Inorg. Chem. 1991, 30, 2990–2993

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Cocondensation Reaction of Arsine and Fluorine: Matrix Infrared Spectrum of AsH_2F

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Received October 16, 1990

The cocondensation reaction between arsine and fluorine in excess argon produced major new product infrared absorptions at 2117, 2108, and 649 cm^{-1} in solid argon at 12 K. Mixed and complete deuterium substitution showed that the former two As–H stretching bands are due to the vibration of two equivalent hydrogen atoms and that the 649-cm^{-1} As–F stretching absorption is coupled to two equivalent hydrogen atoms, hence the identification of AsH_2F. The spontaneous reaction is believed to proceed through AsH_3F_2, which was characterized by a 610-cm^{-1} infrared absorption.

Introduction

The increased reactivity of second-row hydrides as compared to first-row hydrides extends to third-row hydrides,[1,2] which can be demonstrated by cocondensation reactions of NH_3, PH_3, and AsH_3 with molecular F_2. All of these reactions are rapid at room temperature; however, on 12 K condensation of the room-temperature reagents with excess argon, NH_3 and F_2 form a molecular complex, and PH_3 and F_2 react in a controlled manner to give PH_3F_2, PH_2F, and PHF_2.[3,4] Similar arsine reactions were done to test reactivity and to prepare the new reactive compound fluoroarsine, AsH_2F. The only references to simple monosubstituted arsine compounds in the literature concern experimental and theoretical studies of the hydroxy analogue, arsinous acid, AsH_2OH.[5,6]

Experimental Section

The cryogenic apparatus and experimental techniques have been described in earlier papers.[3-5] Fluorine (Matheson) was diluted to Ar/F_2 = 50/1, 100/1, and 200/1 ratios in a passivated stainless-steel system used only for fluorine samples; care was taken to minimize water and HF impurity in the matrix samples. Arsine was prepared by adding 30% H_2SO_4 to powdered Zn_3As_2 in a 100-mL glass bulb under vacuum. The desired product gas was condensed on $CaCl_2$ pellets at 77 K, and the remainder was evacuated.[5,7] Several deuterium-enriched arsine samples were prepared by using D_2SO_4 or H_2SO_4 in D_2O. Arsine samples were diluted with argon to Ar/AsH_3 = 50/1, 100/1, and 200/1 ratios and codeposited with fluorine samples at rates of 2 mmol/h for 4–6 h on a 12 ± 1 K CsI window. Infrared spectra were recorded on a PE 983 spectrometer before and after sample annealing or photolysis using a high-pressure mercury arc. Wavenumber accuracy is better than 1 cm^{-1}.

Results

Arsine and fluorine samples were diluted with argon and codeposited at 12 K. New absorptions for AsH_3 and AsD_3 reaction products will be described in turn.

AsH_3. Seven codeposition experiments were done with AsH_3 and F_2 by using different combinations of argon dilutions. Infrared spectra are illustrated in Figures 1a and 2a, and product absorptions are listed in Table I. In the As–F stretching region, strong new bands were observed at 693, 649, 631, and 610 cm^{-1}. The As–H bending region revealed weak new bands at 984, 894, and 842 cm^{-1}. In the As–H stretching region, strong new absorptions were observed at 2117 and 2108 cm^{-1} and a weak new band was detected at 2099 cm^{-1}. The HF stretching region revealed medium-intensity bands familiar to the HF system[8] at 3962 (A = absorbance = 0.2), 3919, and 3881 cm^{-1}, a weak 3693 cm^{-1} band due to the AsH_3--HF complex,[7] and a new weak absorption at 3722 cm^{-1}. The far-infrared region exhibited bands at 409 and 261 cm^{-1} due to the AsH_3--HF and N_2--HF complexes, respectively.[7-9] The strongest water absorptions at 3756 and 1624 cm^{-1} showed less than 0.1 absorbance unit, indicating minimal water impurity in these experiments. The above new product bands did not appear in the spectrum of similar Ar/AsH_3 samples deposited without fluorine. Finally, the HF impurity absorption intensity in similar Ar/F_2 samples deposited without arsine was approximately 50% of the HF impurity absorption intensity observed in the arsine–fluorine codeposition experiments. On the basis of comparisons with earlier HF experiments,[7] the present HF impurity is 1–2% of the F_2 reagent concentration.

