Photochemistry of Hydrogen Bromide−Acetylene Complexes in Solid Krypton

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Hydrogen-bonded complexes between HBr and acetylene in inert gas matrices were subjected to medium-pressure Hg lamp photolysis at 12 K. For HBr−acetylene, the major product was bromoacetylene, while vinyl bromide was present in trace amounts. When HBr−perdeuterioacetylene and DBr−acetylene complexes were photolyzed, bromoacetylene, deuteriobromoacetylene, and the hydrogen exchange product, DBr(HBr)−C_2HD, were the primary products. Partially deuterated vinyl bromides were present in trace amounts. In HBr−perdeuterioacetylene, the only isomer observed was *cis*-CDBr═CHD. In DBr−acetylene, both *cis*- and *trans*-CHBr═CHD were observed. In neither experiment was the 1,1 addition product formed. The results are interpreted in terms of the supramolecule model of complex photochemistry put forth by Abrash and Pimentel.

Introduction

Recently, there has been growing attention focused on the photochemistry of hydrogen-bonded complexes. Wittig and coworkers have studied the photochemistry of several gas phase complexes,[1] and Abrash and Pimentel have completed both broad-band[2] and laser[3] photolysis studies of the photochemistry of T-shaped complexes of HI and acetylene. In these studies, both the geometry of the precursor complexes and the mere fact of the proximity of the species which make up the complex have been strongly implicated in control of the reaction dynamics. In the HI−acetylene studies, the wavelength dependence of the photochemistry was explained by invoking the concept of a "supramolecule" containing all six atoms from the complex and applying the Franck−Condon principle to the electronic transitions from a ground state arrangement of the six atoms determined by the structure of the complex. This hypothesis has led to successful interpretation of one of Wittig's experiments,[4] but its generality has not yet been demonstrated. As a preliminary step toward repeating the wavelength studies with the related complex HBr−acetylene, we have studied the mercury lamp photochemistry of this complex to determine the product distribution and growth kinetics.

Experimental Section

The experiment used a typical matrix isolation apparatus. The cryostat was an Air Products Model CS202 closed cycle helium refrigerator capable of cooling our substrate, either cesium iodide, potassium bromide, or sodium chloride (Harshaw), to 12 K. It was equipped with a hydrogen gauge and an Au (0.07% Fe) vs chromel thermocouple or a silicon diode (Scientific Instruments) for temperature determinations as well as a resistance heater for annealing or high-temperature depositions. Matrix temperatures were measured to ±0.5 K. The cryostat was placed in the beam path of an FTIR spectrometer for sample analysis following depositions, photolyses, and warm-ups. It was fitted with CsI windows in the IR ports and a quartz window in the photolysis port. The FTIR was an IBM Model IR97 operated over the spectral range 4000−400 cm^{-1} at 0.25 or 0.5 cm^{-1} resolution and with wavelength accuracy of 0.1 cm^{-1} or a Nicolet 5DX operated over the range 4000−400 cm^{-1} with a resolution of 4 cm^{-1}.

Hydrogen bromide (Matheson, 98%), deuterium bromide (MSD Isotopes, 98% D), acetylene (Pacific Oxygen Co., 99.6%, or MG Industries, 99.6%), and acetylene-d_2 (MSD Isotopes, 99% D) were purified by bulb to bulb distillation. The purified gases were stored in glass bulbs fitted with a Teflon stopcock and Viton O-ring. For experiments in which DBr was used, all vacuum lines were repeatedly passivated with D_2O. The final passivation was with pure DBr. Typical D_2O passivations resulted in sample deuteration between 67% and 85%. Kr (Pacific Oxygen Co., 99.995%, or MG Industries, 99.995%) was used without further purification.

To prepare mixtures, the desired amount of HBr was introduced into the vacuum line. The empty mixture bulb was then opened and the HBr frozen in liquid nitrogen. The bulb was then reclosed and the procedure repeated, first for acetylene and then for krypton (which has a vapor pressure of 2.20 Torr at 77 K). After the Kr was added, the mixture bulb was closed, and the mixture was thawed and then allowed to mix diffusively for at least 6 h.

All matrices were deposited at 20 ± 0.4 K. Deposition rates varied from 0.5 to 2.0 mmol/h, with the amounts deposited varying from 1 to 4 mmol.

The photolysis source for these experiments was a medium-pressure mercury lamp (General Electric AH-4, 100 W) with its Pyrex housing cutoff and the output either focused by a 1.5 in. diameter, 5 cm focal length fused silica lens (Oriel) or a 1.0 in. diameter, 7.5 cm focal length lens (Optics for Research), or the source was placed within approximately 3 in. of the substrate and used unfocused.

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 min. Thereafter, the cryostat was rotated to place the matrix sample in the beam path. Photolyses took place on the front face of the CsI substrate unless otherwise specified; i.e., the light did not pass through the substrate before reaching the sample. After each photolysis a new IR spectrum was recorded in order to obtain kinetic information. After sufficient kinetic information was obtained, the sample was annealed by warming,

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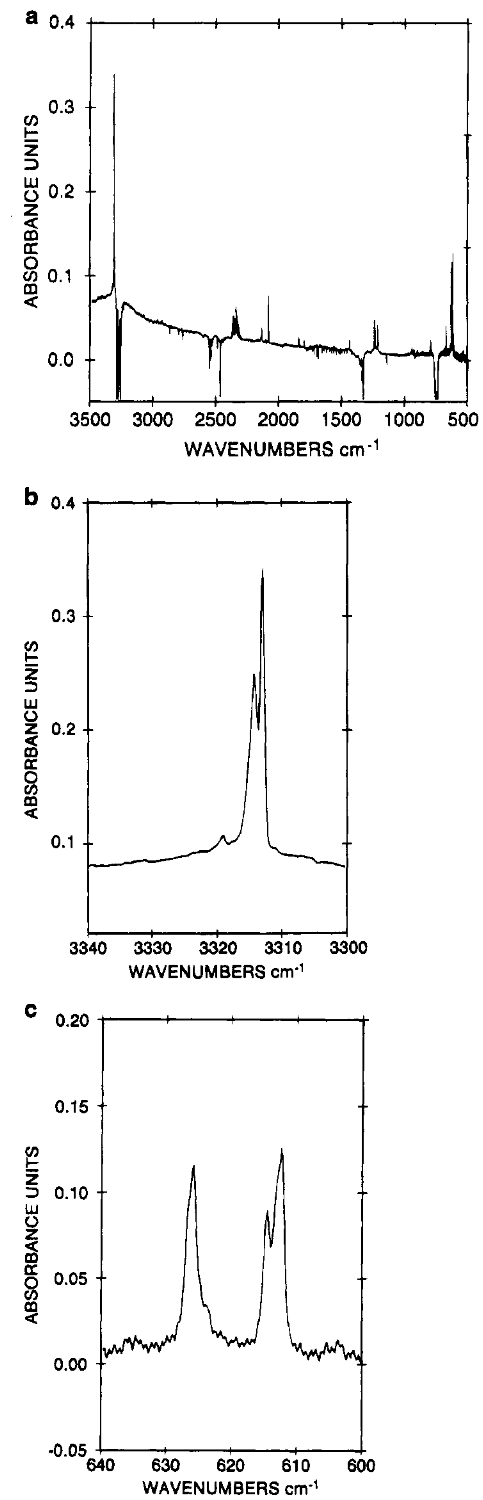

Figure 1. Products after 302 min medium-pressure Hg lamp photolysis, $HBr/C_2H_2/Kr$ = 1/1/100. (a) 500−3500 cm^{-1}; (b) C−H stretching region, 3300−3340 cm^{-1}, (c) C−H bending region, 600−640 cm^{-1}.

usually at the rate of 0.5 K min^{-1}, to a temperature between 45 and 50 K followed by cooling at an approximate rate of 1 K min^{-1}. When the substrate temperature returned to 12 K, an IR spectrum was recorded.

