structure. A weaker interaction of HF with tetramethylsilane supports the contribution of the bonding between the hydrogen of HF and the silvl hydrogens of the other three methyl silanes. The red-shifted Si-H stretching fundamentals in the HF complexes shows a slightly greater perturbation with DF owing to the smaller DF amplitude of motion and its correspondingly closer average distance to the silvl hydrogens. Further calculations performed on the silane--HF complex resulted in a new structure

for this complex, although the acid hydrogen-hydride hydrogen interaction remains intact and important.

Acknowledgment. We gratefully acknowledge financial support from NSF Grant CHE 85-16611, financial support from the Naval Research Laboratory, and helpful discussions with Frank A. Carey.

Registry No. DS, 1590-87-0; MS, 992-94-9; DMS, 1111-74-6; TMS, 993-07-7; TeMS, 75-76-3; HF, 7664-39-3; DF, 14333-26-7.

Infrared Spectra of Arsine–Ozone Complexes, Reaction Products, and Photolysis Products in Solid Argon

Lester Andrews,* Robert Withnall, and Brian W. Moores[†]

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901 (Received: May 23, 1988)

Codeposition of AsH₁ and O₁ at high dilution in argon gave a large yield of AsH₃-O₃ complex and a small yield of reaction products identified as cis- and trans-H₂AsOH. The complex photolyzed with red light, which showed that a specific interaction within the complex markedly increased the red photodissociation probability for the O₃ submolecule. The red photolysis products were H₃AsO, H₂AsOH, and an intermediate species tentatively identified as HAsO. Further blue and near-UV irradiations destroyed HAsO and produced HOAsO₂. This AsH₃ and O₃ study parallels earlier PH₃ work and shows that AsH₃ is slightly more reactive than PH_3 with O_3 .

Introduction

Although several simple oxyhydrides of phosphorus have been characterized in the gas phase¹ and in solid argon,²⁻⁴ no information is available on the corresponding arsenic species. Arsenic monoxide, AsO, is the only well-characterized arsenic-oxygen species;⁵ hence studies of other arsenic oxides are needed. Phosphine has been subjected to three detailed matrix oxidation studies, the first involving PH_3 and N_2O photolysis,² the second on the PH_3-O_3 complex⁶ and its rich photochemistry,³ and the third using O atoms produced by microwave discharge,⁴ aimed at characterizing phosphorus oxyhydrides. Similar gas-phase reactions appear to go through oxyhydrides to the oxides.⁷⁻⁹ A study of chemiluminescent reactions between AsH₃ and ozone reveals sharp AsO and broad continuum emission.⁷ Although no spectroscopic data exist for arsenic oxyacids, their derivatives and soluble anions are important in toxicology, pharmacology, and electrochemistry. Matrix isolation studies have been done on the ion-pair species $M^+AsO_2^-$ and $M^+AsO_3^-$.¹⁰⁻¹³ Arsine oxide itself has not been prepared; however, solid films of trimethylarsine have been examined.^{14,15} The present study reports matrix reactions of arsine and ozone and photolysis of the AsH₃-O₃ complex, which provide infrared spectra of several new arsenic species including molecular arsinous and arsenic acids and arsine oxide.

Experimental Section

The apparatus and techniques for matrix experiments with ozone have been described previously.^{3,6,16} Arsine was prepared by adding 30% H₂SO₄ to powdered Zn₃As₂ under vacuum; the evolved gas was condensed and evacuated, and the first fraction to distill from the reaction vessel was used in these experiments.¹⁷ An AsD₃ sample was prepared by using D_2SO_4 in D_2O in like manner. Arsine and ozone were diluted with argon (150/1, 200/1,and 300/1) and codeposited from separate manifolds at rates of 2 mmol/h for 6-10 h. Infrared spectra were recorded before and after photolysis on a Perkin-Elmer 983 spectrometer and data station; wavenumber accuracy is ± 0.2 or ± 1 cm⁻¹ depending on the spectrum recorded. Samples were subjected to high-pressure mercury arc photolysis for 20-min periods using Corning glass and water filters.

