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Photolysis of Argon Matrices Containing Tribromoboron and Dihydrogen: Synthesis of Hydroboranes via Dibromoboron

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Ultraviolet irradiation (λ = 254 nm) of argon matrices containing BBr_3 and high concentrations of H_2 produces an intermediate, BBr_2, which reacts with H_2 to form $HBBr_2$, H_2BBr, and HBr. The intermediate is completely destroyed by irradiation at 680 nm, the position of a broad absorption band, producing the same hydrogenation products that form by using ultraviolet radiation. The reaction of BBr_2 with HD gives HBr and $DBBr_2$ 1.6 times more readily than DBr and $HBBr_2$. The spectrum of BBr_2 has been reported earlier; herein we reassign the totally symmetric B–Br stretching mode to a weak band at 551.0 cm^{-1}. There is no evidence that either BBr_2 or BBr_3 forms a ground-state complex with hydrogen in spite of the fact that BBr_2 forms more readily in the presence of H_2 and that it is readily converted into $HBBr_2$ and H_2BBr by H_2. However, a complex of hydrogen and BBr_2 in its first excited state may lead to the hydrogenation products. The yield of H_2BBr is greatest when the concentration of hydrogen in the matrix is greater than about 10 mol %. Both hydrogen atoms that make up the H_2BBr come from the same molecule of hydrogen. Mixtures of H_2 and D_2 give H_2BBr and D_2BBr with only a trace of HDBBr whereas matrices containing HD produce only HDBBr.

The bonding between dihydrogen and transition metals involves both the acid and base character of the hydrogen; the HOMO of hydrogen acts as a σ-donor orbital while the LUMO acts as a π-acceptor orbital.[1] We have attempted to explore the acid or base behavior of hydrogen in situations in which it could act as only an acid or only as a base. Recently, we reported the characterization of weak van der Waals associations of hydrogen and Lewis bases that cannot π bond.[2] For strong, neutral bases, the H–H stretching vibration is red-shifted by 20 cm^{-1} from the position of an unperturbed H–H stretch. Much larger shifts are observed in complexes of H_2 and transition metals,[3] a fact which makes it appear as if the donor ability of hydrogen far exceeds its acidity. To evaluate the donor capabilities of hydrogen, we undertook a study of a series of Lewis acids which could not easily act as π donors. $Al(CH_3)_3$, $(\eta^5\text{-}C_5(CH_3)_5)Eu$,[4] $BHBr_2$, and BBr_3 have all been examined in H_2-containing matrices. With the possible exception of $BHBr_2$,[5] the study of which is still incomplete, there is no evidence of complex formation upon codepositing the aforementioned acids with H_2 in argon matrices. During the course of these studies, a report of the matrix synthesis of H_2CuCl has appeared. In this association, copper is thought to behave as a simple Lewis acid.[6] In the course of these studies we discovered that the ultraviolet irradiation of BBr_3 in H_2-containing matrices did produce new products, including HBr, $HBBr_2$, and H_2BBr. An intermediate forms in that reaction which we initially assigned the formula H_2BBr_3.[7] We acknowledge the assistance of a reviewer in reassigning the identity of that intermediate to BBr_2, a species which had been reported earlier albeit with one mistaken band assignment.

Experimental Section

BBr_3 was obtained from the Aldrich Chemical Co. Just prior to its use, it was stripped of HBr by vacuum. $BHBr_2$ was prepared by passing BBr_3 through a heated tube containing $NaBH_4$ at 250 °C just prior to deposit.[8] In addition to $BHBr_2$, B_2H_6 and unreacted BBr_3 were detected in the matrix. Argon and deuterium (Air Products) and hydrogen (Matheson) were nominally over 99.99% pure. HD (MSD Isotopes) was of 98% purity. Oxygen was 99.99% pure. Some experiments were conducted with argon that was contaminated with CO_2. In subsequent experiments, CO_2 was removed by a column of Ascarite.

Matrices of BBr_3 were made either by subliming it directly into the cryostat as Ar/H_2 mixtures were being admitted or, alternatively, by the use of previously-mixed $BBr_3/H_2/Ar$ mixtures. The extreme moisture sensitivity of BBr_3 made it difficult to achieve deposits of uniform composition at low concentration because of surface reactions with water and possibly adsorption. As a result of these reactions, HBr was a ubiquitous impurity. In order to minimize these reactions, most matrices were made by diffusing BBr_3 into a gas stream from a glass vessel with a 2-mm orifice at temperatures ranging from 180 to 200 K. Also, the entire apparatus was exposed to BBr_3 prior to cool-down in order to scavenge adsorbed water. This procedure was used especially after the system had been exposed to atmospheric gases. BBr_3 causes Buna-N rubber O-rings to swell dramatically, and it darkens Apiezon stopcock grease. Once the severity of the problem was appreciated, the BBr_3 in the sublimation source was stored in a liquid-nitrogen bath when it was not in use in order to reduce the exposure of these components to BBr_3. BCl_3 has been reported to react with Teflon, but the Teflon valve parts that were exposed to BBr_3 showed no evidence of deterioration.[9]

Matrices contained from 5 to 20 mol % H_2. Because of the extreme volatility of the hydrogen, the actual composition of the matrix is probably less than the nominal concentration in the gas mixture. The deposits were usually made while the cold-end was being pumped by a diffusion pump through a partially-open valve so that some of the hydrogen is removed during deposition.