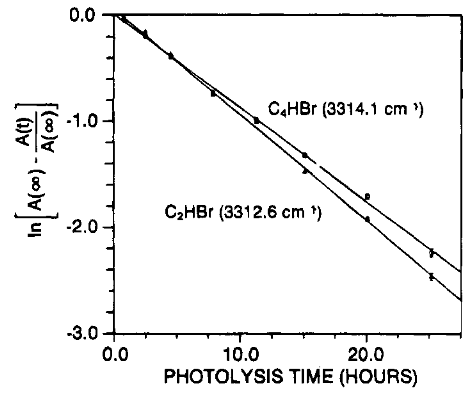

Figure 2. Semilog plot of product growth vs time in the photolysis of $HBr/C_2H_2/Kr$ = 1/1/100.

TABLE 1: Product Frequencies and Intensities after 302-min Mercury Lamp Photolysis of $HBr/C_2H_2/Kr$ = 1/1/100

freq. cm^{-1}	rel peak abs	assignt	freq. cm^{-1}	rel peak abs	assignt
3314.1	65.5	ν_1 (C_4HBr)	897.1	2.0	ν_{11} (C_2H_3Br)
3312.6	100.0	ν_1 (C_2HBr)	792.2	6.7	
2083.2	19.8	ν_2 (C_2HBr)	625.4	41.5	ν_6 (C_4HBr)
1237.5	13.1	$2\nu_6$ (C_4HBr)	614.5	32.3	ν_3 (C_2HBr)
1212.7	11.3	C_2HBr	612.4	45.6	ν_3 (C_2HBr)
947.0	2.3	ν_{10} (C_2H_3Br)	603.9	4.1	

Results

$HBr/C_2H_2/Kr$ = 1/1/100. After photolysis, difference spectra reveal growth of a number of products. Table 1 lists the product frequencies and peak intensities after 302 min of photolysis. Figure 1a shows a survey difference spectrum over the range 500−3500 cm^{-1}, while parts b and c of Figure 1 show key spectral ranges, 3300−3350 and 600−640 cm^{-1}, respectively. The most prominent feature is at 3312.6 cm^{-1} and grows in concert with peaks at 2083.2, 1212.7, 614.5, and 612.4 cm^{-1}. 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[6] and McDonald.[7] Hunt and Wilson report only the one peak 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 shifts consistent with these assignments. The peaks appear at distinct frequencies in our experiment presumably because the matrix shifts the energies of the accidentally degenerate stretch and bend by different amounts. In addition to the fundamentals tabulated in the Hunt and Wilson paper, the spectra show a feature at 1220 ± 10 cm^{-1}, which Hunt and Wilson do not discuss.

Conservation of matter suggests that C_2HBr is formed with an H_2 nearest neighbor—however, we cannot observe this cage partner directly, nor do we see evidence for it in the form of splitting of the bending vibration. It is likely that the H_2 is present, but unobserved because the splitting caused by its presence is too small to be resolved under our experimental conditions.

The second most intense peak is at 3314.1 cm^{-1} and grows in with peaks at 1237.5 and 625.4 cm^{-1}. These peaks are close in wavelength to gas phase absorptions at 3335, 1234.5, and 623 cm^{-1} given by Klaboe et al.[8] for bromodiacetylene, C_4HBr. Since the matrix shifts are similar to that observed in Ar by McDonald for bromoacetylene[7] and are therefore clearly reasonable for bromodiacetylene, the bands are assigned to bromodiacetylene. Figure 2 shows a semilog plot of bromoacetylene and bromodiacetylene growth as a function of photolysis time. Both products show first-order growth kinetics.

TABLE 2: Product Frequencies and Intensities after 1532.5 min Mercury Lamp Photolysis of $HBr/C_2D_2/Kr$ = 1/1/100

freq. cm^{-1}	rel peak abs	assignt	freq. cm^{-1}	rel peak abs	assignt
3333.8	12.2	ν_1 (C_2HD)	869.8	4.1	ν_{10} (*cis*-$CDBr{=}CHD$)
3325.8	43.9	ν_1 ($C_2HD{\cdot}DBr$)	745.7	9.2	ν_5 ($DBr{\cdot}C_2H_2$)
3312.8	30.8	ν_1 (C_2HBr)	733.6	9.4	ν_5 ($DBr{\cdot}C_2H_2$)
3275.7	6.4	ν_3 ($C_2H_2{\cdot}DBr$)	709.5	6.8	ν_{11} (*cis*-$CDBr{=}CHD$)
2596.2	60.2	ν_1 (C_2HBr)	692.9	94.2	ν_5 ($DBr{\cdot}C_2HD$)
2585.6	24.9	ν_1 (C_4DBr)	680.4	100.0	ν_5 (C_2HD)
2581.9	19.7	ν_3 (C_2HD)	613.0	6	ν_3 (C_2HBr)
2575.9	45.3	ν_3 ($C_2HD{\cdot}DBr$)	525.8	30	ν_4 ($C_2HD{\cdot}DBr$)
2083.0	4.0	ν_2 (C_2HBr)	516.8	32	ν_4 (C_2HD)
1950.5	1.9	ν_2 (C_2DBr)	516.1	30	ν_4 (C_2HD)
1849.4	3.1	ν_2 ($C_2HD{\cdot}DBr$)	494.0	21	ν_6 (C_4DBr)
1771.5	76.7	ν_{DBr} ($C_2HD{\cdot}DBr$)			