Results

Infrared spectra of arsine and arsine-ozone in solid argon revealed new reaction and photolysis product absorptions, which will be described for isotopic precursors.

 $A_{SH_{3}}$ + ¹⁶O₃. The Ar/AsH₃ samples contained strong arsine absorptions and very little impurity such as the weak band (labeled I) in Figure 1a. On codeposition with Ar/O_3 samples in four separate Ar/AsH₃ experiments, two types of new bands appeared: (1) complexes involving precursor molecules characterized by sharp bands near precursor absorptions which were decreased by visible photolysis, and (2) products of a chemical reaction between AsH₃ and O_3 during sample condensation. The complex bands are labeled C in Table I and the figures, and the reaction products formed on sample codeposition are labeled with numbers that correspond to the species formed. Several different reaction products were trapped during condensation: the bands labeled 2 were weak in the deposited sample but grew markedly (5-fold) during the photolysis sequence whereas other bands labeled 3 and

- (8) Hamilton, P. A.; Murrells, T. P. J. Phys. Chem. 1986, 90, 182.
- (9) Hamilton, P. A. J. Chem. Phys. 1987, 86, 33.
 (10) Ogden, J. S.; Williams, S. J. J. Chem. Soc., Dalton Trans. 1982, 825. (11) Ogden, J. C.; Sibley, T. J.; Williams, S. J. J. Chem. Soc., Dalton Trans. 1983, 851.
 - (12) Bencivenni, L.; Gingerich, K. A. J. Mol. Struct. 1983, 99, 23.
- (13) Bencivenni, L.; Gingerich, K. A.; Teghie, R. Inorg. Chim. Acta 1984, 85, LÍ1.
- (14) Watari, F. Spectrochim. Acta 1975, 31A, 1143.

- (16) Andrews, L.; Spiker, Jr., R. C. J. Phys. Chem. 1972, 76, 3208.
- (17) Arlinghaus, R. T.; Andrews, L. J. Chem. Phys. 1984, 81, 4341.

[†]On leave from Department of Chemistry, Randolph-Macon College, Ashland, VA 23005.

⁽¹⁾ Larzilliere, M.; Damany, N.; Lam Thanh, M. Chem. Phys. 1980, 46, 401

⁽²⁾ Larzilliere, M.; Jacox, M. E. J. Mol. Spectrosc. 1980, 79, 132.

Withnall, R.; Andrews, L. J. Phys. Chem. 1987, 91, 784.
 Withnall, R.; Andrews, L. J. Phys. Chem. 1988, 92, 4610

⁽⁵⁾ Anderson, U. M.; Callomon, J. H. J. Phys. B: Atom Mol. Phys. 1973, 6, 1664

⁽⁶⁾ Withnall, R.; Hawkins, M.; Andrews, L. J. Phys. Chem. 1986, 90, 575. (7) Fraser, M. E.; Stedman, D. H. J. Chem. Soc., Faraday Soc. 1 1983, 79, 527.

⁽¹⁵⁾ Rojhantalab, H.; Nibler, J. W. Spectrochim. Acta 1976, 32A, 947.

TABLE I: New Infrared Absorptions (cm⁻¹) Observed in Arsine-Ozone Codeposition and Photolysis Experiments in Excess Argon at 15 K

-			
¹⁶ O ₃	¹⁸ O ₃	appearance	ident ^b
3652.7	3640.4	wR	2
3613	3602	uP	5
3566	3556	Р	?
2173.5	2173.6	rP	1
2170.1	2070.0	rP	1
2162	2162	С	С
2157	2157	С	С
2092.0	2092.0		3
2086.3	2086.8	wR	2
2080.7	2080.8	wR	2
1964	1964	R	?
1931.0	1929.5	rР	4
1341	1338	sR	3
1102	1041	С	С
1061.4	1033.5	uP	5
1035.5	978.2	С	С
1032.7	975.2	С	С
1009	с	Р	?
983.4		Р	1
979.8		Р	1
976.5		R	3
974.7	972.2	R	2
972		Р	?
964		Р	?
948	932	uP	5
937.8	894.0	rP	1
932.2	885.6	uP	5
929.7	888.1	rP	1
905.7	905.6	С	С
902.7	902.9	С	С
817.1	815.4	rP	1
813	812	R	3
806.7	805.5	rP	2
760	726	uP	?
738.2	702:2	uP	?
725	699	uP	5
709		Р	?
687.2	686.5	rP	2
687.2	677.6	sR	3
673		uP	?
647.9	619.4	wR	2
424, 414	422, 413	uP	5
367	364	sR	3
297.5	296.5	wR	2