Descriptions of our use of infrared and Raman spectroscopy have already appeared.[2,10] In addition to the routine use of the Perkin-Elmer FTIR, spectra were made by using a Beckman 4260 infrared spectrometer to observe the region between 450 and 275 cm^{-1}. Additionally, spectroscopic observations were made by using a Cary 17 spectrometer in the ultraviolet, visible, and near infrared regions. In every instance, an infrared spectrum was recorded so that changes that were observed

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(5) As an outgrowth of this study, experiments have begun on $BHBr_2$. In the presence of H_2, new features are present at higher wavenumber than the positions of $HBBr_2$ in argon.

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in the electronic spectrum could be correlated with changes in the infrared spectrum. Deposits were made at a rate of approximately 1 mmol/h. The matrices were photolyzed with two low-pressure mercury penlamps placed on opposite sides of the cryostat for as long as 8 h. A phosphor-coated, mercury penlamp (Hammatsu Corp., Model 80-1025-01/351) was used to produce a broad fluorescence spectrum centered at 351 nm in addition to the mercury lines in the near-ultraviolet and visible regions of the spectrum. A projector fitted with a 400-W projector lamp was used for its visible irradiance. In several experiments, a Metrologic helium/neon laser, Model ML820, was used for its irradiance at 633 nm. It was defocused so that the entire matrix was illuminated.

ESR spectra were recorded on a Varian E-3 spectrometer. The cryogenic equipment was configured in a similar fashion as illustrated elsewhere.[11] Matrices were irradiated by a penlamp through a grid window in the front of the ESR cavity for as long as 5 h. No attempt was made to rotate the rod; thus, not all regions of the matrix were irradiated.

Results

Argon matrices of BBr_3 are characterized by two infrared absorptions at 849.0 and 812.8 cm^{-1} which are assigned to the E symmetry, B–Br stretching vibrations of $^{10}BBr_3$ and $^{11}BBr_3$, respectively. In addition to these absorptions, two shoulders are present at 845 and 808 cm^{-1}. The shoulders are not due to aggregates because there is no correlation between the intensities of these features and the concentration of BBr_3. The shoulders are present in pure argon matrices of varying concentrations of BBr_3, as well as in matrices containing H_2, D_2, or Ne. By contrast, BF_3 strongly associates in matrices producing more complex band patterns than those observed for BBr_3 matrices.[12] In addition to the aforementioned features and those ascribed to common impurities in vacuum systems, two sets of absorptions were occasionally noted which were due to impurities which sublime with BBr_3. One set which includes absorptions at 775 and 753 cm^{-1} had previously been noted and assigned to $HBBr_2$,[13] an assignment which is inconsistent with work reported herein.[14] A second set of impurity bands are observed, the most intense of which occurs at 1350 cm^{-1}. When this impurity was most concentrated, there were additional features present in the region of the E mode of BBr_3, principally at 830 cm^{-1}. Neither set of impurities are significantly affected by ultraviolet radiation whereas BBr_3 undergoes dramatic changes.

There is no evidence of an association of H_2 with BBr_3 prior to ultraviolet irradiation. When hydrogen is present in the matrix, the infrared bands are shifted by only 2 cm^{-1} to larger wavenumber and are usually somewhat broadened. The frequency of the totally symmetric stretching vibration remains near 274 cm^{-1} as measured by Raman methods.[15] Moreover, the optical transition at 253 nm is not affected by the presence of H_2 nor is it sensitive to the substitution of Kr for Ar. Finally, nothing appears in the region of 4135–3000 cm^{-1} of the Raman or the infrared spectrum that can be assigned to a perturbed H–H stretch.

When hydrogen-containing matrices of BBr_3 are irradiated in the 253-nm band with a low-pressure mercury lamp, new absorptions appear at the same time as the bands of BBr_3 become attenuated. Some of the new absorptions can be assigned to $HBBr_2$, on the basis of comparisons with independently synthesized $HBBr_2$ and gas-phase data.[16–19] Others are assigned to the largely uncharacterized H_2BBr. These absorptions are most prominent in matrices containing greater than 10 mol % of hydrogen (vide infra). Also, a weak band at 2496.5 cm^{-1} appears in a position which has been assigned to HBr aggregates.[20] In addition to the above, bands at 870.3, 833.2, and 551.0 cm^{-1} behave as though they belong to intermediates. (A single intermediate, I, is responsible for the bands; vide infra.) Rather than continuously growing with longer photolysis times, they reach a maximum intensity after which they then decline. Dramatically, the bands are bleached by visible light; even short periods of irradiation with a 400-W projector lamp cause the bands to vanish with concomitant growth in the bands due to BBr_3, HBr, $HBBr_2$, and H_2BBr. (See Figures 1 and 2.)