Table I. Infrared Absorptions (cm^{-1}) of New Products Formed upon Codeposition of Argon/Arsine and Argon/Fluorine Samples at 12 K

$AsH_3 + F_2$	$AsD_3 + F_2$	identification[a]
3962	2896	HF, R(0)
3919	2877	HF, Q induced
3881	2846	N_2--HF
3776	2771	?
3722	2734	AsH_2F–HF
3693	2716	AsH_3--HF
2117[b]	1526[b]	AsH_2F (3)
2108[c]	1518[c]	AsH_2F (3)
2099	1513	$AsHF_2$ (2)
984[b]		AsH_2F (3)
894	644	AsH_3F_2 (1)
842[c]	606[b]	AsH_2F (3)
693	698	AsH_xF_y
668	668	$AsHF_2$ (2)
649[b]	662[b]	AsH_2F (3)
631	620	AsH_xF_y
618	590	shoulder
610	583	AsH_3F_2 (1)
409	309	AsH_3--HF
261	212	N_2--HF

[a] Identifications for hydrogen species also apply to the perdeuteriated species by replacement of H with D. (1), (2), and (3) refer to the species as identified in the text, figures, and equations. [b] Full width at half-maximum is 2.0 cm^{-1}. [c] Full width at half-maximum is 3.0 cm^{-1}.

Similar experiments have been done with water and fluorine in this laboratory. Fluorine does not react with water on codeposition; full arc photolysis is required. In an experiment with water at the impurity level observed here from desorption of water from the walls of the vacuum chamber, photolysis produced weak H_2O/F_2 product bands that are not common with the present arsine/fluorine experiments. Finally, a series of experiments[7] has been done with AsH_3 and HF by using HF concentrations 50–100 times greater than that of the HF impurity in the fluorine used here. The AsH_3--HF complex products identified earlier are minor contributors to the present product spectrum.

The F_2/AsH_3 mole ratio in the matrix was varied in this series of experiments. Increasing the F_2 concentration at constant AsH_3 concentration increased absorbances of the product bands. The 693- and 631-cm^{-1} bands were weak with F_2/AsH_3 mole ratios <1, but their relative absorbances increased with F_2/AsH_3 ratios >1, as shown in Figure 1.

Sample annealing into the 28–32 K range typically increased the weak bands due to HF complexes at the expense of isolated

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(1) Manocha, A. S.; Setser, D. W.; Wickramaartchi, M. A. *Chem. Phys.* **1983**, *76*, 129.
(2) Agrawalla, B. S.; Setser, D. W. *J. Phys. Chem.* **1986**, *90*, 2450.
(3) Andrews, L.; Lascola, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6243.
(4) Andrews, L.; Withnall, R. *Inorg. Chem.* **1989**, *28*, 494.
(5) Andrews, L.; Withnall, R.; Moores, B. W. *J. Phys. Chem.* **1989**, *93*, 1279.
(6) Schneider, W.; Thiel, W.; Komornicki, A. *J. Phys. Chem.* **1990**, *94*, 2810.
(7) Arlinghaus, R. T.; Andrews, L. *J. Chem. Phys.* **1984**, *81*, 4341.
(8) Andrews, L.; Johnson, G. L. *J. Phys. Chem.* **1984**, *88*, 425.
(9) Andrews, L.; Kelsall, B. J.; Arlinghaus, R. T. *J. Chem. Phys.* **1983**, *79*, 2488.

