same as for the vinyl bromide experiments with the following exceptions. The spectrometer for these experiments was a Nicolet 5DX FTIR, with a resolution of 4 cm^{-1}. Gas mixtures were prepared by transferring the desired quantity of each gas into our vacuum line and allowing to mix for 6 h. The matrix gas for these experiments was Ar (Mg Industries, 99.9995%). In these experiments depositions were carried out at 25 K, at a rate between 3–5 mmol/h, and all photolyses and spectroscopy were done at 9.8 K.

Vinyl iodide was synthesized by the reaction of diiodoethane and sodium ethoxide.[12] Sodium ethoxide was prepared by reaction of 4.51 g of sodium metal with 68 mL of ethanol. Diiodoethane (56.52 g, 0.200 mol) was added to the reaction vessel, which was connected to a distillation apparatus. The reaction began at room temperature, and then the reaction vessel was warmed as the reaction proceeded. Product was collected in a cold bath maintained at −55 to −70 °C. The crude product was distilled twice to remove excess ethanol. The product was then washed with sodium thiosulfate to remove unreacted iodine and dried with $CaCl_2$. The vinyl iodide was characterized by GC-MS and ^1H-NMR.

TABLE 1: Product Frequencies and Intensities after 450 Min of Mercury Lamp Photolysis of CH_2CHBr/Kr (1/100)

freq (cm^{-1})	rel peak abs (arb units)	assignt
3888.5	1.7[a]	$\nu_3 + \nu_4$ $HBr\cdot C_2H_2$[b]
3873.0	2.3	$\nu_2 + 2\nu_4 + \nu_5$ $HBr\cdot C_2H_2$
3313.0	15.4	ν_1 C_2HBr
3292.8	29.3	$\nu_2 + \nu_4 + \nu_5$ $HBr\cdot C_2H_2$[c]
3275.2	>100	ν_3 $HBr\cdot C_2H_2$[c]
3267.2	26.9	
3255.2	10.8	
3252.5	9.7	
3250.6	10.3	
2465.1	100	νHBr $HBr\cdot C_2H_2$
1969.9	5.3	$HBr\cdot C_2H_2$
1334.4	28.2	$\nu_4 + \nu_5$ $HBr\cdot C_2H_2$
1214.1	3.1	C_2HBr
1213.2	3.1	C_2HBr
744.5	>100	ν_5 $HBr\cdot C_2H_2$
733.2	>100	ν_5 $HBr\cdot C_2H_2$
614.5	6.3	C_2HBr[d]
612.6	6.7	C_2HBr[d]

[a] The uncertainty for all bands listed here was less than one in the final digit. [b] We have numbered the fundamentals for $HBr\cdot C_2H_2$ as for isolated C_2H_2. [c] The observed frequencies for these two features are a result of a Fermi resonance between ν_3 and $\nu_2 + \nu_4 + \nu_5$. [d] As noted in the Results section, these bands correspond to ν_3, or ν_3 and ν_4 of C_2HBr. We do not have the data necessary to determine which is ν_3 and which is ν_4, or if both are due to an isotopic splitting of the ν_3.

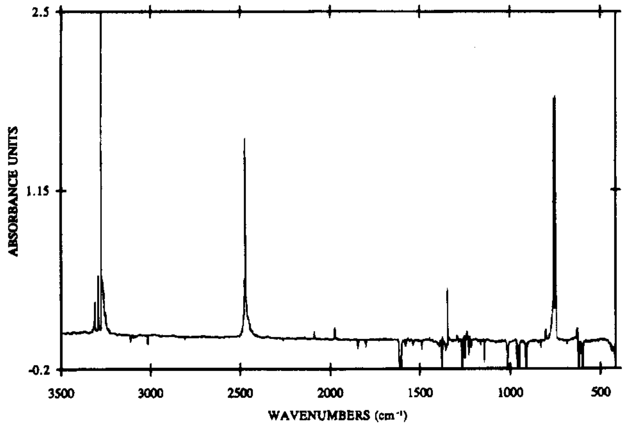

Figure 1. FTIR difference spectrum after 450 min Hg lamp photolysis of C_2H_3Br/Kr (1/100).