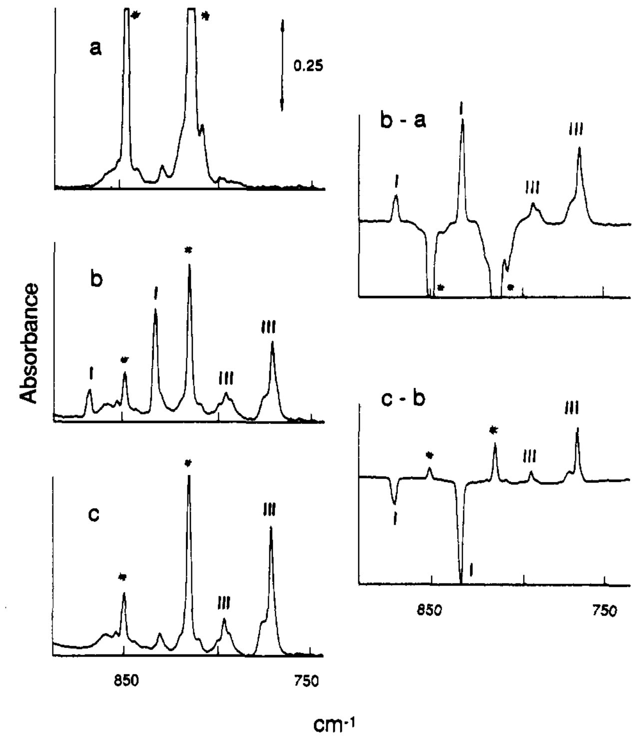

Figure 1. Spectra taken of an argon matrix containing BBr_3 and 18 mol % H_2: (a) After 120 min of deposit; (b) after 280 min of irradiation with two low-pressure mercury lamps; (c) after 90 min of irradiation with an unfiltered projector lamp. Also plotted are difference spectra on the right side. Asterisks mark the positions of absorptions due to BBr_3. I marks the asymmetric stretch of BBr_2; III denotes bands due to $HBBr_2$. All spectra are plotted with the same scaling.

BBr_3 in D_2- and HD-containing matrices behaves similarly, but there are several key differences. Because of mixing between the B–D deformation and B–Br stretching modes, the appearance of the spectrum of $DBBr_2$ is quite different from that of $HBBr_2$.[18,19] (See Figure 2.) In HD-containing matrices, bands of both $HBBr_2$ and $DBBr_2$ grow with irradiation by either ultraviolet or visible light, but the amount of $DBBr_2$ which is formed is approximately 1.6 times that of $HBBr_2$.[21] Also, in HD-containing matrices none of the bands associated with D_2BBr and H_2BBr are observed to grow; only HDBBr is produced. By contrast, the photolysis of BBr_3 in mixtures of H_2 and D_2 yields H_2BBr and D_2BBr, while there is little growth of the band at 1079 cm^{-1} that is assigned to HDBBr. (See Figure 4.) Thus, it is clear that both hydrogen

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(21) The relative extinction coefficients for the absorption at 769 cm^{-1} of $HBBr_2$ and the absorption at 864 cm^{-1} $DBBr_2$ were calculated by noting the amount of intensity that was produced by the loss of unit absorbance of the band at 833 cm^{-1} of I. This estimate is most accurate if $HBBr_2$ and HBr are the sole products produced by I when it is destroyed by visible light, but H_2BBr is also produced. The rigor is not lost if the yields of H_2BBr and D_2BBr are the same. However, this event is unlikely. Because D_2 is probably more efficiently trapped in the matrix than H_2, the concentration of D_2 is higher for a given nominal H_2 concentration. This would likely lead to a greater yield of D_2BBr than H_2BBr. As a consequence, we have probably underestimated the relative oscillator strength of the bands of $DBBr_2$. The estimate of 1.6 molecules of $DBBr_2$ formed for every $HBBr_2$ then should be viewed as a lower limit.

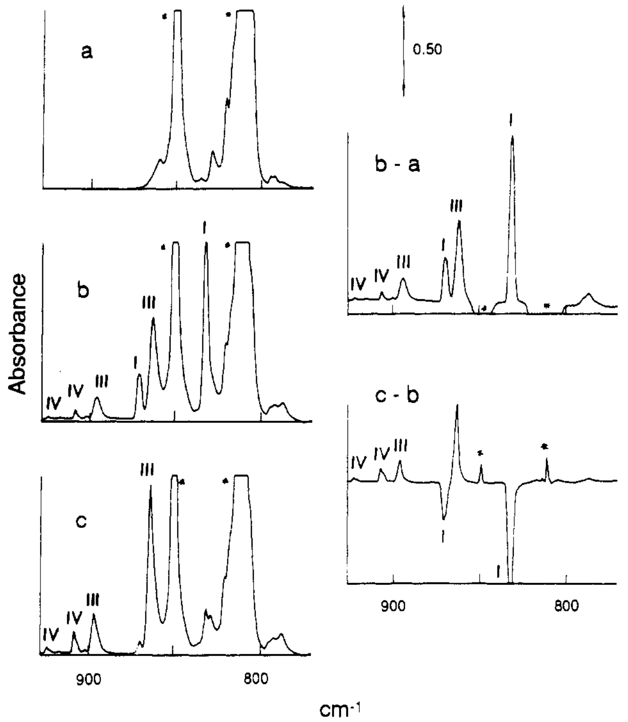

Figure 2. Spectra taken of an argon matrix containing BBr_3 and 19 mol % D_2: (a) After 25 min of deposit; (b) after 160 min of irradiation with two low-pressure mercury lamps; (c) after 15 min of irradiation with an unfiltered projector lamp. Also plotted are difference spectra on the right side. Asterisks mark the positions of absorptions due to BBr_3. I marks the asymmetric stretch of BBr_2; III and IV denote bands due to $DBBr_2$ and D_2BBr, respectively. All spectra are plotted with the same scaling.