TABLE 3: Product Frequencies and Intensities after 1260 min Mercury Lamp Photolysis of $DBr/HBr/C_2H_2/Kr$ = 0.57/0.43/1/100

freq. cm^{-1}	rel peak abs	assignt	freq. cm^{-1}	rel peak abs	assignt
3334.5	6.8	ν_1 (C_2HD)	922.4	0.7	ν_{10} (*cis*-$CHBr{=}CHD$)
3325.8	5.4	ν_1 ($C_2HD{\cdot}HBr$)	896.6	0.9	ν_{11} (C_2H_3Br)
3314.2	47.5	ν_1 (C_4HBr)	804.0	1.3	ν_{11} (*cis*-$CHBr{=}CHD$)
3312.8	100.0	ν_1 (C_2HBr)	692.4	4.7	ν_5 ($C_2HD{\cdot}HBr$)
2596.3	13.6	ν_1 (C_2DBr)	679.4	24.8	ν_5 (C_2HD)
2585.6	0.4	ν_1 (C_4DBr)	625.9	29.1	ν_6 (C_4HBr)
2582.2	5.7	ν_3 (C_2HD)	614.3	30.8	ν_3 (C_2HBr)
2576.3	2.7	ν_3 ($HBr{\cdot}C_2HD$)	612.4	46.2	ν_3 (C_2HBr)
2083.2	21.2	ν_2 (C_2HBr)	603.4	1.9	
1237.5	9.9	$2\nu_6$ (C_4HBr)	516.2	8.7	ν_4 (C_2HD)
1212.7	12.3	C_2HBr	476.9	4.0	ν_4 (C_2DBr)
946.5	1.0	ν_{10} (C_2H_3Br)			

The weak peaks at 947.0 and 897.1 cm^{-1} indicate the presence of vinyl bromide. These two features correspond to the two strongest peaks of vinyl bromide in Kr.[9] The two relevant peaks of vinyl bromide in Kr are ν_{10} = 946.5 cm^{-1} and ν_{11} = 896.9 cm^{-1}. Although the frequencies match very well, the intensities of these two peaks are reversed in ref 9 compared to those in Table 1. The intensity reversal of the 946.5 and 896.9 cm^{-1} peaks is probably due to the poor signal-to-noise ratio for these peaks in the HBr/C_2H_2 experiment.

$HBr/C_2D_2/Kr$ = 1/1/100. The product frequencies and intensities for this experiment are shown in Table 2. In addition, a difference spectrum showing all products, and expanded spectra of the CH and CD stretching regions, are shown as Figure 3a−c. In this experiment six products were observed. The two most prominent have absorptions at 3333.8, 2581.7, 680.4, 516.8, and 516.1 cm^{-1} and at 3325.8, 2575.9, 1849.4, 1771.5, 692.9, and 525.8 cm^{-1}. The frequencies of both products were close to fundamentals reported for C_2HD in the gas phase,[10] at 3334.8, 2584, 1851.2, 683, and 518.8 cm^{-1}, and for C_2HD in a nitrogen matrix,[11] at 3332.5, 2580, 694.5, and 689.5 cm^{-1}. The only peak not contained in these spectra for isolated C_2HD is the 1771.5 cm^{-1} feature of the second product, which is at a reasonable frequency to be DBr hydrogen bonded to acetylene.[6,7] Coupled with the observations that in the second product the stretching features are all at lower frequencies than those of the first and that all the bends are at higher frequency, assignment of the second product to $C_2HD{\cdot}DBr$ and of the first to C_2HD is clear. Bromoacetylene was a third product, with frequencies as in the HBr/C_2H_2 experiment. Once again conservation of matter suggests that the bromoacetylene has D_2 as a nearest neighbor. The fourth product had peaks at 2596.2 and 1950.5 cm^{-1}, which agree well with gas phase values for C_2DBr given by Hunt and Wilson,[5] at 2600 and 1950 cm^{-1}. This molecule, again by conservation of matter, should have HD as a nearest neighbor. The fifth product had absorptions at 2585.6 and 494 cm^{-1}, which grew in concert. Its assignment will be considered in the Discussion section. In addition to these products two weak bands were observed at 869.8 and 709.5 cm^{-1}. Comparison with gas phase spectra of deuterated vinyl bromides[12] leads to their assignment as *cis*-$CDBr{=}CHD$, as noted in Table 2.

The ratio of the peak intensities of ν_1 of C_2DBr to ν_1 of C_2HBr varied between 1.35 and 2.00 but not in a monotonic fashion with respect to photolysis time. The overall average was 1.7 ± 0.3. We can approximate the number ratio by assuming that ν_1 is nearly a pure CH stretching motion. In this case the ratio of the absorption coefficient of C_2HBr to that of C_2DBr will be 2:1, which yields an average number ratio of 3.4 ± 0.7. The number ratios as a function of photolysis time are shown in Figure 4. Despite a good deal of scatter in the data, the figure suggests that there is an early rise in the ratio followed by a decay at later times. The ultimate value of the ratio is poorly defined but appears to be about 2.7. Since the ratio of D to H in the starting material is 2:1, this suggests that the hydrogen or deuterium in the C_2HBr or C_2DBr comes most frequently from the acetylene.

The growth curves for bands in the CH and CD stretching regions are shown in Figure 5, a and b, respectively. They can be divided into two groups. The bands corresponding to C_2HD and $C_2HD{\cdot}DBr$ all showed first-order growth curves, and all seemed to reach asymptotic limits to their growth by the end of photolysis. The other group, consisting of bromoacetylene and deuteriobromoacetylene, had more complex growth curves. Both peaks had predominantly first-order behavior, but neither had reached an asymptotic limit by the end of photolysis. It is important to note that, because two different growth patterns exist, the relative yield of products is a function of time. Furthermore, the presence of more than one class of growth curve shows that all products cannot be due to branching from a single process.

This system was also studied with both the Corning 9-54 and CsI filters. In both experiments all products were formed, indicating that the observed chemistry is indeed due to HBr photolysis and not to excitation of the acetylene.

$DBr/HBr/C_2H_2/Kr$ = 0.57/0.43/1/100. The frequencies and relative peak intensities for photolysis of this system after 1260