Results

C_2H_3Br/Kr = 1/100. A 1/100 sample of vinyl bromide in Kr was prepared and photolyzed. Frequencies and intensities of all product bands are given in Table 1, and the difference spectrum following the final photolysis is given as Figure 1. Absorptions at 3292.8, 3275.2, 2465.1, 1969.9, 1334.4, 745.0, and 733.2 cm^{-1} were very close to the frequencies observed by McDonald[9] for HBr–acetylene in Ar and are assigned to that complex. Due to the relatively high concentrations of our matrices, it is likely that most or all of the absorptions between 3250 and 3270 cm^{-1} are contributed by aggregates of C_2H_2. In addition, peaks at 3313.0, 1214.1, 1213.2, 614.5, and 612.6 cm^{-1} are clearly due to bromoacetylene. These features closely correspond to gas phase spectra of bromoacetylene reported by Hunt and Wilson[5], with bands at 3325, 2085, 618, and 295 cm^{-1}, and to the spectra of the same molecule in Ar matrices reported by Andrews[10] and McDonald.[9] Hunt and Wilson report only one peak in the vicinity of 600 cm^{-1}, at 618 cm^{-1}, but assign it to both the CBr stretch and the CH bend, attributing the coincidence of the features to accidental degeneracy. Their assignment was supported by the appearance of two bands in the appropriate regions in the spectrum of C_2DBr, with isotope

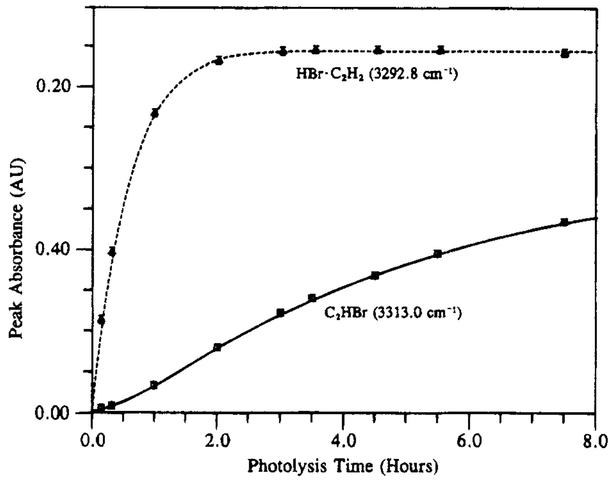

Figure 2. Growth behavior of HBr−C_2H_2 complexes and C_2HBr as a function of Hg lamp photolysis time (C_2H_3Br/Kr = 1/100).

shifts consistent with these assignments. In addition to the fundamentals tabulated in the Hunt and Wilson paper, their spectra show a feature at 1220 ± 10 cm^{-1}, which Hunt and Wilson do not discuss.

Despite our general agreement with Hunt and Wilson, we note that the splitting between the 612.6 and 614.5 cm^{-1} features is consistent with the ^{81}Br/^{79}Br isotope shift for a CBr stretching motion which suggests that it is possible that both of these absorptions are due to ν_3. However, if this is correct, we would then be unable to account for the absence of ν_4, the CH bend.

The splitting between the combination bands at 1213.2 and 1214.1 cm^{-1} suggests that the CBr stretch is a component of these peaks. Conservation of matter suggests that C_2HBr is formed with an H_2 nearest neighbor; however, we cannot observe this cage partner directly. It is likely that the H_2 is present but unobserved because the shift in the bromoacetylene vibrational frequency caused by its presence is too small to be resolved under our experimental conditions.

The growth kinetics of the two products, which were not reported by Andrews[10] or McDonald,[9] were significantly different. They are shown in Figure 2. The HBr−acetylene complexes grow in immediately, showing normal first order kinetics and indicating that the HBr-acetylene complexes are primary photolysis products of vinyl bromide. The bromoacetylene has a sigmoidal growth curve, with a slope of zero at early stages of the photolysis. This indicates that the bromoacetylene is a secondary photolysis product, not a primary product of the photolysis of vinyl bromide. Coupled with the growth curve of HBr−acetylene, this shows that the HBr−acetylene complexes are necessary precursors of bromoacetylene.