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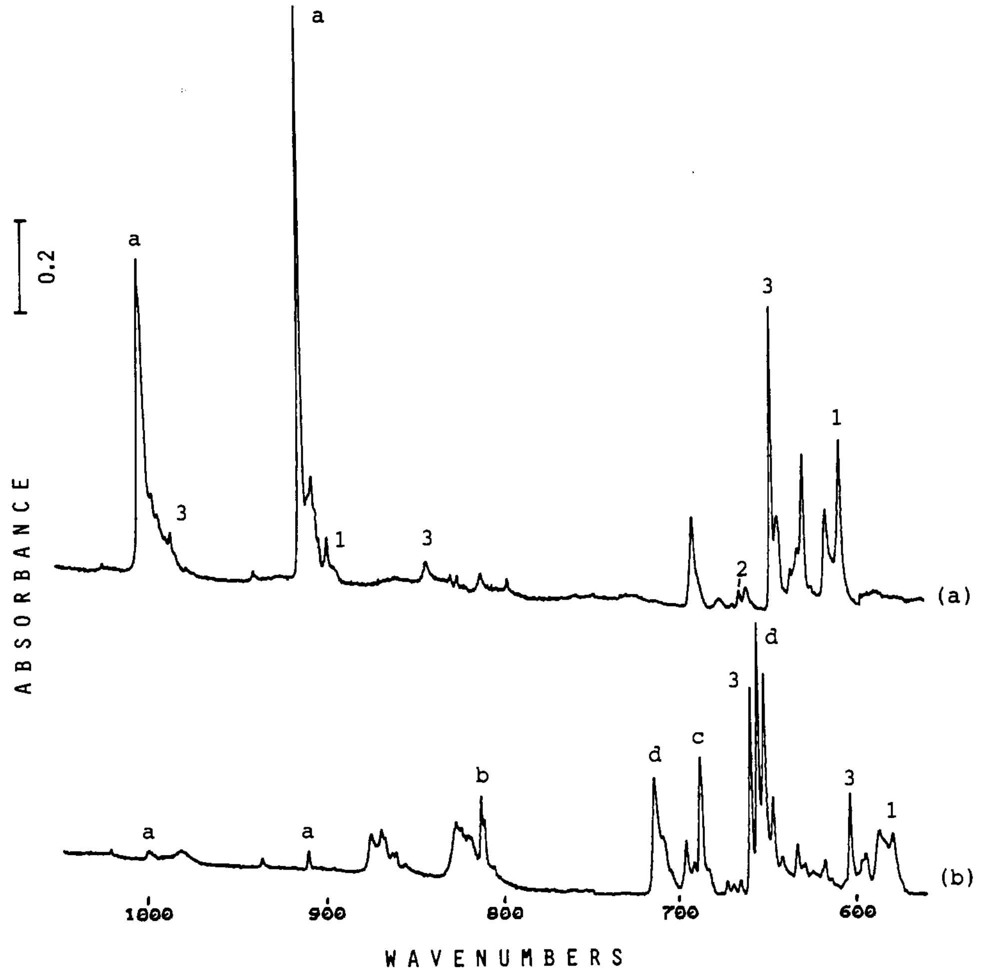

Figure 1. Infrared spectra in the 1050-550-cm^{-1} region following codeposition of arsine and fluorine samples at 12 K: (a) Ar/AsH$_3$ = 200/1 and Ar/F$_2$ = 50/1, 15 mmol of each sample; (b) Ar/AsD$_3$ = 200/1 and Ar/F$_2$ = 50/1, 17 mmol of each sample, approximately 90% deuterium enrichment. a donotes AsH$_3$, b identifies AsH$_2$D, c denotes AsHD$_2$, and d identifies AsD$_3$. Numbers refer to species formed in reactions 1–3. Absorbance scale: 0.0–2.0. Resolution: 0.5–1.0 cm^{-1}.