^aR = reaction product, C = precursor complex, P = complex photolysis product, w denotes weak and s denotes strong for reaction products, r denotes red and u denotes ultraviolet for photolysis. ^b Identification code defined in text and mechanism. ^c Obscured by intense ¹⁸O₃ band at 982 cm⁻¹.

still others noted R in Table I grew much less (about 20%). Photolysis with 750–1000-nm radiation slightly reduced C bands and increased the 2 and 3 bands, and produced a weak, new 937.8-cm⁻¹ band (A = 0.02) (labeled 1). Irradiation at 630–1000 nm reduced the C bands 20%, increased the 1 and associated bands

10-fold and the 2 bands 4-fold, and produced a new band at 1931.0 cm⁻¹ (labeled 4). Photolysis with 515-1000-nm radiation increased the 1, 2, and 3 absorptions to their maximum intensity, as illustrated in Figure 1b, decreased the 4 band, and produced new bands at 3613, 1061, 932, 449, and 725 cm⁻¹ and a 424-, 414-cm⁻¹ doublet (labeled 5).

Ultraviolet photolysis (380- or 290-nm filters) in these experiments further decreased 4 and increased 5 absorptions, without changing 1, 2, and 3 bands. A final 220-1000-nm irradiation increased the 5 absorptions and produced several new bands (labeled uP). Sample annealing revealed decreases in most of the product absorptions without discrimination.

Figures 2, 3, and 4 show expanded scale regions of the spectrum at different stages in the photolysis. Figure 2 illustrates the O-H stretching region (a) after deposition, (b) after 515-nm photolysis, and (c) after 220–1000-nm irradiation. Figure 3 illustrates similar spectra for the As-H stretching region, and Figure 4 shows corresponding spectra for the O-H torsional region.

Two experiments were performed with O atoms from microwave discharge of an Ar/O_2 stream⁴ codeposited with an Ar/AsH_3 sample. Sharp weak bands were observed at 983.3, 979.1, and 937.9 cm⁻¹ for species 1, but the strongest species 2 band (647.9 cm⁻¹) was not detected.

 $AsH_3 + {}^{18}O$ -Enriched Ozone. Experiments were done with both 98% and 55% ¹⁸O-enriched ozone samples. In the former ¹⁸O counterparts for most product absorption were measured; these isotopic bands are listed in Table I. In the latter mixed isotopic experiments, isotopic multiplets were observed for a number of the product absorptions; most notably, the 1 species exhibited a strong doublet at 937.8 and 894.0 cm⁻¹ and the 2 species gave rise to a strong 647.9- and 619.4-cm⁻¹ doublet and a weaker 3652.6- and 3641.4-cm⁻¹ doublet. The species 5 band at 1061 cm⁻¹ exhibited a broad 1048-cm⁻¹ band with double the intensity of the full ¹⁸O counterpart at 1033 cm⁻¹ (the 1061-cm⁻¹ band was masked by ozone-16-18-18); unfortunately the mixed isotopic counterpart of the 932-cm⁻¹ band falls under AsH₃ at 907 cm⁻¹. The isotopic ozone v_3 sextet reveals five of six complex components with 1:2:1:(obscured by AsH₃):2:1 relative intensities. However, with AsD₃ the spectrum in Figure 5a shows the complete complex sextet with relative intensities tracking the ozone precursor, and Figure 5b illustrates the loss of complex bands and growth of the species 1 doublet at 938.2 and 894.9 cm⁻¹; note the very small deuterium shift on the latter bands.