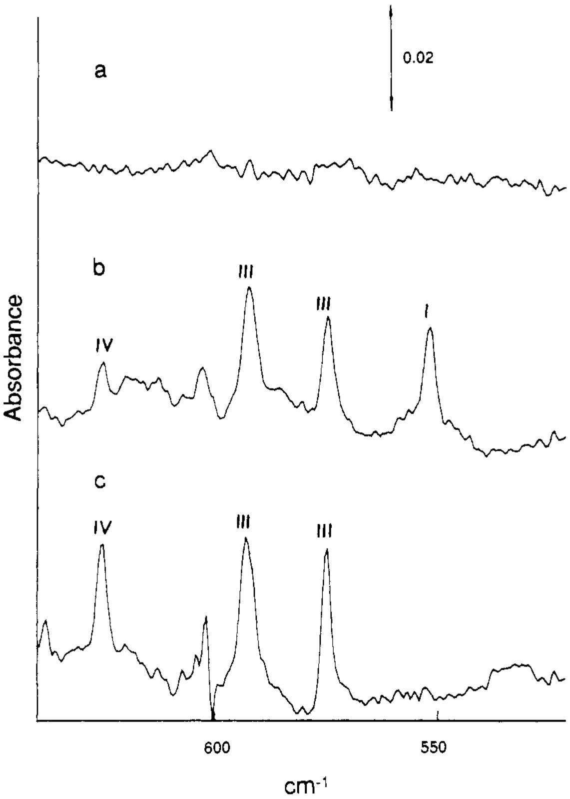

Figure 3. Spectra taken from the same experiment which was used for Figure 2, a matrix containing 19 mol % of D_2 in argon: (a) After 25 min of deposit; (b) after 160 min of irradiation with two low pressure mercury lamps; (c) after 15 min of irradiation with an unfiltered projector lamp. I marks the symmetric stretch of BBr_2; III and IV denote bands due to $DBBr_2$ and D_2BBr, respectively.

atoms that make up H_2BBr must come from the same molecule of H_2. Finally, there is no evidence that H_2BBr can be produced from $HBBr_2$; matrices of $HBBr_2$ can be photolyzed with low-pressure mercury lamps in D_2-containing matrices for long periods without loss.

HBr is also observed as a product of the photolysis of BBr_3 in H_2-containing matrices. Its identification as a product is made more difficult because of the usual presence of HBr in the unphotolyzed matrix. Matrix isolated HBr freely rotates in argon, and the Q vibrations of both DBr and HBr are weak[20,22] and have not been observed in these experiments. Photolyzed matrices of BBr_3 that contain hydrogen show absorptions at 2496.5 and 1792 cm^{-1} for HBr and DBr, respectively, which are coincident with the strongest absorptions of $(HBr)_2$.[20] Observations in the spectral regions of the weaker absorptions of the dimer species are complicated by absorptions of other molecules. Although it is conceivable that $(HBr)_2$ forms, other associations of HBr might also give rise to such an absorption. The growth at 2496.5 cm^{-1} cannot be ascribed to light-induced changes in the spectrum of impurity HBr because no analogous growth is noted when D_2-containing matrices of BBr_3 are treated in a similar fashion. DBr has never been an impurity in these experiments; thus, the source of the band at 1792 cm^{-1} can be unambiguously ascribed to the reaction of D_2 with BBr_3.

The bands which are assigned to H_2BBr are only observed when the concentration of H_2 is greater than about 10 mol %, suggesting the involvement of more than a single molecule of hydrogen. The frequencies for H_2BBr with various isotopic compositions are tabulated in Table II. The bands could be differentiated from those of other species by exceptionally rapid growth as a result of visible and cadmium lamp irradiation. In some instances, assignments are more ambiguous. The H–B and H–Br stretching regions overlap. Two bands have been reported for HBr dimers at 2496.4 and, weakly, at 2550.3 cm^{-1}.[20] A band at 2548 cm^{-1} must be attributed to a H–B stretching vibration of H_2BBr because it is not observed in HD-containing matrices in which no H_2BBr is produced. Also, when the band at 2548 cm^{-1} is observed, it is too intense relative to the HBr band at 2496 cm^{-1} for all of it to arise from $(HBr)_2$. Two vibrations are of A_1 symmetry and are close enough in energy to expect mixing, the B–H deformation mode (A_1, in-plane scissor motion) and the B–Br stretch. The deformation mode exhibits an isotopic ratio $\bar{\nu}_H/\bar{\nu}_D = 1.30$, which is unexpectedly low, and the band assigned to the B–Br stretch is strongly dependent on the hydrogen mass. This latter mode is assigned to a band at 679 cm^{-1} in H_2BBr, close to the position of the B–Br stretch of BBr at 678 cm^{-1}.[23] Bands appear at 625.5 and 638.6 cm^{-1}, which are assigned to the same mode for $D_2{}^{11}BBr$ and $D_2{}^{10}BBr$, respectively. The large shift to smaller wavenumber relative to H_2BBr and the small boron isotopic splitting are both consistent with a large amount of mixing between the B–Br stretch and the B–D in-plane deformation mode. Weak bands observed at 714 and 756 cm^{-1} for HDBr and D_2BBr, respectively, may be due to overtones. The band at 756 cm^{-1} is nearly as intense as the band assigned to the B–Br stretch, indicative of possible mixing with the fundamentals.