HF. In addition, a 30% *growth* was found for the 894- and 610-cm^{-1} bands (labeled 1 in the figures), the 2099- and 668- cm^{-1} bands (labeled 2) were unchanged, and a 20% *reduction* was observed for the 2117-, 2108-, 984-, 842-, and 649-cm^{-1} bands (labeled 3 in the figures). Mercury arc photolysis also substantiated this grouping of bands; the 610-cm^{-1} band increased by 20% whereas the bands labeled 3 increased only 5% in absorbance, and the 693- and 631-cm^{-1} bands were unchanged. The same behavior was found when photolysis was performed before annealing.

AsD$_3$. Six experiments were performed with AsD$_3$ samples using two different deuterium enrichments. The spectra revealed DF at 2896, 2877, and 2857 cm^{-1}, the N$_2$--DF complex at 2846 and 212 cm^{-1}, and the AsD$_3$--DF complex at 2716 and 309 cm^{-1}, demonstrating a reaction between AsD$_3$ and F$_2$; the HF region revealed much weaker bands in the positions described above for AsH$_3$ experiments. New bands were observed at 2734, 2771, and 3776 cm^{-1}, as are listed in Table I.

Figure 1b compares the spectrum in the As–F stretching region for the AsD$_3$ reaction with F$_2$. Isotopic precursor bands are labeled a–d for AsH$_3$, AsH$_2$D, AsHD$_2$, and AsD$_3$, respectively.[5,7] The major new product bands at 662.0 and 654.2 cm^{-1} bracket the sharp AsD$_3$ band at 657.9 cm^{-1}; the sharp 649.0-cm^{-1} band from the AsH$_3$ experiments was also observed. The relative intensities of the 662.0-, 654.2-, and 649.0-cm^{-1} bands follow the degree of deuterium enrichment, the 662.0-cm^{-1} band being strongest with the higher and the 654.4- and 649.0-cm^{-1} bands being stronger with lower deuterium enrichment. These three bands are appropriate for the As–F stretching fundamental of a molecule with two equivalent hydrogen atoms. The sharp 605.6-cm^{-1} band exhibits constant relative intensity with the 662.0-cm^{-1} band throughout the series of AsD$_3$ experiments.

Other major bands in this region included a new band at 583 cm^{-1} with a shoulder at 590 cm^{-1} that behaved on annealing like the 610-cm^{-1} band and 618-cm^{-1} shoulder in the AsH$_3$ studies.

Figure 2c shows the As–D stretching region; strong new bands were observed at 1526 and 1518 cm^{-1} with weaker new bands at 1522 and 1513 cm^{-1}; new bands were observed at 2113 and 2099 cm^{-1} in the As–H stretching region. Figure 2b shows the spectrum in both regions for a sample with less deuterium enrichment. Notice that the intermediate 1522-cm^{-1} band is stronger than the 1526- and 1518-cm^{-1} bands while the 1513-cm^{-1} band is unaffected in the As–D stretching region and the 2113-cm^{-1} band has 2117- and 2108-cm^{-1} shoulders while the 2099-cm^{-1} band is also unaffected in the As–H stretching region. These observations reveal one mixed H/D absorption in the As–H stretching region at 2113 cm^{-1} and one in the As–D stretching region at 1522 cm^{-1} for this new species.

Discussion

Products of the arsine and fluorine codeposition reaction will be identified, and the reaction mechanism will be discussed.

Identification. The corresponding phosphine and fluorine matrix reaction products PH$_3$F$_2$, PHF$_2$, and PH$_2$F are expected to be a model for the present studies.[4] Unfortunately, no data exist for any of the corresponding small AsH$_x$F$_y$ species. The strongest evidence for a new species from the present experiments is for the identification of AsH$_2$F from the product bands labeled 3 in the figures.