Vinyl Iodide/Ar. *Deposition.* Vinyl iodide/Ar mixtures were prepared at dilutions of 1/1000 and 1/10 000. A spectrum of the 1:10 000 mixture after deposition at 25 K and cooling to 9.8 K is shown as Figure 3, and the observed frequencies and intensities are reported in Table 2. Sixteen absorptions showed constant relative intensities at both concentrations: 3106, 3082, 3011, 1894, 1862, 1825, 1590, 1371, 1239, 991, 953, 908, and 543 cm^{-1}. The observed frequencies, once normal matrix shifts are taken into account, correspond well with those reported by Torkington and Thompson,[14] also given in Table 2, with $\nu_1-\nu_8$, $\nu_{10}-\nu_{12}$, and four combination bands in the matrix spectrum assigned. One exception is ν_{12}, which Torkington and Thompson report at 435 cm^{-1}, but we observe at 543 cm^{-1}. Our observation is consistent with the reassignment of this fundamental to 540 cm^{-1} by Elst and Oskam.[15] In addition to the 16 absorptions assigned to vinyl iodide monomers, we observed three weak peaks at 3072, 3060, and 2967 cm^{-1} which are tentatively assigned to vinyl iodide dimers based on intensities which change with concentration relative to those of the monomer.

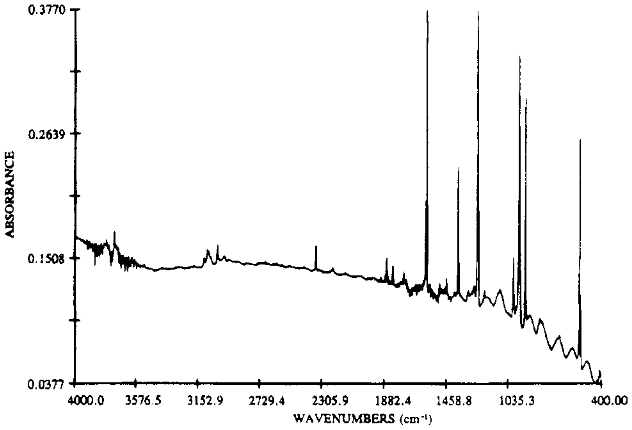

Figure 3. FTIR spectrum of vinyl iodide/Ar (1:10 000). The negative going fine structure near 3700 and 1600 cm^{-1} is due to interference from gas phase water.

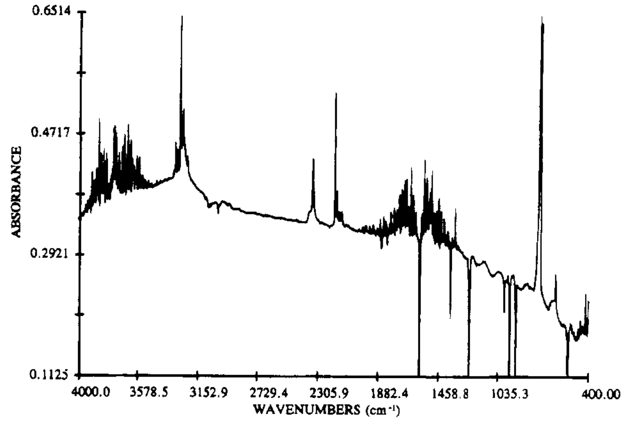

Figure 4. FTIR difference spectrum after 360 min Hg lamp photolysis of C_2H_3I/Ar (1/10 000). The fine structure near 3700 and 1600 cm^{-1} is due to water vapor.