The maximum intensity in the bands due to I is achieved when the H_2 concentration is at its greatest, approximately 18 mol %. Yet, it does not appear that H_2 is required for the appearance of I. Weak bands are observed in the positions of those of I even when no hydrogen had been introduced into the argon, albeit at much lower yields. For instance, an argon matrix of BBr_3 produced an optical density at 833 cm^{-1} of 0.2 after 1100 min of irradiation, in sharp contrast to the 160 min it took to achieve

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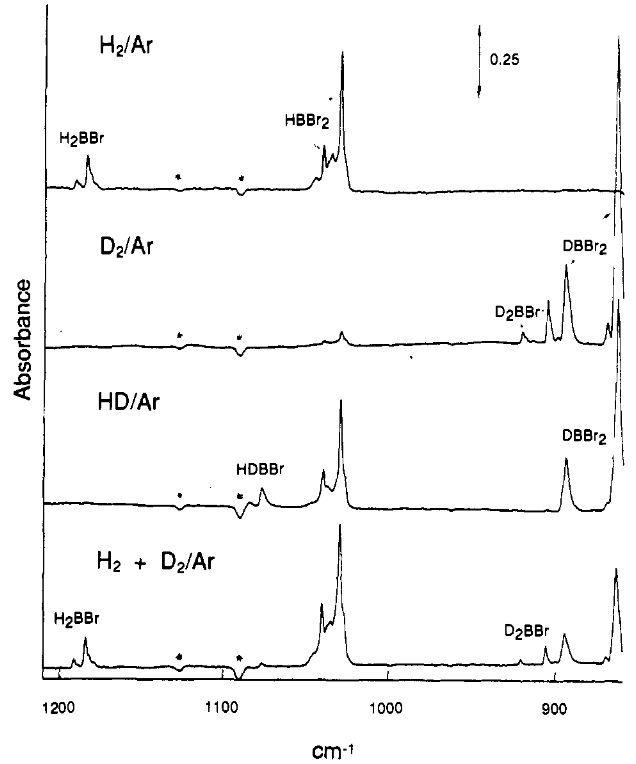


Figure 4. Difference spectra made from a series of experiments. The spectra are the result of subtracting the spectrum made from the initial deposit from that obtained after the use of the unfiltered projector lamp. Asterisks mark the positions of a combination band of BBr_3. The appearance of some $HBBr_2$ in the D_2-containing matrix is the result of reaction of BBr_3 with adventitious HBr and H_2.

an absorbance of 1.0 in the presence of 18 mol % D_2. If an argon matrix of BBr_3 is annealed prior to ultraviolet irradiation, then the probability of forming I is even less than for an unannealed matrix.

In contrast to the bands of $HBBr_2$ and H_2BBr, there is no hydrogen mass effect in the spectrum of the intermediate, I. Of the bands that are assignable to I, the bands at 870.3 and 833.2 cm^{-1} are clearly correlated; the correlation with the band at 551.0 cm^{-1} was less clear because of variations in the width of the band at 833 cm^{-1} from one experiment to another. The ratio of intensities of the bands at 833 and 551 cm^{-1} averaged 40:1 over 12 determinations with a standard deviation of 10. An experiment was designed in which the formation and subsequent destruction of the intermediates was monitored 6 times during which the signal to noise at 551 cm^{-1} never was less than 4. Fortunately, the shape of the band at 833 cm^{-1} was not significantly altered over the course of the experiment. Then, the ratio of intensities of the bands at 833 and 551 cm^{-1} averaged 42.6 with a standard deviation of 1.6 when the intensity ratio was measured at various stages of ultraviolet irradiation and subsequent bleaching with a He–Ne laser.

The photolysis of H_2-containing matrices causes new absorptions to grow in the visible and ultraviolet spectrum, principally at 297, 432, and 384 nm, as well as a shoulder at 326 nm. The bands at 384 and 432 nm are almost 50-nm wide at half-height, whereas the band at 297 nm is quite narrow. On the long wavelength side of the band at 432 nm is a broad featureless absorption. By using a phosphor-coated, low-pressure mercury lamp, all the new bands could be attenuated except the bands at 297 cm^{-1} and the broad feature which is centered at 630 nm. It was evident from the infrared spectrum that I was unaffected. Irradiation with a helium–neon laser at 633 nm caused the broad band at 630 nm and the infrared spectrum of I to become attenuated. No infrared absorptions could be assigned to the species which gave rise to the bands that disappear with 351-nm irradiation. From the behavior of the optical bands, one can identify at least three different species that form due to irradiation with 254-nm light. These species may be related to the chemistry that causes the ESR spectrum that is assigned to matrix impurities.

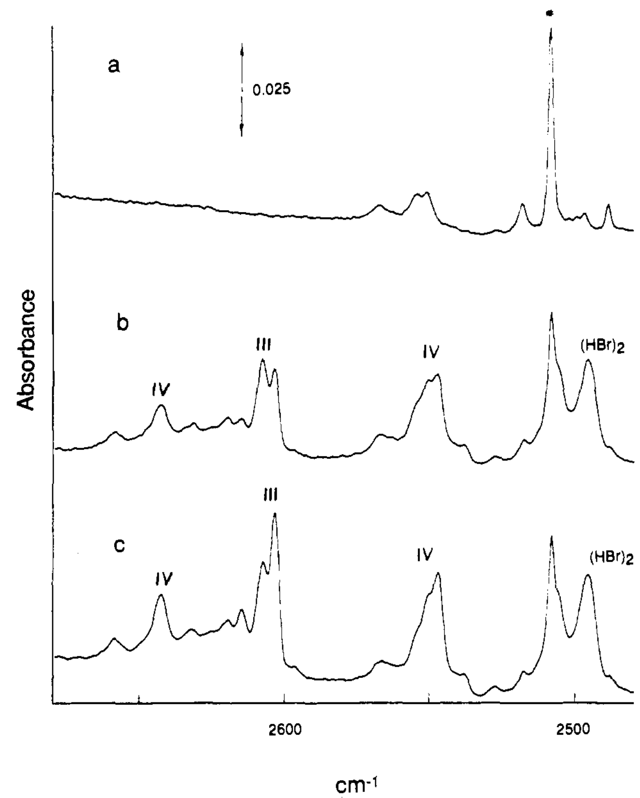


Figure 5. Spectra taken from an argon matrix containing BBr_3 and 9 mol %, each, of D_2 and H_2: (a) After 30 min deposit; (b) after 650 min of irradiation with two low-pressure mercury lamps; (c) after 20 min of irradiation with an unfiltered projector lamp. An asterisk marks the position of absorptions due to HBr which was initially present. III and IV denote bands due to $HBBr_2$ and H_2BBr, respectively. The integrated intensity of the band at 2508.5 cm^{-1}, marked by an asterisk, remains unchanged throughout the experiment.