The 2117-, 2108-, 984-, 842-, and 649-cm^{-1} bands maintained constant relative intensities throughout this series of experiments, and thus these five bands are assigned to a single new species. The 649-cm^{-1} band is the strongest of these absorptions (*A* =

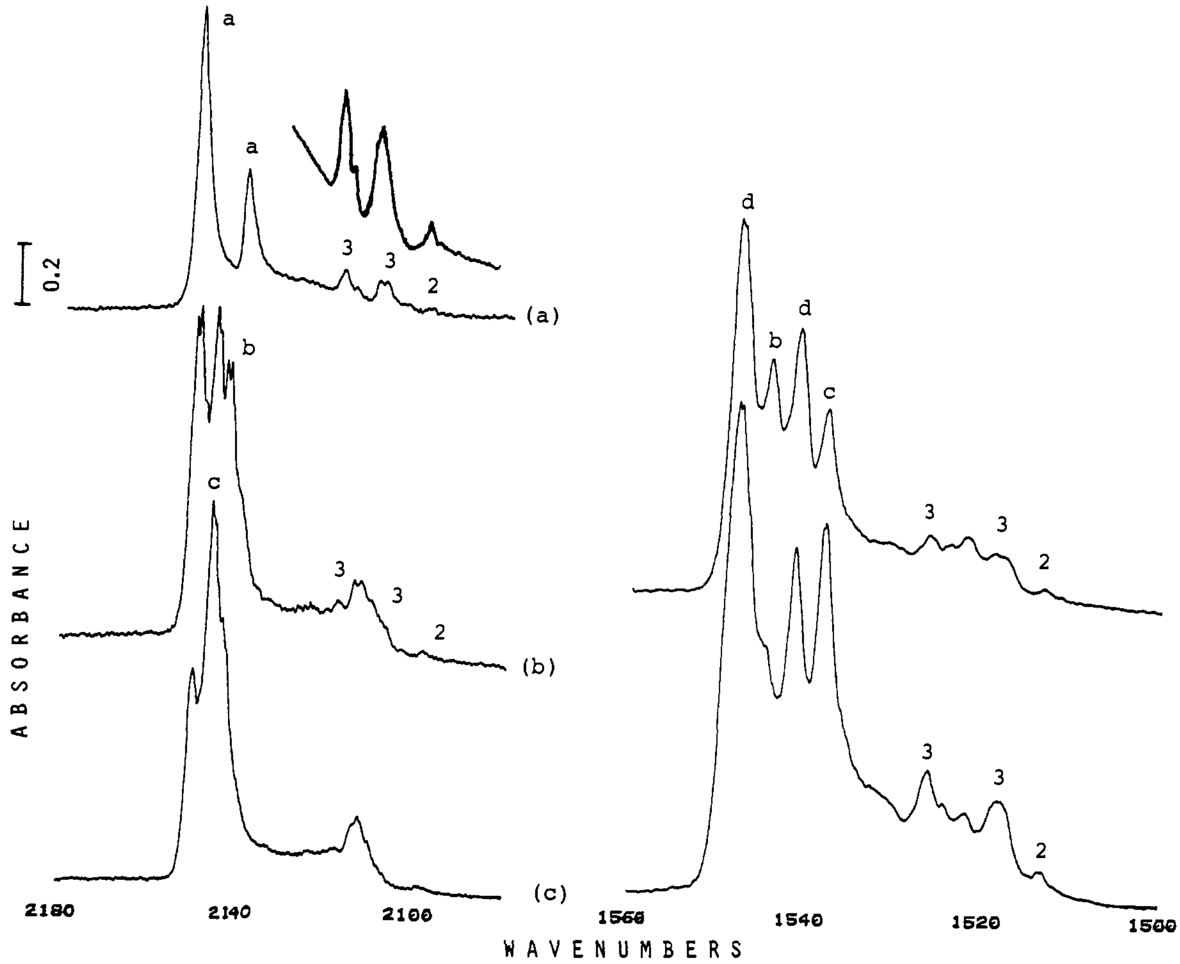

Figure 2. Infrared spectra in the As–H and As–D stretching regions for arsine and fluorine samples codeposited at 12 K, with Ar/arsine = 200/1 and Ar/F_2 = 50/1: (a) AsH_3; (b) mixed AsH_xD_y, approximately 65% deuterium enriched; (c) AsD_3, approximately 90% deuterium enriched. Numbers refer to species formed in reactions 1–3. Absorbance scale: 0.0–3.0. Resolution: 1–2 cm^{-1}. The spectra in Figure 2 were recorded during the first half of sample deposition, except the inset scan in Figure 2a, which was recorded after full sample deposition. Product bands were stronger but noise was higher in these regions after full sample deposition.

absorbance = 0.66 in Figure 1a); in the same spectrum, the 2117- and 2108-cm^{-1} bands are 25% as intense as the 649-cm^{-1} band. The 984- and 842-cm^{-1} bands are weaker, with A = 0.03 and 0.04, respectively, in Figure 1a.