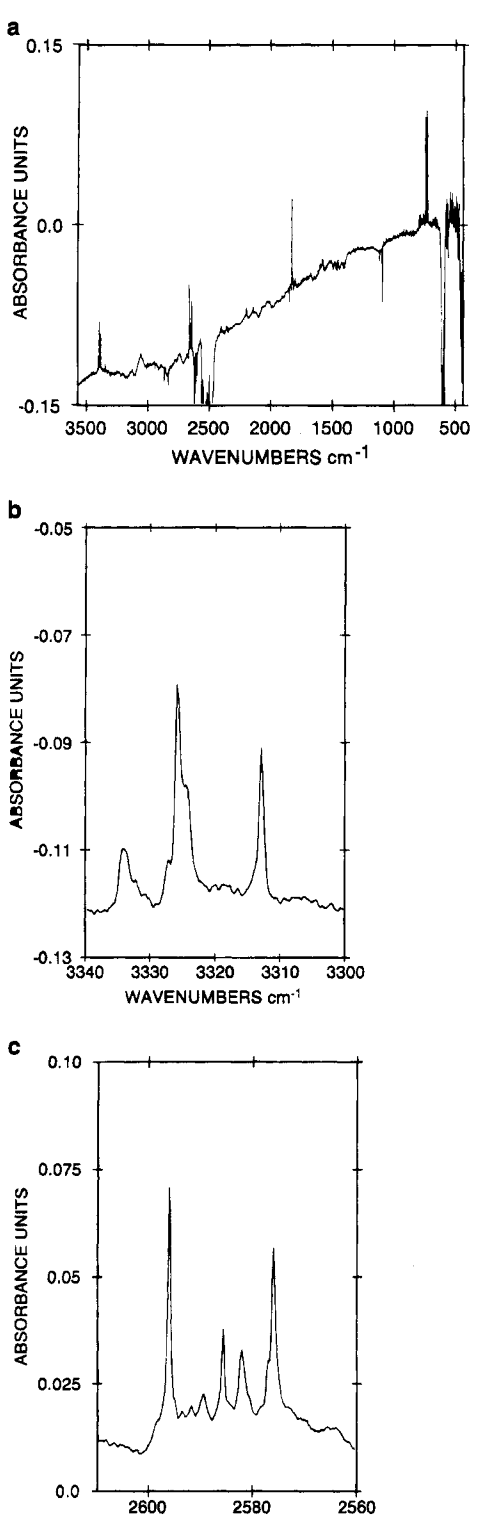

Figure 3. Products after 1532 min medium-pressure Hg lamp photolysis, $HBr/C_2D_2/Kr$ = 1/1/100. (a) 400–3500 cm^{-1}; (b) C–H stretching region, 3300–3340 cm^{-1}; (c) C–D stretching region, 2560–2610 cm^{-1}.

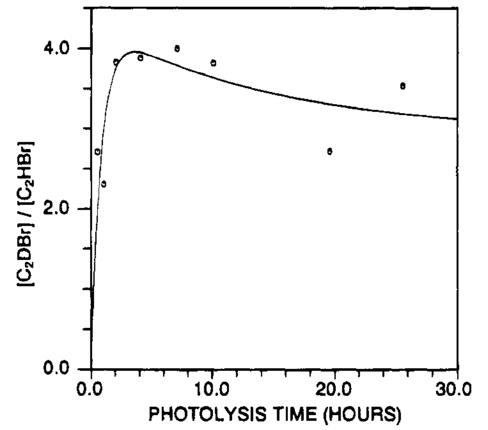

Figure 4. Relative yield of C_2DBr/C_2HBr, $HBr/C_2D_2/Kr$ = 1/1/100.

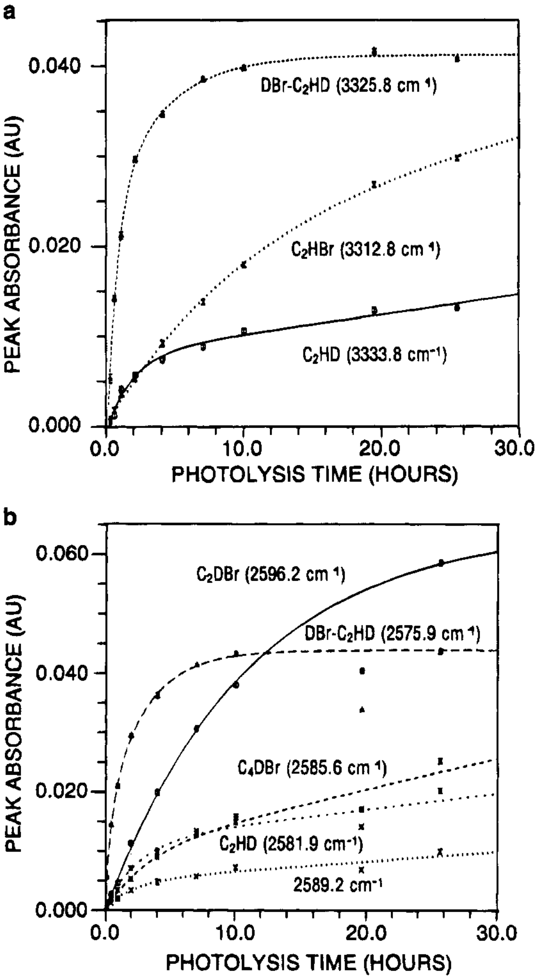

Figure 5. Product growth during photolysis, $HBr/C_2D_2/Kr$ = 1/1/100: (a) C–H stretching region; (b) C–D stretching region.

min of photolysis are given in Table 3. A survey difference spectrum is given as Figure 6a, and spectra of the CH and CD stretching regions are given as Figure 6, b and c. The results in this experiment were complicated by the high concentration of HBr, determined by the intensity of the 2465.1 cm^{-1} $HBr\cdot C_2H_2$ feature.[6] The range of products was the same as in the $HBr\cdot C_2D_2$ experiment, with the exception that, as expected, $HBr\cdot C_2HD$ rather than $DBr\cdot C_2HD$ was the acid–deuterioacetylene product. In addition, the very weak peaks at 922.4 and 804.0 cm^{-1} are assigned to ν_{10} and ν_{11} of *cis*-CHBr=CHD on the basis of strong correlation to gas phase spectra.[12]

As in the previous experiment, we wish to determine the ratio of bromoacetylene to deuteriobromoacetylene. This number ratio is plotted as Figure 7. Unlike the previous experiment, the number ratio of C_2HBr to C_2DBr was not constant over any interval during the course of the experiment. The ratio rose from 3.15 to 4.93 over the first 50 min of photolysis and fell to an asymptotic value of 3.5 over the next 1210 min. The peak ratio is slightly higher than the H:D ratio in the reactant, 4.3:1, and again suggests that the H or D atom from the hydrohalide is preferentially eliminated.