Irradiation of argon matrices containing BBr_3 and H_2 produced an ESR spectrum of the hydrogen atom and also a feature in the region of $g = 2.00$. Both features can be detected in the absence of BBr_3 and H_2; thus, they can be assigned to minor photolysis products which arise from contaminants in the matrix. Moreover, the same products were observed when the matrix was doped with D_2. When CO was also present in the matrix, HCO was detected, a species which could even be seen occasionally by IR. With D_2 present, DCO was not detected.

Although the bands due to I can be readily photobleached, it is difficult to study the effects of annealing. Matrices containing large quantities of H_2 cannot be raised to temperatures above 17 K without losing large quantities of hydrogen. Then, the temperature often rises uncontrollably. If the matrix survives, the spectral quality of the remaining species will often be substantially degraded. On one occasion it was possible to warm a matrix containing 10 mol % hydrogen and BBr_2 to 25 K. The bands due to I were somewhat attenuated at 17 K while there was a small increase in the peak heights of bands due to both BBr_3 and $HBBr_2$. On further heating to 25 K, more I was lost as additional growth was observed in the region of, but not coincident with, the BBr_3 antisymmetric stretch. Similar annealing behavior is noted in the absence of hydrogen.

A number of observations were made to determine whether I might originate from a reaction of BBr_3 and an impurity in the vacuum system. BBr_3 was deposited in matrices with as much as 20 mol % HBr in order to ascertain whether I could be formed from HBr and BBr_3. Although $HBBr_2$ could be formed by

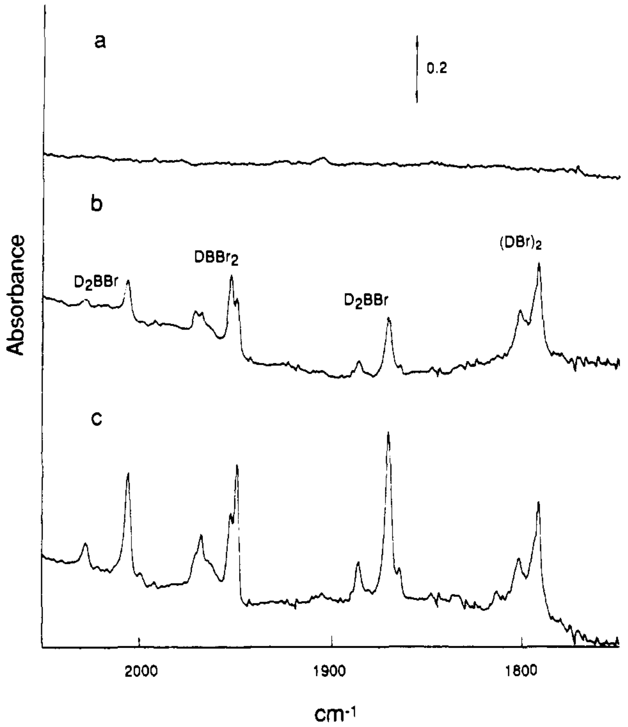


Figure 6. Spectra of the D–B stretching region taken from the same experiment which was used for Figure 2, a matrix containing 19 mol % of D_2 in argon: (a) After 25 min of deposit; (b) after 160 min of irradiation with two low-pressure mercury lamps; (c) after 15 min of irradiation with an unfiltered projector lamp.

Table I. Positions of Infrared Absorptions (cm^{-1}) Due to BBr_2 (I) and $HBBr_2$

	$HBBr_2$		
BBr_2 (I)	generated in situ[a]	Ar matrix[b]	$DBBr_2$[a]
870.3		2613.5	1967.5[c]
833.2	2604.5[c]	2602.0	1949.0
551.0	1042.5[d]	1041.6	895.5
	1032.0[d]	1031.0	864.0
	1047.2[d]		656.0
	1037.5[d]		593.3
	794.5	793.8	574.3
	769.0	768.0	
		741.7	
	730.4	730.6	
		617.3	
	595.6	595.2	

[a] $HBBr_2$ generated in situ in Ar matrices. [b] $HBBr_2$ generated from $NaBH_4$ and BBr_3 prior to deposit. [c] Peaks are prominent over a broad plateau of new absorptions. [d] Spectrum is split into pairs of pairs.