TABLE 2: Frequencies and Intensities of 25 K Deposition of Vinyl Iodide/Ar (1/10 000) after Cooling to 9.6 K

exptl freq (cm^{-1})	exptl int (arb units)	lit. freq (cm^{-1})	assignt
3106	3	3110	ν_1 C_2H_3I
3082	5	3060	ν_2 C_2H_3I
3072	<1		$(C_2H_3I)_2$
3060	<1		$(C_2H_3I)_2$
3011	5	3000	ν_3 C_2H_3I
2967	<1		$(C_2H_3I)_2$
1894	1	1898	$\nu_4 + \nu_9$ C_2H_3I
1862	7	1858	$\nu_{10} + \nu_{11}$ C_2H_3I
1825	5	1817	ν_{11} C_2H_3I
1590	100	1593	ν_4 C_2H_3I
1371	38	1376	ν_5 C_2H_3I
1239	93	1229	ν_6 C_2H_3I
991	16	990	ν_7 C_2H_3I
953	75	946	ν_{10} C_2H_3I
908	65	909	ν_{11} C_2H_3I
543	66	540	ν_{12} C_2H_3I

Vinyl Iodide Photolysis. Figure 4 shows the 4000−400 cm^{-1} spectrum of a 1/10 000 mixture of vinyl iodide in Ar after 360 min of medium pressure mercury lamp photolysis. The frequencies, intensities and assignments of the product peaks in this spectrum appear in Table 3. The most intense feature in this spectrum is at 746 cm^{-1}. This feature grows in concert with features at 3301, 3282, 2188, 1338, and 737 cm^{-1}. All

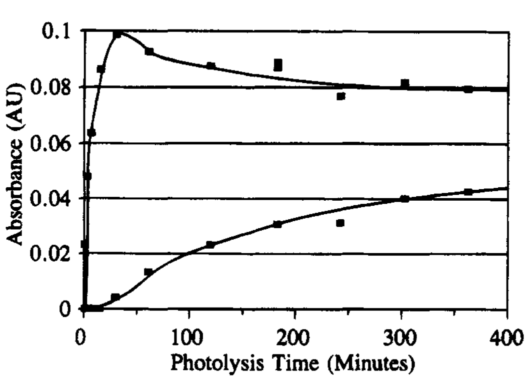

Figure 5. Growth behavior of HI–C_2H_2 complexes and C_2HI as a function of Hg lamp photolysis time (C_2H_3I/Ar = 1/1000).

TABLE 3: Product Frequencies and Intensities after 360 min of Mercury Lamp Photolysis of CH_2CHI/Ar (1/10 000)

freq (cm^{-1})	int (arb units)	assignt
3315	12.2	ν_1 C_2HI
3301	9.2	$\nu_2 + \nu_4 + \nu_5$ HI•C_2H_2
3282	55.42	ν_3 HI•C_2H_2
3260	24.88	ν_3 (HI)n•$(C_2H_2)_m$
3242	5.6	ν_3 (HI)n•$(C_2H_2)_m$
3231	7.4	ν_3 (HI)n•$(C_2H_2)_m$
2188	54.99	ν_s HI•C_2H_2
2171	12.2	ν_s $(HI)_2$•$(C_2H_{2)n}$
2157	4.4	ν_s $(HI)_3$•(C_2H_2)n
2140	4.8	ν_s $(HI)_3$•(C_2H_2)n
1338	14.0	$\nu_4 + \nu_5$ HI•C_2H_2
746	100.0	ν_5(xz) HI•C_2H_2
737	96.08	ν_5(xy) HI•C_2H_2
624	14.2	ν_4 C_2HI