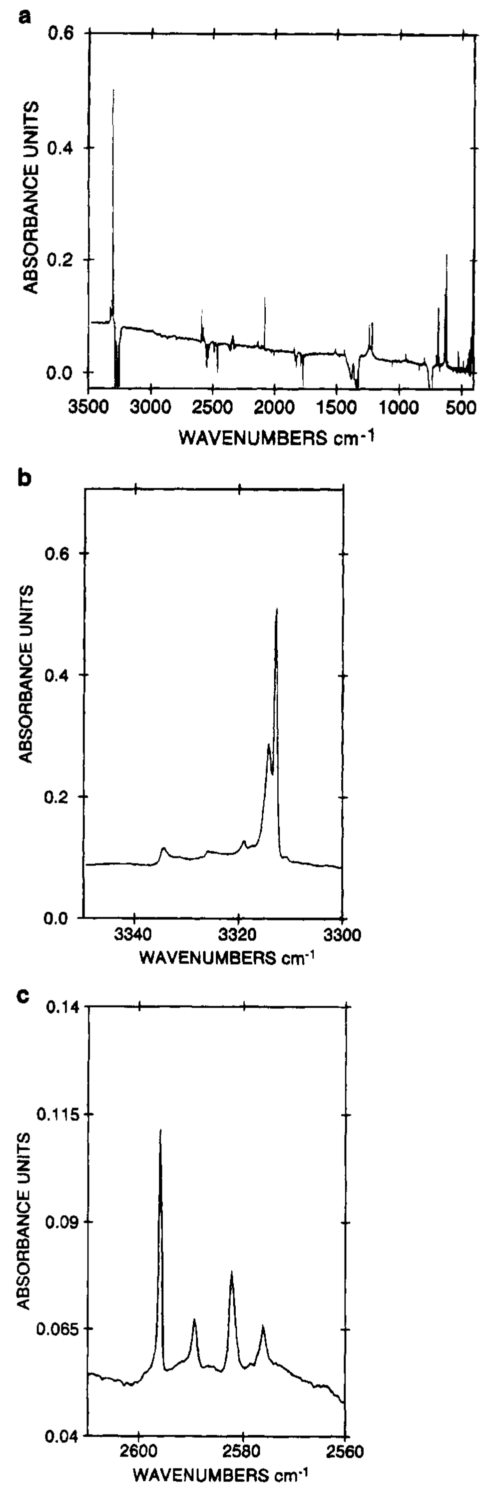

Figure 6. Products after 1260 min medium-pressure Hg lamp photolysis, $DBr/HBr/C_2H_2/Kr = 0.57/0.43/1/100$: (a) 400−3500 cm^{-1}; (b) C−H stretching region, 3300−3350 cm^{-1}; (c) C−D stretching region, 2560−2610 cm^{-1}.

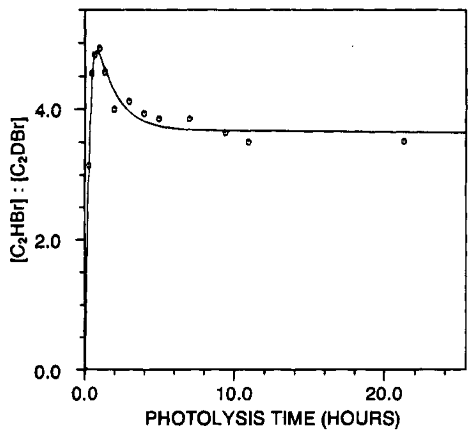

Figure 7. Relative yield of C_2HBr/C_2DBr, $DBr/HBr/C_2H_2/Kr = 0.57/0.43/1/100$.

$DBr/HBr/C_2D_2/Kr = 0.74/0.26/1/100$. Product frequencies and intensities for this experiment are shown in Table 4. As expected from the results reported above, C_2DBr, C_2HD, and $DBr\cdot C_2HD$ were the major products observed. The peaks at 2585.6 and 494.5 cm^{-1} which were observed in the $HBr/C_2D_2/Kr$ experiment are observed here as well. In addition, several new peaks were observed. One group consisted of peaks at 1521.0, 1025.6, 979.3, and 694.1 cm^{-1} which grew in concert. On the basis of comparison to gas phase spectra,[12] these are assigned to ν_4, ν_5, ν_6, and ν_{11} of C_2D_3Br, respectively. In addition, peaks are observed at 1546.1, 709.5, 709.0, and 690.5 cm^{-1}. The peaks at 709.5 and 709.0 cm^{-1} are assigned to ν_{11} of *cis*-CDBr=CHD while the peak at 690.5 cm^{-1} is assigned to ν_{11} of *trans*-CDBr=CHD. The peak at 1546 cm^{-1} could be assigned to ν_4 of either the cis or the trans isomer.[12] The peaks at 709.5 and 709 cm^{-1} are assumed to be the same mode split by some matrix effect.

Discussion

Matrix Concentrations. From the known bond lengths and van der Waals radii, C_2H_2 clearly occupies two adjacent Kr sites in the lattice. Although HBr may be too large to fit a single site, as in the case of HI,[2] we shall assume it does, therefore placing the $HBr\cdot C_2H_2$ complex in a three-site vacancy, with 32 nearest neighbors.

At matrix ratios $HBr/C_2H_2/Kr = 1/1/100$, the statistical fraction of isolated HBr will be 70%, 17% of the HBr molecules will have one C_2H_2 neighbor, and 8% will have one HBr neighbor. This implies that about 5% will have two or more acetylene neighbors. Because of its larger size, only 59% of the C_2H_2 molecules will be isolated, 11% will have a single HBr neighbor, and 21% will have another C_2H_2 neighbor but no HBr.

There remains the question of the number of complexes, $HBr\cdot C_2H_2$, that are isolated. With 32 nearest neighbors, this turns out to be about 40%. The fraction of complexes with another acetylene in the same cage is almost as large, 33%. The remaining 27% is distributed among a variety of multiple nearest-neighbor situations, each present in small amounts. As in our study of HI−acetylene photochemistry, those complexes with other acetylenes in the same cage presumably account for the C_4 products.

Vinyl Bromide. The $HBr\cdot C_2H_2$ experiment offers an unequivocal identification of vinyl bromide. The peaks at 947 and 841 cm^{-1} match the two most intense peaks from the spectrum of vinyl bromide in a Kr matrix.[10] The absence of other peaks, including the third most intense peak at 1596 cm^{-1}, indicates that the concentration is small. Since the concentration maintains a low steady state level, and since it is well-known that vinyl bromide undergoes photolysis at these wavelengths,[6,7] we conclude that vinyl bromide is a primary product which undergoes secondary photolysis.

In addition, isotopically substituted vinyl bromides were clearly identified in each of our other experiments. In the $DBr/HBr/C_2H_2/Kr$ experiment, trace amounts of ν_{10} and ν_{11}. In the $HBr/C_2D_2/Kr$ experiment, *cis*-CDBr=CHD is observed. Finally, in the $DBr/HBr/C_2D_2/Kr$ experiment, C_2D_3Br and both *cis*- and *trans*-CDBr=CHD are observed. In no experiment were either CD_2=CHBr or CH_2CDBr observed.

TABLE 4: Product Frequencies and Intensities after 393 min Mercury Lamp Photolysis of DBr/HBr/C_2D_2/Kr = 0.74/0.36/1/100

freq. cm^{-1}	rel peak abs	assignt	freq. cm^{-1}	rel peak abs	assignt
3333.8	15.8	ν_1 (C_2HD)	979.3	11.7	ν_6 (C_2D_3Br)
3325.6	14.5	ν_1 ($DBr\cdot C_2HD$)	709.5	18.9	ν_{11} (*cis*-CDBr=CHD)
3312.6	10.2	ν_1 (C_2HBr)	709.0	18.0	ν_{11} (*cis*-CDBr=CHD)
2596.3	100.0	ν_1 (C_2DBr)	694.1	27.6	ν_{11} (C_2D_3Br)
2585.6	57.8	ν_1 (C_4DBr)	692.9	34.0	ν_5 ($DBr\cdot C_2HD$)
2581.7	23.6	ν_3 (C_2HD)	690.5	12.7	ν_{11} (*trans*-CDBr=CHD)
2576.0	18.6	ν_3 ($DBr\cdot C_2HD$)	679.1	71.9	ν_5 (C_2HD)
1950.7	3.2	ν_2 (C_2DBr)	525.8	10.1	ν_4 ($DBr\cdot C_2HD$)
1546.1	3.5	ν_4 (CDBr=CHD)	516.2	25.4	ν_4 (C_2HD)
1521.0	7.2	ν_4 (C_2D_3Br)	494.5	42.7	ν_4 (C_4DBr)
1025.6	8.1	ν_5 (C_2D_3Br)	476.7	26.0	ν_4 (C_2DBr)

The amount of vinyl bromide (or the appropriate deuterated form) stabilized relative to bromoacetylene seems to increase sharply when perdeuterioacetylene rather than acetylene is used as a starting material. This can be seen by comparing the relative intensities of ν_{11} of the vinyl bromide to ν_1 of the bromoacetylene.