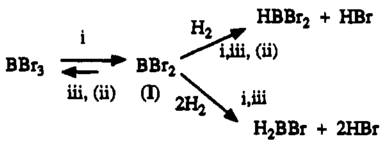
Table II. Positions of Infrared Absorptions Due to H_2BBr (IV)[a]

H_2BBr	HDBBr	D_2BBr	assgnt	mode sym[b]
2659.5		2027.5	$\nu_s(^{10}B–H,D)$	A_1
2643.5	2597.6	2005.2	$\nu_s(^{11}B–H,D)$	A_1
	1941.0	1885.5	$\nu_a(^{10}B–H,D)$	B_2
2548.5	1926.6	1870.0	$\nu_a(^{11}B–H,D)$	B_2
1198.5	1086.4	921.5	$\delta(^{10}BH_2,HD,D_2)$	A_1
1185.5	1079.0	906.5	$\delta(^{11}BH_2,HD,D_2)$	A_1
	713.8	756.0	overtones?	A_1
		638.6	$\nu_s(^{10}B–Br)$	A_1
679.0		625.5	$\nu_s(^{11}B–Br)$	A_1

[a] All data are taken from Ar matrices, in cm^{-1}. [b] C_{2v} symmetry, *y* axis is assumed to lie in the plane.

irradiating the matrix with a low-pressure mercury lamp, the bands due to I were not observed. The yield of $HBBr_2$ was not nearly as large as with H_2-containing matrices for the same duration of exposure to ultraviolet light. Matrices were formed of BBr_3 and argon doped with H_2O, CO_2, O_2 CO, N_2, and CH_4. In no case could the production of I be correlated with the concentration of impurity. The irradiation of BBr_3 in O_2-containing matrices causes a rapid reaction, but the spectrum of products was not that of I.

Scheme I



i Irradiation with 254 nm light

ii Annealing to 25 K (minor changes)

iii Irradiation with visible light

I has been formed in high yields in matrices that were as dilute as 0.1 mol % of BBr_3 suggesting that I does not require more than a single BBr_3 molecule to form. In matrices that are much more concentrated in BBr_3, there are no few features that would suggest that the reaction follows a different course at high concentration. To determine if the spectrum of I was due to some matrix-dependent phenomenon, BBr_3 was photolyzed in a Kr/H_2 matrix; the behavior of BBr_3 in Kr mimics its behavior in Ar.

Discussion

The observations are consistent with Scheme I. The fact that only three bands can be assigned to I and that no impurity or concentration effects correlate with its formation suggests that I forms by a unimolecular photodecomposition of BBr_3. The bands at 833 and 870 cm^{-1} had been assigned to BBr_2 by Miller and Andrews.[13] For I to be BBr_2, however, it is necessary to correct the previous assignment of the totally symmetric B–Br stretch.[25] Consistent with the claim that I is BBr_2 is the absence of any deuterium-isotope effect on the spectrum of I and the sensitivity of photolyzed BBr_3 to O_2 in contrast to its reactivity with other contaminants. The novel products that are formed by O_2 may result from the insertion of O_2 into the fragmented B–Br bond. Radical coupling products were not detectable by either ESR or infrared spectroscopies, however.[24]

The ability to form I in the absence of H_2 suggests that H_2 is not required although the presence of H_2 has a dramatic influence on the yield. From annealing experiments in pure argon, it is clear that the BBr_3 which successfully loses a bromine atom is in a unique site. The increased yield of homolysis products in the presence of H_2 may be ascribed to a variety of causes. Local softening of the matrix in the vicinity of the H_2 may occur, or the presence of hydrogen may assist in removing thermal energy from the fragments, thereby retarding their recombination. The increased yield cannot be ascribed to the formation of H_2BBr_2. The most intense vibrational features of BBr_2 shift by less than 2 cm^{-1} as a result of the presence of H_2. This behavior is similar to the effect of H_2 on the spectrum of BBr_3. By contrast, coordination of H_2 on CuCl results in a 10-cm^{-1} shift in the Cu–Cl stretching frequency.[6] Hay has performed preliminary

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(25) In the reported spectrum of BBr_2 there is a band at 596 cm^{-1} which is assigned to the totally symmetric B–Br stretching vibration.[13] We observe nothing in the region of 596 cm^{-1} which can be assigned to I, although a band appears at 596 and 593 cm^{-1}, which is due to $HBBr_2$ and $DBBr_2$, respectively.[18] It is unlikely that a band due to I can escape notice unless it is exceedingly weak because visible irradiation should cause it to disappear. Using intensity ratios from the published spectrum of BBr_2, we anticipated an absorbance of at least 0.05 absorbance units for the band in several experiments using both hydrogen and deuterium. We have observed intensities in this region of 0.02 or less, and the intensity is not diminished by visible irradiation. Moreover, using the published intensity ratios we have found that all the intensity found by Miller and Andrews at 596 cm^{-1} [13] must be attributed to $HBBr_2$.

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Scheme II

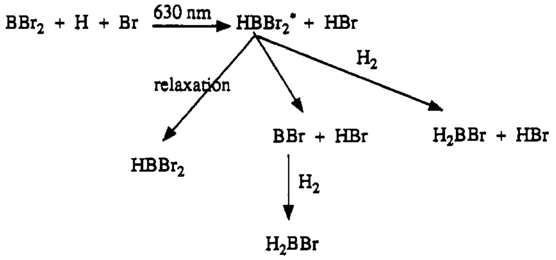
$$H_2 + BBr_2 + Br + \text{photon} \rightarrow HBBr_2 + HBr$$

Scheme III

$$H_2 + BBr_2 + \text{photon} \rightarrow HBBr_2 + H$$

$$H + Br \rightarrow HBr$$

Scheme IV



calculations on the system $BBr_2 + H_2$, which also suggests that H_2 and ground-state BBr_2 do not interact significantly.[27]

If I is BBr_2, then there are four questions which must be addressed. What is the role of the bromine atom in the observed reactions? How can both $HBBr_2$ and H_2BBr be formed from the same intermediate? Is there any interaction between I and H_2 prior to the reaction that leads to $HBBr_2$ and H_2BBr? Why did the radical products escape ESR detection?