 AsD_3 and Ozone. A series of isotopic ozone experiments was done with AsD₃, and the new product bands are listed in Tables II-V for specific molecular species. Several points are noteworthy. Arsine is a sufficiently weak base that isotopic exchange contamination of the AsD₃ does not occur. Reaction products were not observed in the deposited sample in contrast to AsH₃. Relative intensities of species 1 and 2 bands favored species 1 (about 5:1) whereas with AsH₃, the major 1 and 2 bands were of comparable intensity.

Figure 6 illustrates the As-D stretching region of the spectrum for AsD₃ and ${}^{16}O_3$. The weak complex bands at 1557 and 1553 cm⁻¹ give way to very strong 1 bands at 1568.2 and 1559.8 cm⁻¹

TABLE II: Infrared Absorptions (cm⁻¹) Due to Isotopic Ozone and Arsine Submolecules and Arsine-Ozone Complexes^a

16-16-16	16-16-18	18-16-18	16-18-16	18-18-16	18-18-18	ident
1039.9	1026.2	1017.8	1006.6	992.0	982.8	ν3
(1035.5)	(1022.3)	(1012.8)	(1002.2)	(988.2)	(978.6)	v3 ^c
4.4	3.9	4.3	4.4	3.8	4.2	$\Delta \nu_3$
1104	1091			1062	1043	ν_1
(1102)	(1088)			(1059)	(1041)	vic
2	3			3		ν_1^c
AsH3	b	AsH ₂ D	AsHD ₂	As	D ₃ ^c	
912		813	690	658		<i>v</i> ₂
(905.7, 9	002.7)	(807.5, 806.0)	(685.9)	(653.6	, 651.5)	ν_2^c
2150				1549		ν_3
(2162, 2157)				(1557,	1553)	V3C

^a Precursor bands with complex bands below in parentheses. Bands for one submolecule in complex did not vary for isotopic substitution of the other submolecule. ^bReference 17. ^cThe other AsD₃ fundamentals $\nu_1 = 1540$ cm⁻¹ and $\nu_4 = 717$ cm⁻¹ in solid argon, did not exhibit complex bands.



Figure 1. Infrared spectra of AsH₃ and O₃ in the 1100-600-cm⁻¹ region: (a) $Ar/AsH_3 = 200/1$ codeposited with $Ar/O_3 = 200/1$ at 15 K for 6 h, (b) after 515-1000-nm photolysis for 30 min, and (c) after 220-1000-nm photolysis for 30 min.

TABLE III: Infrared Absorptions (cm^{-1}) Assigned to Species 2 (H_2AsOH)

H ₂ As ¹⁶ OH	H ₂ As ¹⁸ OH	D ₂ As ¹⁶ OD	D ₂ As ¹⁸ OD	assign
3652.2	3640.4	2694.6	2678.3	ν(O-H)
2086.3ª	2086.8	1504.2	1504.6	v(As-H)
2080.7	2080.8	1498.9	1499.2	$\nu(As-H)$
974.5	972.2	697.7	697.6	$\delta(AsH_2)$
		762.0	753.0	δ(AsOH)
806.7	805.5			δ(HAsO)
647.9	619.4	647.8	623.5 ^b	ν(AsO)
687.2	686.5	516.1°	512.7	$\rho(AsH_2)$
297.5	296.5		223	$\tau(H_2AsOH)$

^aCounterparts at 2083.2 and 1500.8 cm⁻¹ for mixed H, D species. ^bCounterparts at 623.5, 619.4, and 616.9 cm⁻¹ for mixed H, D species. ^cCounterparts at 564.8, 552.6, and 525.5 cm⁻¹ for mixed H, D species.