Since the intensity of a vibrational feature is reduced by deuteration, we need to introduce a correction factor in order to compare the relative yields of the deuterated and nondeuterated vinyl bromides. According to Crawford,[23] the intensity of a deuterated normal mode is related to the intensity of the nondeuterated mode by

$$\frac{I_D}{I_H} = \left(\frac{\nu_D}{\nu_H}\right)^2$$

Thus, to make a direct comparison of the yields of the deuterated and nondeuterated species, we will multiply the intensity of each deuterated peak by a factor of $(\nu_H/\nu_D)^2$. Thus, the intensity of ν_1 of C_2DBr is multipled by $(3312.6\ cm^{-1}/2596.2\ cm^{-1})^2 = 1.628$, ν_{11} of *cis*-CDBr=CHD by 1.599, ν_{11} of *cis*-CHBr=CHD by 1.244, ν_{11} of *trans*-CDBr=CHD by 1.674, and ν_{11} of C_2D_3Br by 1.669.

In some experiments, there is more than one isotopic form of bromoacetylene or vinyl bromide. We treat this problem in the simplest possible way—by adding the intensities, corrected for isotope effect, of the various forms. Given these two corrections, for loss of intensity on deuterium substitution and for branching among isotopic forms, we obtain the following ratios of ν_1 of C_2HBr to ν_{11} of C_2H_3Br. In the HBr/C_2H_2/Ar experiment, the ratio is 0.020. In the DBr/HBr/C_2H_2 experiment, the ratio is 0.030. In the HBr/C_2D_2/Ar experiment the ratio is 0.084. Finally, in the DBr/HBr/C_2D_2/Ar experiment, the ratio is 0.564. Thus, even by these crude measures it is seen clearly that the relative yield of vinyl bromide increases with the extent of deuteration of the initial complex.

We can suggest a relatively simple explanation for the higher relative yield of vinyl bromides for complexes containing C_2D_2. Since vinyl bromides have increasing numbers of lower frequency modes as the number of deuterium atoms is increased, stronger coupling of the molecular vibrations to the matrix phonons increases observed yields of the deuterated vinyl bromides. This is entirely consistent with our observation that yield increases with the number of deuterium atoms present in the initial complex.

We also note that in the DBr/HBr/C_2D_2/Kr experiment, the only experiment in which both cis and trans isomers of the deuterated vinyl bromides was observed, ν_{11} of the cis isomer is 50% more intense than ν_{11} of the trans isomer. This difference in intensity is sufficient to account for our failure to observe the trans isomer in the other experiments, where the observed intensity of the vinyl bromides was much smaller.

In order to interpret our HBr−acetylene chemistry, it is critical to identify the products of the secondary photolysis of vinyl bromide. MacDonald[7] and Andrews[6] photolyzed vinyl bromide in argon matrices and found bromoacetylene and HBr−acetylene complexes as products. Abrash has studied the photochemistry of vinyl halides in inert gas matrices.[9,13] These studies will be the topic of a separate publication. In short, both the product distribution and the growth behavior of the products were studied in a krypton matrix. Abrash also found two products, the $HBr\cdot C_2H_2$ complex and bromoacetylene, but with quite distinct growth behaviors. Whereas $HBr\cdot C_2H_2$ grew immediately, the bromoacetylene grew with strongly sigmoidal behavior and zero slope at short photolysis times. Plainly, vinyl bromide undergoes primary photolysis to eliminate HBr, whereas HCCBr is formed only through secondary photolysis of the $HBr\cdot C_2H_2$ complex.

HCCD. When matrices which contain HBr and C_2D_2 are photolyzed, product absorptions appear which are readily associated with the spectrum of monodeuterioacetylene. By growth behavior, they can be divided into two sets, each assignable to C_2HD. One set, 3333.8, 2581.9, 680.4, and a doublet at 516.8 and 516.1 cm^{-1}, matches our observed frequencies for C_2HD from photolysis of matrices containing HI and C_2D_2 to within less than one wavenumber[2] and is therefore assigned to isolated C_2HD. The other set, 3325.8, 2575.9, 1771.5, 692.9, and 525.8 cm^{-1}, is assigned to the photolytically produced complex, $DBr\cdot C_2HD$. The assignment is based on three arguments. First, the shifts in frequency from isolated C_2HD are consistent with well-known trends in hydrogen bonding: the stretching vibrations shift to lower frequency while the bending vibrations shift to higher frequency. Second, the acetylenic bands correlate with the feature at 1771.5 cm^{-1}, which is at an appropriate frequency to be assigned to DBr in a π-type hydrogen bond. Third, the acetylenic bands are close in frequency to those assigned in our previous paper to $HI\cdot C_2HD$ but have slightly greater shifts, as one would expect for a complex containing a more polar hydrohalide. In addition, we tentatively assign the weak feature at 1849.4 cm^{-1} to this complex. This feature is close to the gas phase value of 1851.2 cm^{-1} reported by Herzberg.[10] The growth behavior of the peak does not correlate particularly well to the other features assigned to $HBr\cdot C_2HD$, but this may be attributed to the low absorption intensity of the feature. It is assigned to the complex simply on the basis that the stretching features of the complex are considerably more intense than that of the isolated C_2HD and that a weak feature appearing out of the noise is more likely to be due to the more concentrated molecule.