It is clear that photoexcitation of BBr_2 leads to the formation of $HBBr_2$. There are two plausible routes to its formation that can be differentiated using ESR evidence (Schemes II and III). In the first alternative, the production of HBr and $HBBr_2$ are accomplished in the same reaction whereas the reactions are uncoupled in the second alternative. We favor Scheme II. The simultaneous interaction of three particles is not unreasonable because H_2 is so abundant in the matrix and Br and BBr_2 are close neighbors, having been generated from a precursor BBr_3 in a rigid environment. If Scheme III correctly described the behavior, one should be able to detect H atoms. Indeed, we do observe protium atoms and HCO by ESR. However, adventitious hydrogen atoms are ubiquitous even when there is no obvious source of hydrogen. What is inconsistent with this second model is our failure to observe deuterium atoms or DCO in D_2-containing matrices of BBr_3.

The model for the formation of H_2BBr must be consistent with the following observations. H_2BBr is formed from BBr_2 and H_2 simultaneously with the formation of $HBBr_2$. Moreover, the concentration of H_2 must be greater for the formation of H_2BBr than for forming $HBBr_2$. Ground-state $HBBr_2$ cannot be converted to H_2BBr by using 254-nm radiation. Finally, the two hydrogens of H_2BBr must come from the same molecule of H_2. We propose a model which starts with the formation of a very excited $HBBr_2$ (Scheme IV). The energy content of the nascent $HBBr_2$ stems from the visible photon that initiates the reaction (189 kJ/mol) and the new B–H and H–Br bonds, which yield 389 and 362 kJ/mol, respectively.[26] Since only an H–H bond is broken, the products must dissipate as much as 500 kJ/mol. Such an energy is more than sufficient to fragment $HBBr_2$ into HBr and BBr, although BBr has not been detected. If BBr is formed as a transient, it could react rapidly with either H_2 or HBr. The reaction with H_2 would be more favored as the concentration of H_2 in the matrix was larger, as is observed. On the other hand, the reaction of BBr with HBr gives no new products.

Alternatively, BBr may not have to form if an excited state will react directly with H_2 to yield HBr as H_2 is added. An alternative mechanism involving bromine atom abstraction from H_2BBr_2 (vide infra) by Br must be excluded. No molecular bromine is detected by optical spectroscopy. Moreover, the different H_2-concentration dependence for H_2BBr formation relative to $HBBr_2$ formation cannot be explained by bromine atom abstraction.

The first excited state of BBr_2 results from the excitation of a single electron from a nominally sp^2 hybrid orbital in the BBr_2 plane into the vacant p orbital. Such an excited BBr_2 resembles a coordinatively unsaturated transition metal complex by having a filled (albeit half-filled) orbital of π symmetry and a vacant σ orbital in the BBr_2 plane. Hay found a significant bond between this excited BBr_2 and H_2.[27] It may be that the photoreactions that have been observed in this study result from the interactions of H_2 and the excited state of BBr_2. Once coordinated, a hydrogen molecule can react with bromine atoms to yield $HBBr_2$ and HBr as described in Scheme II. The reaction of an excited state BBr_2 with hydrogen mimics the behavior of atoms in the gas phase and in matrices.[28] The population of a metal orbital capable of donating electron density into the H_2 σ^* orbital appears to be a prerequisite for reaction.

BBr_2 would be expected to be of C_{2v} symmetry with a lone electron in a sp^2-hybridized orbital. As such, there should be a large coupling between the boron nucleus and the unpaired electron, analogous to what is observed in the ESR spectrum of BCl_2[29] and BF_2.[30] The broad features that were seen could be observed in the absence of hydrogen and even BBr_3. They must be assigned to impurities. The inability to detect BBr_2 by ESR is the most unsettling feature of this report.

This study was begun in order to identify simple complexes of Lewis acids with H_2 in which there was no potential for significant π interactions. The spectrum of BBr_3 is so little perturbed that it offers no hint of an interaction. Perhaps the most diagnostic feature for the interaction is the ultraviolet transition at 253 nm which arises from an excitation of a lone pair electron of the bromines into the boron p_z. The insensitivity of this transition to the presence of hydrogen, or a switch from argon to krypton, suggests there is an insignificant interaction with these donors. This behavior contrasts with $Cr(CO)_5$ which shows a significant shift in its optical transitions as a function of the atom in the sixth coordination site.[31] One can only conclude that the acidity at boron is significantly satisfied by the presence of the bromine lone pairs. Ab initio calculations on the boron halides support this view.[32]

Although we have failed to observe complexes of H_2 wherein the hydrogen acts as a simple base, it is important to note that H_2 has been observed in association with several acids, most notably H^+.[33] Hydrogen has also been reported to selectively adsorb at cation sites in zeolites.[34] The only neutral complexes of hydrogen that have been reported is H_3F, a molecule which is T-shaped, with the HF molecule pointed into the H–H bond via its hydrogen[35] and H_2CuCl.[6] Of particular relevance to this study, the isotope exchange which results from acid attack on BH_4^- has been taken as evidence for the transitory existence of BH_5.[36] This view has recently been supported by calculations.[37] If such a molecule is at least weakly bound, then the existence of H_2BBr_3 should not have been surprising because BBr_3 is thought

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to be a stronger acid than BH_3.[38] What has precluded the formation of H_2BBr_3 is the attenuated acidity of boron due to the π interactions between boron and bromine. It seems clear that, for BBr_3 to be a stronger acid than BH_3, there must be a sufficiently strong interaction between a base and BBr_3 in the early stages of the reaction to power the trigonal distortion of BBr_3 and the loss of π-bonding.

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