In the As–H stretching region, two bands at 2117 and 2108 cm^{-1} below the strong stretching fundamentals of AsH_3 at 2150 and 2140 cm^{-1} are assigned to the antisymmetric and symmeteric As–H stretching fundamentals of AsH_2F. These bands shift to 1526 and 1518 cm^{-1}, respectively, with an H/D ratio of 1.387, which is near the isotopic frequency ratio for arsine. Of more importance, each pair of isotopic stretching fundamentals is replaced by a single intermediate band in the only observed mixed H/D isotopic species at 2113 and 1522 cm^{-1}. As is shown in Figure 2, with 65% deuterium substitution in the precursor, the 2113-cm^{-1} band replaced the 2117- and 2108-cm^{-1} bands in the As–H region and the 1522-cm^{-1} band dominated the As–D product region, and with deuterium substitution increased to 90%, the 1526- and 1518-cm^{-1} bands superseded the intermediate 1522-cm^{-1} band. The observation of one As–H and one As–D stretching mode for the mixed H/D isotopic species indicates the involvement of two equivalent hydrogen atoms in the new molecule.

The strong, sharp 649-cm^{-1} band is in the region below the stretching modes of AsF_3 at 731 and 689 cm^{-1}.[10] The sharp 649-cm^{-1} product band exhibits one mixed isotopic counterpart at 654 cm^{-1} and a fully deuteriated counterpart at 662 cm^{-1}, which indicates a small vibrational interaction with two equivalent hydrogen atoms and further characterizes the new product as a species with two equivalent hydrogen atoms. The 649-cm^{-1} band is assigned to the As–F stretching fundamental in the AsH_3F molecule. Vibrational assignments for the AsH_2F, AsHDF, and AsD_2F isotopic species are summarized in Table II. Fluoroarsine is a pyramidal molecule with a plane of symmetry and six vibrational modes; only five of these were observed here.

Table II. Infrared Absorptions (cm^{-1}) for AsH_2F Isotopic Species, PH_2F, and AsH_2OH in Solid Argon

PH_2F[a]	AsH_2F	AsHDF	AsD_2F	assignment	AsH_2OH[b]
2310	2117	2113	1526	$\nu_5(a'')$, As–H(D) str	2086
2304	2108	1522	1518	$\nu_1(a')$, As–H(D) str	2081
1090	984			$\nu_2(a')$, H–As–H(D) bend	975
934	842		606	$\nu_3(a')$, As–$H_2(D_2)$ def	807
795	649	654	662	$\nu_4(a')$, As–F str	648

[a] Reference 4. [b] Reference 5.

The two weaker bands at 984 and 842 cm^{-1} exhibit constant relative intensity with the stronger bands assigned above to AsH_2F. These bands are assigned to AsH_2 bending and deformation modes, respectively. Note that the AsH_2F bands appear below the analogous bands of AsH_3 at 1002 and 912 cm^{-1}. In the AsD_3 experiments, the sharp 605.6-cm^{-1} band is appropriate for the fully deuteriated counterpart of the 842-cm^{-1} AsH_2F deformation mode. Interaction between the 662.0- and 605.6-cm^{-1} fundamentals intensifies the latter and blue-shifts the former from its 649.0-cm^{-1} position in AsH_2F.