The DCCBr/HCCBr Ratio. In our paper on the photochemistry of HI−acetylene complexes, the DCCI/HCCI ratio was particularly revealing, demonstrating unequivocally that for this complex the hydrogen (deuterium) atom in the hydrohalide

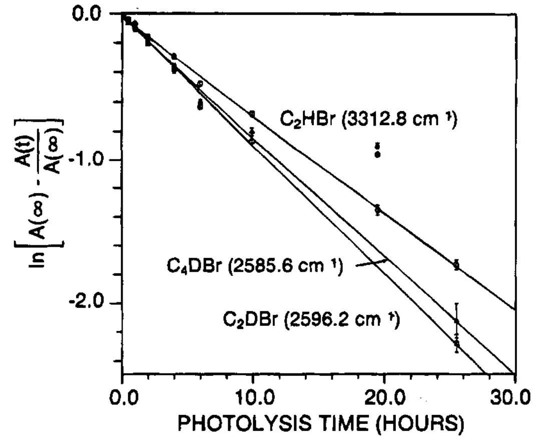

Figure 8. Semilog plot of product growth as a function of photolysis time, $HBr/C_2D_2/Kr$ = 1/1/100.

is preferentially eliminated. The DCCBr/HCCBr ratio is somewhat more complex and more difficult to interpret. As in the previous experiment, the ratio is high at short times and decays with time, although the rate of decay is small. However, unlike the previous experiment, there is an observable rise in the ratio. The first observed value for this ratio is greater than 2:1, and it quickly rises to a maximum value of 4:1, thereafter slowly decaying to an asymptotic value of approximately 3.2: 1.

This contrast in the ratio is consistent with the growth curves for the two molecules. In the HI experiment, the HCCI and DCCI both showed sigmoidal growth behavior, with the difference that the DCCI had a finite initial slope, while the HCCI had an initial slope of zero. In the HBr experiment both products show simple first-order growth curves, as indicated by the semilog plot in Figure 8. Both products appear at short times. It may be suggested that the rise in the ratio is due to the low intensity of the products at short times which would result in a high percentage error in the ratio. However, this growth behavior is reproducible and has been observed on experimental setups both at the University of Richmond and at the University of California. The situation is reversed for the $DBr/HBr/C_2H_2$ experiment, as shown in Figure 7, although the substantial HBr impurity masks the behavior to a certain extent. This time, the HCCBr is favored in the ratio and demonstrates a rise from 3.2:1 to a maximum of 5:1 followed by a fairly rapid decay to an asymptotic limit of approximately 3.8. The differences in the decay time and asymptotic ratios can be explained by the HBr impurity.

We can find no simple explanation for the rise in the DCCBr/HCCBr ratio, except that there is more than one reaction which produces bromoacetylene. This is consistent with the observed behavior in HI−acetylene, as demonstrated by the sigmoidal growth curves. What is important to note is that the greater than 2:1 initial population ratio of DCCBr/HCCBr indicates that at least for one of these processes, the hydrogen or deuterium originating with the hydrohalide is preferentially eliminated. It is simplest to assume that, as in the case of HI−acetylene, in this process, which from the growth curve accounts for the bulk of the bromoacetylene formation, the hydrohalide hydrogen is exclusively eliminated. We can find no evidence which indicates what the second process is.

Isotopic Combinations. We now have four experimental premises with which to interpret the mixed-isotope studies. When the hydrogen bromide−acetylene complex is photolyzed in krypton, (i) vinyl bromide is a primary product, (ii) acetylenic isotope exchange is another primary process, (iii) formation of bromoacetylene is a primary process in which the hydrogen bromide hydrogen exclusively ends up in the hydrogen molecule, and (iv) vinyl bromide undergoes secondary photolysis, giving only hydrohalide elimination.

CHART 1

MIXTURE		PRIMARY PRODUCTS		SECONDARY PRODUCTS
(A) $HBr \bullet C_2H_2$	$\xrightarrow{h\nu_1}$	$H_2 \bullet HCCBr$		
	$\xrightarrow{h\nu_1}$	$CH_2 = CHBr$	$\xrightarrow{h\nu_2}$	$HBr \bullet C_2H_2$
(B) $HBr \bullet C_2D_2$	$\xrightarrow{h\nu_1}$	$HD \bullet DCCBr$		
	$\xrightarrow{h\nu_1}$	$D_2 \bullet HCCBr$		
	$\xrightarrow{h\nu_1}$	cis - $CDBr = CHD$	$\xrightarrow{h\nu_2}$ $\xrightarrow{h\nu_2}$	$HBr \bullet C_2D_2$ $DBr \bullet C_2HD$
	$\xrightarrow{h\nu_1}$	trans - $CDBr = CHD$	$\xrightarrow{h\nu_2}$ $\xrightarrow{h\nu_2}$	$HBr \bullet C_2D_2$ $DBr \bullet C_2HD$
	$\not\rightarrow$	$CHBr = CD_2$		
	$\xrightarrow{h\nu_1}$	$DI \bullet C_2HD$		
(C) $DBr \bullet C_2H_2$	$\xrightarrow{h\nu_1}$	$HD \bullet HCCBr$		
	$\xrightarrow{h\nu_1}$	$H_2 \bullet DCCBr$		
	$\xrightarrow{h\nu_1}$	cis - $CHBr = CHD$	$\xrightarrow{h\nu_2}$ $\xrightarrow{h\nu_2}$	$DBr \bullet C_2D_2$ $HBr \bullet C_2HD$
	$\xrightarrow{h\nu_1}$	trans - $CHBr = CHD$	$\xrightarrow{h\nu_2}$ $\xrightarrow{h\nu_2}$	$DBr \bullet C_2D_2$ $HBr \bullet C_2HD$
	$\xrightarrow{h\nu_1}$	$CH_2 = CDBr$		
	$\xrightarrow{h\nu_1}$	$HI \bullet C_2HD$		
(D) $DBr \bullet C_2D_2$	$\xrightarrow{h\nu_1}$	$D_2 \bullet DCCBr$		
	$\xrightarrow{h\nu_1}$	$CDBr = CD_2$		

The premises lead to the expectations for the mixed-isotope experiments shown in Chart 1. We see that in Chart 1, reactions A and C, HCCBr and DCCBr are primary products, although HCCBr is stongly favored. Therefore, in these experiments both products will have finite growth at short time. The situation should reverse in reactions B and D, where DCCBr should be favored over HCCBr. All observed growth curves are consistent with these four premises. We note that the data are not fully consistent with premise three, although we can find no better premise to explain our results. This is in contrast to the observed photochemistry of HI−acetylene complexes, where the HI hydrogen exclusively ends up in the hydrogen. The thermochemistry of the complexes, as seen below, is not sufficiently different to account for the observed differences in the chemistry.