TABLE IV: Infrared Absorptions (cm⁻¹) Assigned to Species 1 (H₃AsO)

H ₃ As ¹⁶ O	H ₃ As ¹⁸ O	D ₃ As ¹⁶ O	D ₃ As ¹⁸ O	assign	
2173.5ª	2173.6	1568.2ª	1568.2	v(As-H)	
2170.1	2170.0	1559.8	1559.6	$\nu(As-H)$	
983.4 ⁶		707.8	707.2	$\delta(AsH_3)$	
979.8		704.9	704.8	$\delta(AsH_3)$	
937.9	894.0	938.2	894.9	$\nu(As=O)$	
817.1	815.4	576.3	574.2	δ(HAsO)	

^aCounterparts at 2172.1 and 1561.8 cm⁻¹ for mixed H, D species. ^bCounterparts at 896.5 and 889.7 cm⁻¹ for mixed H, D species.

and medium intensity, sharp 2 bands at 1504.2 and 1498.9 cm⁻¹. The 1050–880-cm⁻¹ region in the spectrum for AsD₃ and ^{16,18}O₃ has already been presented in Figure 5; the 775–475 cm⁻¹ region from this experiment is shown in Figure 7. The original spectrum, Figure 7a, shows AsD₃ bands at 716.7 and 657.7 cm⁻¹ and a complex doublet at 653.7 and 651.4 cm⁻¹. Photolysis with 515–1000-nm radiation gave the new product bands shown in Figures

TABLE V: Infrared Absorptions (cm⁻¹) Assigned to Species 5 (HOAsO₂)

H~16	H-18	D -16	D-18	assign	
3613	3602 sh	2664 sh	2649	ν(OH)	-
1061.4ª	1033.5	masked	1009.4	$\nu_{a}(AsO_{2})$	
948	932	masked	978	δ(HOAs)	
932.2	885.6	951.3 ^b	907.6	$\nu_{\rm s}({\rm AsO}_2)$	
725	699	778	762	$\nu(As-O)$	
424, 414	422, 413			$\tau(O_2AsOH)$	

^a Intermediate component at 1048 cm⁻¹ in ${}^{16,18}O_3$ experiment. ^b Intermediate component at 930 cm⁻¹ in ${}^{16,18}O_3$ experiment.

5b and 7b, which include the **2** doublets at 762.0-753.0, 647.7-623.7, and 516.1-512.7 cm⁻¹ and band at 697.7 cm⁻¹ and the **1** doublet at 938.2-894.9 cm⁻¹, bands at 707.4 and 704.9 cm⁻¹, and an unresolved doublet at 575 cm⁻¹. Further ultraviolet photolysis gave a 929.6-cm⁻¹ intermediate component for the 951.3-cm⁻¹ ¹⁶O and 907.6-cm⁻¹ ¹⁸O bands for species **5**. Ultraviolet photolysis of AsD₃ and ¹⁸O₃ samples gave new 678- and 762-cm⁻¹ bands; the ¹⁶O₃ counterpart of the former was masked by stronger products and the former ¹⁶O₃ counterpart appeared at 778 cm⁻¹.

 AsH_xD_{3x} (x = 0, 1, 2, 3) and Ozone. Mixed isotopic arsines were prepared with a mixture of isotopic acids, and the symmetric bending modes of AsH₃, AsH₂D, AsHD₂, and AsD₃ at 906, 813, 690, and 658 cm⁻¹, respectively, provided a measure of the degree of enrichment. Ozone complex bands were observed on the red side of each of the above precursor bands as are given in Table II. The spectra of AsH₂D and AsHD₂ photolysis products were complicated by the presence of AsH₃ and AsD₃; nevertheless, new bands provide some information about the photolysis products. New product bands were observed in the As-H and As-D stretching regions at 2172.1, 2083.2 cm⁻¹ and 1561.8, 1500.8 cm⁻¹, respectively. These new intermediate bands were twice as strong as the pure isotopic product bands. The strong, sharp species 1 bands were observed at 939.1 cm⁻¹ with ¹⁶O₃ and 895.3 cm⁻¹ with



Figure 2. Infrared spectra of AsH_3 and O_3 in the 3660–3560-cm⁻¹ region for the experiment described in Figure 1.