the features except that at 2188 cm^{-1} are close to the gas phase fundamentals of acetylene at 3294, 3287, 1328.1, and 729.1 cm^{-1} [16] and to the acetylenic features of a hydrogen bonded complex of HBr with acetylene reported by Andrews.[10] The feature at 2188 cm^{-1} is shifted 56 cm^{-1} from the value for isolated HI[17,18] and corresponds closely to the value of 2187 cm^{-1} reported by Barnes et al for ν_{HI} for the HI-acetylene complex.[18] Thus, we assign these features to a hydrogen bonded complex of HI and acetylene, HI•C_2H_2. There are several features which appear as lower frequency satellites to the acetylenic CH features, at 3260, 3242, and 3231 cm^{-1}. These features are close in frequency to those assigned as CH stretches of acetylene multimers in Ar by Bulanin et al.[19], and as such we assign them to multimers of HI and C_2H_2. Similarly, a set of features at 2171, 2157, and 2140 cm^{-1}, which appear on the low-frequency side of ν_{HI}, correspond to features reported at 2178, 2157, and 2141 cm^{-1}, by Barnes et al. [18] for HI multimers. Following Barnes, the feature at 2171 cm^{-1} is assigned to an HI-acetylene complex containing two HI moieties, the feature at 2157 cm^{-1} is assigned to a complex containing three HI moieties in a linear configuration, and the feature at 2140 cm^{-1} is assigned to a complex containing three HI moieties in a cyclic configuration. This leaves two features at 3315 and 624 cm^{-1}, which grow in concert. These features are close to those reported for the spectrum of C_2HI isolated in a krypton matrix,[5] at 3306 and 624 cm^{-1}, and to those reported by Carpenter[20] and Rogstad[21] for gas phase C_2HI, at 3326 and 630 cm^{-1}. We assign these features to iodoacetylene, C_2HI.

Kinetic Behavior during Photolysis. Figure 5 shows the peak intensities of the 3282 cm^{-1} absorption of the HI–acetylene complexes and the 3315 cm^{-1} absorption of the iodoacetylene as a function of photolysis time for the 1:1000 vinyl iodide/Ar sample. The concentration of HI–acetylene complexes grows exponentially at early photolysis times but reaches a peak concentration at 60 min of photolysis time and decays thereafter. This is consistent with the HI–acetylene complexes being primary photolysis products which subsequent to formation undergo secondary photolysis. The iodoacetylene concentration shows a different growth behavior, with a sigmoidal growth pattern with zero initial slope. This behavior is consistent with a product which is formed by secondary photolysis of a species produced by direct photolysis of the vinyl iodide. The photolysis time behaviors of the HI–acetylene concentration and of the iodoacetylene concentration was identical for the more dilute 1/10 000 matrix.

Discussion

Product Distribution and Growth. The two products from photolysis of vinyl bromide showed distinct growth curves. The HBr–acetylene complexes showed immediate growth which reached an asymptotic limit. This behavior is consistent with that of the first order growth of a primary photolysis product from a limited reactant pool. The bromoacetylene shows a sigmoidal growth pattern with an initial slope of zero. The sigmoidal growth curve is typical of a product which is formed by secondary photolysis, i.e., the bromoacetylene is being formed by a process with the kinetic scheme

$$\text{vinyl bromide} \xrightarrow{h\nu} \text{B} \xrightarrow{h\nu} \text{bromoacetylene}$$

In addition, the zero initial slope indicates that this secondary photolysis process is the only process by which bromoacetylene is formed—bromoacetylene, despite its presence, is not a primary photolysis product of vinyl bromide. It remains only to identify the intermediate B which is photolyzed to yield the bromoacetylene. However, there is an obvious candidate for this intermediate—the HBr–acetylene complexes which are the vinyl bromide photolysis products.

The growth curves for the vinyl iodide photolysis products show nearly identical behavior. The HI–acetylene complexes grow in immediately, reach a maximum intensity at 61 min photolysis time, and decay thereafter. The iodoacetylene grows with a sigmoidal pattern with zero initial slope. The only observable difference between the growth curves for the vinyl bromide and vinyl iodide is that for vinyl iodide the secondary photolysis of the HX–acetylene complexes is observable on the time scale of the experiment, while for vinyl bromide it is not. Thus, we come to a parallel conclusion for the vinyl iodide photolysis: HI–acetylene pairs are primary photolysis products whose secondary photolysis yields iodoacetylene.