The AsH_2F fundamentals are also compared to PH_2F and AsH_2OH values[4,5] in Table II. The shift to lower wavenumbers from PH_2F to AsH_2F follows the relationships between PH_3 and AsH_3 and between PF_3 and AsF_3.[7,10] The As–H stretching and

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[10] Downs, A. J.; Gaskill, G. P.; Savill, S. B. *Inorg. Chem.* **1982**, *21*, 3385.

bending fundamentals for AsH_2F and AsH_2OH are quite similar as expected, and the As–F and As–O stretching modes are almost identical. These comparisons support the present assignments to the new molecule AsH_2F.

The weak 2099-cm^{-1} band in AsH_3 experiments has a single 1513-cm^{-1} counterpart in AsD_3 studies that identifies the vibration of one hydrogen atom. These bands exhibit the same 1.387 H/D ratio as the stronger 2117- and 2108-cm^{-1} product bands. Following the relationship between PH_2F and PHF_2, the 2099-cm^{-1} band is assigned to the As–H stretch in $AsHF_2$. A weak band at 668 cm^{-1} in both AsH_3 and AsD_3 studies that remained unchanged with the 2099-cm^{-1} band on annealing is tentatively assigned to one of the As–F stretching modes of $AsHF_2$; the other As–F stretching mode is probably masked by different product absorptions. (This 668-cm^{-1} band is not to be confused with the weak 663-cm^{-1} band due to CO_2 impurity in solid argon).

The remaining weak 894-cm^{-1} band and the strong product band at 610 cm^{-1}, with a satellite at 618 cm^{-1}, and deuterium counterparts at 590 and 583 cm^{-1} are the only new bands that increase substantially on sample annealing; this suggests a simple reaction product. The 610-cm^{-1} band is assigned to the antisymmetric As–F stretching mode of the new AsH_3F_2 species with fluorine in the axial positions. The phosphorus analogue, PH_3F_2, prepared by the analogous PH_3 and F_2 reaction,[4,11] absorbed strongly at 755 cm^{-1}. The pentafluorides PF_5 and AsF_5 are well-known and exhibit antisymmetric axial P–F and As–F stretching modes at 947 and 787 cm^{-1}, respectively.[12] The trichlorodifluoroarsorane and -phosphorane compounds have both been observed, and the antisymmetric axial P–F and As–F stretching modes are 859 and 677 cm^{-1}, respectively.[13] These values predict 595- or 627-cm^{-1} absorptions for AsH_3F_2 by using a simple ratio with PH_3F_2, which nicely bracket the observed 610-cm^{-1} value assigned here to difluoroarsorane, AsH_3F_2.

The possibility that the 610- and 590-cm^{-1} bands are due to AsH_2F--HF and AsD_2F--DF, respectively, instead of AsH_3F_2 and AsD_3F_2 must be considered because the stoichiometries are the same. On the basis of previous work with HF complexes,[7] the HF perturbation in an arsine base complex (the As lone pair is clearly more basic than F lone pairs in AsH_2F) should not shift the As–F stretching mode more than 10 or 20 cm^{-1} and certainly not from 649 to 610 cm^{-1}. It is, therefore, unlikely that the 610-cm^{-1} band is due to AsH_2F--HF; the AsH_3F_2 assignment is preferred.

Two other bands, 693 and 631 cm^{-1}, show a higher order fluorine concentration dependence than the 649- and 610-cm^{-1} bands. The observation of higher order reaction products reinforces the above interpretation of the 649- and 610-cm^{-1} bands as arising from the reaction of one F_2 molecule. One or both of the 693- and 631-cm^{-1} bands could be due to AsH_2F_3.