 $^{18}O_3$; however, the strong species 2 band at 647.7 cm⁻¹ exhibited a satellite at 644.5 cm⁻¹ and the ^{18}O band became a 623.4-, 619.4-, 616.9-cm⁻¹ triplet. Additional sharp species 1 bands were observed at 896.5 and 889.7 cm⁻¹. In the low-frequency region, new species 2 bands were observed at 564.8, 552.6, and 535.5 cm⁻¹, which showed 3-cm⁻¹ ¹⁸O shifts in a separate $^{18}O_3$ study.

Discussion

The new arsenic oxyhydride species produced here will be identified and compared to phosphorus analogues. The arsineozone system is unfortunately complicated by overlapping of precursor and product band regions; however, a fairly complete picture of the arsine-ozone complex photochemistry can be drawn from the spectra.

Arsine–Ozone Complex. The AsH₃–O₃ complex is characterized by red-shifted O₃ stretching modes, a red-shifted AsH₃ symmetric bending mode, and a blue-shifted AsH₃ stretching mode as compared to isolated submolecule values. The complex involves symmetrical binding of O₃ to AsH₃ as attested by the 1:2:1:1:2:1 sextet for mixed isotopic ozone submolecules in the complex. A similar sextet was observed for the PH₃–O₃ complex,⁶ and a symmetrical structure was calculated for the NH₃–O₃ complex,¹⁸ and determined for the (CH₃)₃N–SO₂ complex by X-ray crystallography.¹⁹

It appears, however, that a slightly stronger interaction operates between AsH₃ and O₃ than in the PH₃-O₃ complex based on the 1.2-1.6-cm⁻¹ larger red shift for $\nu_3(O_3)$ in the arsine complex. The



Figure 3. Infrared spectra of AsH_3 and O_3 in the 2200–2060-cm⁻¹ region: (a) $Ar/AsH_3 = 300/1$ and $Ar/O_3 = 150/1$ codeposited for 5 h at 15 K, and after 515–1000-nm photolysis for 20 min.

red shift on $\nu_2(AsH_3)$ (6.3–9.3 cm⁻¹) is almost as large as the 10-cm⁻¹ red shift for AsH₃-HF whereas the 7–12-cm⁻¹ blue shift for $\nu_3(AsH_3)$ is smaller than the 30-cm⁻¹ value found for As-H₃-HF,¹¹ which suggests a comparable interaction for AsH₃-O₃.

The AsH₃-O₃ complex clearly photolyzes efficiently with 630-1000-nm radiation, which is in the weak Chappuis band of ozone.²⁰ In fact some photoproduct was observed following 750-1000-nm irradiation. It is obvious that a specific interaction between arsine and ozone enhances the reactivity of the excited state in the complex and facilitates the photoinduced transfer of an O atom from ozone to arsine.

Arsine–Ozone Reaction Products. All of the AsH₃ and ${}^{16}O_3$ experiments gave new species 2 and 3 bands in the deposited sample that were not present with either reagent alone. As can be seen from the figures, the 3 bands produced by reaction during deposition are stronger than their 2 counterparts in the same region, but on photolysis the 2 bands increased about 5-fold and the 3 bands about 20%. Deuterium counterparts for neither of these species were observed on sample deposition. The spectrum of species 2 is more complete so it will be considered first.

The isotopic data for species 2 are given in Table III. These data clearly identify the 3652.2-cm⁻¹ band as an O-H stretching mode and the 2086.3- and 2080.7-cm⁻¹ bands as As-H stretching modes. The observation of extra As-H and As-D bands in mixed H/D experiments suggests that this vibration involves more than one equivalent hydrogen. Note the expected increase in H/D ratios for the ν (OH) (1.355) and ν (AsH) (1.387) modes as the

⁽¹⁸⁾ Lucchese, R. R.; Haber, K.; Schaeffer, III, H. F. J. Am. Chem. Soc. 1976, 98, 7617.

⁽¹⁹⁾ v. d. Helm, D.; Childs, J. D.; Christian, S. D. J. Chem. Soc., Chem. Commun. 1969, 887.