What makes these observations particularly fascinating is that it is a natural conclusion that the T-shaped geometry of our hydrogen bonded complexes lends itself to formation of chemically activated vinyl halides which then eliminate H_2 to form a haloacetylene. This claim is supported by the following evidence. First, under any circumstances, addition of H to acetylene is favored over H atom abstraction.[22,23] Second, calculations by Harding et al.[24] show that the transition state for formation of vinyl radical from H + acetylene is similar to the T-shaped geometry of our complex. Third, experiments by Kiel et al.[23] on the H + acetylene reaction have demonstrated that the nascent vinyl radicals are chemically activated. Finally, our own experimental evidence that the primary products of vinyl halide photolysis include no new products shows that the reaction between vinyl radical and the halide radical trapped in the cage is facile and yields only vinyl halides.

This argument leads to an interesting paradox. Vinyl halide photolysis leads to only one primary product in an inert gas matrix, an HX–acetylene complex. Again, we see no evidence that H_2 eliminations are even a minor channel in the vinyl halide photolysis. In contrast, photolysis of a T-shaped HX−acetylene complex, occurring through an energized vinyl halide intermediate, yields a haloacetylene as one of its products, as shown both by this experiment and by previously published work by our group.[5,7] Thus, the conclusion we draw is that somehow when we create an energized vinyl halide by photolysis of HX−acetylene complexes, we obtain products which are never formed by vertical excitation of vinyl halides at similar energies. Presumably this is because we are populating states of the vinyl halide which are not Franck−Condon allowed on direct excitation.

Structure of Complexes. Interpretation of the product spectra shows that both HI−acetylene and HBr−acetylene complexes form T-shaped complexes. For HBr−acetylene this was already shown conclusively by Andrews et al.,[10] and our results in krypton are completely consistent with theirs in argon. That hydrogen bonding is occurring is evident from the substantial shift of the HBr absorption from that of isolated HBr at 2565.8 cm^{-1}.[17] The key feature which demonstrates that the complex is T-shaped is the nature of the splitting of the doubly degenerate ν_5 mode of acetylene. Both T-shaped and linear complexes will result in a splitting of this mode but with different characteristic patterns. Formation of a linear complex results in a symmetric splitting of the two vibrations, with one moving to higher frequency and one to lower frequency. In contrast, in a T-shaped complex, the vibration in the plane containing the HBr($\nu_5(xz)$) will be shifted to higher frequency due to the increased repulsive interactions, while the vibration perpendicular to this plane ($\nu_5(xz)$) will be nearly unshifted.[10] Since the latter behavior is observed for HBr−acetylene complexes in Kr, as in Ar, we can only conclude that in the complex between HBr and acetylene is a T-shaped hydrogen-bonded complex here, too.

In contrast with HBr−acetylene, where the substantial polarity of the acid leads one to suspect that the primary interaction will be hydrogen bonding, there are two plausible structures for an HI−acetylene complex. One is the T-shaped complex observed for the other HX−acetylene complexes.[10] However, because of the small dipole moment of HI and the high polarizability of I, an alternative structure for the complex would be a linear structure, with the slightly acidic acetylene hydrogen interacting with the iodine on the HI. However, our results conclusively show that the T-shaped structure is the correct one for this complex.

The shift in the HI absorption to 2188 cm^{-1} from the frequency of matrix isolated HI in Ar[17] at 2246 cm^{-1} is smaller than that observed for HBr, but indicates clearly that the HI−acetylene interaction is hydrogen bonding. In addition, the splitting pattern in ν_5 is the same as that observed for other HX−acetylene complexes in Ar matrices,[10] demonstrating that the complex is a T shaped hydrogen bonded complex with the HI hydrogen pointing toward the triple bond of the acetylene.

Conclusions. Photolysis of matrix isolated vinyl bromide yields HBr−acetylene complexes as the primary product and bromoacetylene as a secondary product. Photolysis of matrix isolated vinyl iodide yields similar results with HI−acetylene complexes as the primary product and iodoacetylene as a secondary product. The formation of haloacetylenes by secondary photolysis of the HX−acetylene complexes is thought to go through some energized state of a vinyl halide which eliminates H_2 prior to relaxation. Since these experiments unambiguously show that H_2 elimination is not an open channel following vertical electronic excitation of vinyl halides in inert gas matrices, it suggests that the preparation of excited vinyl halides through chemical activation is responsible for formation of otherwise inaccessible products.

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