Mechanism. The most important observation is the *controlled spontaneous reaction* of AsH_3 and F_2 during matrix formation to give the new molecule AsH_2F, which is relaxed by the condensing matrix before decomposition. This parallels work with PH_3 and contrasts similar studies with NH_3, where photolysis was required to initiate the reaction to give NH_2F--HF.[3,4] The AsH_3 and F_2 reaction gave the following three major products:

$$AsH_3 + F_2 \rightarrow [AsH_3F_2]^* \rightarrow AsH_3F_2 \qquad (1)$$

$$\rightarrow AsHF_2 + H_2 \qquad (2)$$

$$\rightarrow AsH_2F + HF \qquad (3)$$

It is proposed that the initial energized intermediate species has the unstable structure with one axial and one equatorial fluorine since this structure would require minimum rearrangement for the original AsH_3 submolecule part of the AsH_3F_2 species. In the case of PH_3F_2, ab initio calculations have shown that the one axial–one equatorial substituted isomer is less stable than the diaxial form.[14]

The energized intermediate species has three choices, as given in the above reactions. The intermediate can rearrange and relax to the more stable diaxial difluoro isomer (eq 1). It is noteworthy that this reaction takes place on diffusion of F_2 in solid argon at 30 K. The lack of much reaction for PH_3 on sample annealing demonstrates that AsH_3 is slightly more reactive than PH_3 toward cold fluorine. The intermediate can eliminate H_2 to give $AsHF_2$ (eq 2) or HF to give AsH_2F (eq 3). As was found in the analogous PH_3 study, on the basis of relative intensities of AsH_2F and $AsHF_2$ product bands, HF elimination is by far the dominant decomposition pathway. Finally, there is no evidence for a reaction of sufficiently higher order to give AsF_3 as a product. Cocondensation with excess argon diluent effectively terminated the AsH_3 and F_2 reaction at the second-order stage, where AsH_2F was the dominant product.

The HF present in the matrix sample is more than impurity in the F_2 sample and in the vacuum system on the basis of similar AsH_3 and NH_3 experiments.[3,7,15] Hence, it must be concluded that reaction has occurred between AsH_3 and F_2 during sample deposition. The observation of DF in the AsD_3 experiments, which cannot be due to impurity in the system, clearly shows that reaction between AsD_3 and F_2 takes place during condensation of reagent samples. Some of the HF and DF byproducts form the AsH_3--HF and AsD_3--DF complexes characterized earlier.[7] It is suggested that the weak 3722-cm^{-1} band, which increases on annealing, is due to the AsH_2F--HF complex. This interaction brings together the products of reaction 3. It is seen that AsH_2F is less basic than AsH_3, on the basis of the 29 cm^{-1} smaller displacement of HF in AsH_2F--HF as compared to AsH_3--HF in these arsine base complexes. Such is the case for NH_2F and NH_3 complexes.[3,15,16]

Two experimental observations demonstrate the greater reactivity of AsH_3 over PH_3. With O_3 matrix reactions AsH_2OH was observed on sample cocondensation, but photolysis was required to produce PH_2OH.[5,17] Sample annealing to 30 ± 2 K increased the yield of AsH_3F_2, whereas PH_3F_2 did not increase on a similar sample-warming operation.

Conclusions

The cocondensation reaction of AsH_3 and F_2 in excess argon gave AsH_2F as the major reaction product. Matrix infrared spectra with partial and complete deuterium substitution provide identification for the new molecule fluoroarsine, AsH_2F. The reaction apparently proceeds through an AsH_3F_2 intermediate, and evidence for difluoroarsorane AsH_3F_2 was also observed in the spectrum. The cocondensation process terminates the reaction at the bimolecular stage and traps the highly reactive AsH_2F species before it can eliminate HF, the most probable fate of AsH_2F in the gas phase.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE 88-20764.

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(11) Seel, V. F.; Vellman, K. *Z. Anorg. Allg. Chem.* **1971**, *385*, 123.
(12) Hoskins, L. C.; Lord, R. C. *J. Chem. Phys.* **1967**, *46*, 2402.
(13) Minkwitz, R.; Prenzel, H. *Z. Anorg. Allg. Chem.* **1989**, *548*, 103.
(14) Keil, F.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 3623.
(15) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1982**, *104*, 3043.
(16) Lascola, R.; Withnall, R.; Andrews, L. *J. Phys. Chem.* **1988**, *92*, 2145.
(17) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1987**, *91*, 784.