⁽²⁰⁾ Levene, H. B.; Nieh, J.-C.; Valentini, J. J. J. Chem. Phys. 1987, 87, 2583.



Figure 4. Infrared spectra of AsH_3 and O_3 in the 440–280-cm⁻¹ region for the experiment described in Figure 1.



Figure 5. Infrared spectra of AsD_3 and ${}^{16,18}O_3$ in the 1050-880-cm⁻¹ region: (a) $Ar/AsD_3 = 300/1$ codeposited with $Ar/{}^{16,18}O_3 = 150/1$ (55% ${}^{18}O)$ at 15 K for 10 h, and (b) after 515-1000-nm photolysis for 30 min.

mass of the heavy atom increases. The strong 647.9-cm⁻¹ band is clearly due to an As–O stretching mode as the 28.5-cm⁻¹ ^{18}O



Figure 6. Infrared spectra of AsD_3 and O_3 samples in the 1630–1470cm⁻¹ region: (a) $Ar/AsD_3 = 300/1$ and $Ar/O_3 = 150/1$ codeposited for 7 h at 15 K, and (b) after 515–1000-nm photolysis for 30 min.



Figure 7. Infrared spectra of AsD_3 and ${}^{16.18}O_3$ in the 775-475-cm⁻¹ region for the experiment described in Figure 5.

shift is almost the predicted value (30.4 cm^{-1}) for a pure As–O bond stretching mode; satellites on this strong absorption with

 AsH_xD_{3-x} (x = 0, 1, 2, 3) precursor show that the molecular species contains more than one hydrogen. Therefore species 2 contains two As-H bonds, one O-H bond, and one As-O bond, and the formula H₂AsOH is indicated. Deformation modes for the AsOH and HAsO groups, a rocking mode of the AsH₂ group, and a torsional mode for H₂As-OH were also observed and further characterize the 2 species as H₂AsOH, arsinous acid.

The 3 species has several bands in regions common to species 2 but the spectrum is not complete. The strong 3 band at 687.2 cm^{-1} is believed to contain absorption due to both species 2 and 3. The 3 component is probably an As-O stretch, and if so, the As-18O counterpart would fall under CO₂ and cannot be detected. Species 3 exhibits a torsional mode at 366 cm⁻¹, a HAsO deformation mode at 813 cm⁻¹, a combination band at 1341 cm⁻¹ $(976 + 366 = 1342 \text{ cm}^{-1})$, an AsH₂ bending mode at 976 cm⁻¹, and an As-H stretching mode at 2092 cm⁻¹. The OH region was sufficiently scattering to preclude detection of a weak band. It is believed that species 3 is the other isomer of H_2AsOH . Based on calculated spectra²¹ for cis- and trans-H₂POH, similar PH₃-O₃ experiments gave a more complete spectrum for the cis isomer, which suggests that the more extensive spectrum observed here for species 2 is likely due to the *cis* isomer and species 3 is probably the trans isomer of H_2AsOH . The observation of more 3 on sample deposition is consistent with the *trans* form being the more stable isomer.21,22

Arsine-Ozone Complex Photolysis Products. The first new bands to appear on photolysis of the AsH₃-O₃ complex are identified as species 1. In addition the strongest three bands of species 1 were observed in discharge experiments where O atoms were reacted with AsH_3 , but species 2 was not detected. The strongest species 1 band (937.9 cm⁻¹) is near the gas-phase AsO fundamental (957 cm⁻¹).²³ The 937.9-cm⁻¹ band shifts to 894.0 cm⁻¹ with ¹⁸O₃, which is within 0.2 cm⁻¹ of a pure As–O oscillator, exhibits a doublet with $^{16,18}O_3$, and shows very little shift with AsD₃ (Figure 5); these observations identify an "As=O" stretching mode. Two strong bands in the As-H stretching region at 2173.5 and 2170.1 cm⁻¹ exhibit slightly different H/D ratios (1.386 and 1.391) and no ¹⁸O shift within experimental error. Two strong bands appear at 983.4 and 979.8 cm⁻¹, just below the degenerate bending mode of AsH_3 ; these bands exhibit almost identical H/Dratios (1.389 and 1.390). A final medium-intensity band at 817.1 cm⁻¹ showed a small (1.7 cm^{-1}) ¹⁸O shift and a large H/D ratio (1.418). These fundamentals are sufficient to identify species 1 as arsine oxide, H₃AsO, a new species. Following the example of H₃PO, H₃AsO probably has a C_{3v} structure.