Thermochemistry. Figure 9 shows the energy relationships that exist among reactants and products.[14] The energies for [HBr]* are vertical transition energies for gaseous HBr, thus ignoring any excited-state interaction with the neighboring C_2H_2.[15] Evidently, no matter which of the allowed transitions of HBr is accessed, there is enough energy to produce vinyl bromide in either its first excited singlet or triplet state. After internal conversion, either state of vinyl bromide would have ample excess energy to eliminate H_2 to produce HCCBr. However, in order to produce the observed ratios in the mixed-isotope experiments, any addition−elimination process would have to be sufficiently rapid to go to completion before isotopic scrambling of the partially deuterated vinyl bromide could occur. Other processes that the electronically excited vinyl bromides would undergo would be H(D)Br elimination to yield either the parent complex or isotope exchange and relaxation to ground

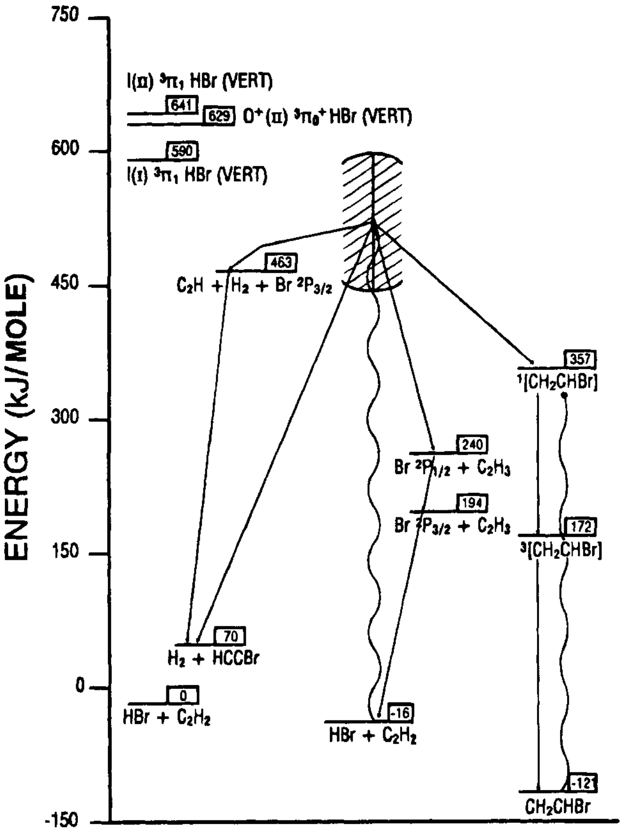

Figure 9. Energy diagram for the photochemistry of hydrogen bromide−acetylene complexes.

state vinyl bromide. We see that photoproduction of vinyl bromide and its secondary photolysis only catalyze isotope exchange.

It is possible to suggest an alternate process by which bromoacetylene is formed as a primary product. We observe, first, that the hydrohalide excitation tends to impart high translational energy to its hydrogen (deuterium) atom. Then we note that our results show that the "ejected" hydrogen (deuterium) atom ends up in product hydrogen molecules. This suggests that the process by which bromoacetylene is formed can be pictured as an abstraction, as in the following sequence of reactions, all within the cage:

$$\mathrm{BrH\cdot\cdot C_2D_2 \rightarrow Br\cdot\cdot C_2D\cdot\cdot HD \rightarrow DCCBr{\cdot}HBr}$$

We speculate that, as in the case of HI−acetylene, the high selectivity is controlled by Franck−Condon factors for the initial excitation and a correlation between these initial excitations and the products formed.

The Identity of the Absorption at 2586.6 cm^{-1}. The most logical molecule to assign to these absorptions is C_4DBr, bromodiacetylene. In the HBr/C_2H_2 experiments, C_4HBr was a very prominent product. The yield of the 2585.6 cm^{-1} feature is highest in experiments with C_2D_2 and falls almost to nil in the DI/C_2H_2 experiment, consistent with our argument that the attacking hydrogen is preferentially eliminated. As noted above, 2585.6 cm^{-1} grows in with an absorption at 494.0 cm^{-1}. The isotope shifts from ν_1 and ν_6 of C_4HBr, at 3314.1 and 625.4 cm^{-1}, are 1.28 and 1.26, respectively, respectable values for these shifts. As a final point, the growth curve for 2585.6 cm^{-1} was similar to that for C_4HBr. For these reasons we assign the features at 2585.6 and 494.0 cm^{-1} to ν_1 and ν_6 of C_4DBr. This is the first observation of any fundamentals of this molecule.

Comparison between HBr·Acetylene and HI·Acetylene. The results of this experiment bear important similarities to HI−acetylene. The dominant processes are haloacetylene formation and isotope exchange. The haloacetylene products are anomalous when compared with gas phase H + acetylene studies and on the basis of simple thermodynamic considerations. In both cases there is evidence that the hydrogen originating from the hydrohalide is exclusively found in the hydrogen molecule. Apparently, the proximity and geometry of the complex are profoundly affecting the product branching.

There are three differences between the photochemistry of the two complexes. (1) The net production of vinyl bromide is much smaller than the production of vinyl iodide. We conclude this because vinyl iodide reaches higher absorbances before depletion.[2] On the basis of the higher electronegativity of bromine, we would expect that the dipole derivatives and therefore the absorption coefficients of equivalent normal modes of vinyl bromide would be higher than in vinyl iodide. Therefore, we can conclude that the higher absorbance of vinyl iodide modes corresponds to higher concentrations. This in turn tells us that the relative rate of production of the vinyl halide to its secondary photolysis is higher for vinyl iodide than for vinyl bromide. This may be easily explained by the fact that while vinyl bromide and vinyl iodide have similar extinction coefficients in the region 200−300 nm,[20,21] HI has a larger extinction coefficient than HBr in this region, even though the peak extinction coefficient of HBr in the vacuum-UV is higher than the HI peak.[22]

An alternative explanation is that relaxation of vinyl bromide in a matrix would be slower than that of vinyl iodide because of the presence of the C−I bend which would couple more effectively to the matrix phonons than the C−Br bend. The result of this would be that relaxation of the chemically activated vinyl iodide would compete more effectively with elimination of HI than the relaxation of vinyl bromide would compete with elimination of HBr. This would result in the relatively small observed yield of vinyl bromide in these experiments.

(2) In the mixed-isotope experiments, bromoacetylene and deuteriobromoacetylene are both initially produced. (3) The ratio of DCCBr to HCCBr in the HBr/C_2D_2 experiment and of HCCBr to DCCBr in the $DBr/HBr/C_2H_2$ experiment show a rise, which was not observed for HI/C_2D_2, and show slower decays than in the HI−acetylene systems. As noted above, these taken together suggest the presence of an unidentified second process which produces haloacetylenes. Since the most obvious difference between HI and HBr is the larger number of electronic states underlying the continuum for HBr,[15] these two processes may correspond to two different states of HBr, both of which correlate to bromoacetylene. This in turn suggests that HBr−acetylene complexes are fruitful subjects for wavelength dependence studies and may show substantially different results than those obtained for HI−acetylene.

Conclusion

The photolysis of hydrogen bromide−acetylene hydrogen-bonded complexes in solid krypton produces both bromoacetylene and vinyl bromide in primary processes. Secondary photolysis of vinyl bromide catalyzes isotopic exchange in isotopic mixtures, but it does not directly produce bromoacetylene. We conclude that the primary production of bromoacetylene involves hydrogen (deuterium) abstraction by the energetic HBr or an extremely rapid addition elimination reaction. The differences between the photochemistry of this complex and the earlier reported photochemistry of HI−acetylene hydrogen-bonded complexes make the study of the wavelength dependence of this system promising.

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