Trimethylarsine oxide is a known compound, and the strongest band in the infrared spectrum $(870 \text{ cm}^{-1})^{14}$ and a strong band in the Raman spectrum (866 cm⁻¹)¹⁵ of solid films, which shows practically no shift on deuteriation, have been assigned to the As=O stretching fundamental. The $\nu_3(a_1)$ As==O fundamental for H₃AsO comes about 70 cm⁻¹ higher, which is the same relationship found for matrix isolated H₃PO and solid (CH₃)₃PO.³ The sharp 2173.5- and 2170.1-cm⁻¹ bands are probably matrix splitting of the antisymmetric AsH₃ stretching mode $v_4(e)$ which are blue-shifted about 22 cm⁻¹ from the $v_3(e)$ mode of AsH₃. Likewise the sharp 983.4- and 979.8-cm⁻¹ bands are likely matrix splittings of the antisymmetric AsH₃ bending mode $\nu_5(e)$, which are red-shifted about 19 cm⁻¹ from the $\nu_4(e)$ mode of AsH₃. Finally, the 817.1-cm⁻¹ band is assigned to the degenerate HAsO deformation mode $\nu_6(e)$ for H₃AsO. The increase in ¹⁸O shift for the D₃AsO mode (2.1 cm⁻¹) indicates more oxygen motion against D than against H where the ¹⁸O shift is 1.7 cm⁻¹.

A weak new band (A = 0.03) appeared at 1931.0 cm⁻¹ on red photolysis and this band was decreased with green radiation and destroyed by near-UV light. This band showed a 1.5-cm⁻¹ ¹⁸O shift. Unfortunately, no deuterium counterpart was detected, and no other bands were found with this photochemical behavior.

SCHEME I

Following the position of HPO in the infrared spectrum of the PH_3-O_3 photolysis products and its photochemical history,³ the 1931.0-cm⁻¹ band is tentatively assigned to HAsO.

Species 5 bands were detected after 515-nm photolysis and these bands increased with UV irradiation while species 1, 2, and 3 bands were approximately constant and the species 4 band was destroyed. The diagnostic bands of species 5 include an O-H stretch (3613 cm⁻¹), two bands in the As=O stretching region (1061 and 932 cm⁻¹), one band in the As=O stretching region (725 cm⁻¹), and absorption in the -OH torsional region (424, 414 cm⁻¹). The 1061-cm⁻¹ band exhibited an intermediate component at 1048 cm⁻¹ in ^{16,18}O₃ experiments, which indicates the presence of two equivalent oxygen atoms. Likewise the 951-cm⁻¹ band in the AsD₃-¹⁶O₃ experiments exhibited an intermediate component at 930 cm⁻¹ revealing two equivalent oxygen atoms. Species 5 is accordingly identified as metaarsenic acid, HOAsO₂, which contains the requisite -AsO₂ and -OH subgroups. It is presumed that HOAsO₂ is a planar molecule like HOPO₂ and HONO₂.²⁴

The isotopic data in Table V substantiate the mode descriptions given above. The O-H stretching fundamental tracks this mode for species 2. The 1061-cm⁻¹ band is assigned to the antisymmetric AsO₂ stretching mode. Assuming a 135° O-As-O angle, near that calculated²⁴ for HOPO₂, the antisymmetric AsO₂ stretching mode is predicted to shift to 1017 cm⁻¹, more than the observed value (1033 cm⁻¹). This and the D shift (to 1009 cm⁻¹) indicate mixing most likely with the HOAs deformation mode. The 932-cm⁻¹ band assigned to the symmetric AsO₂ stretching mode provides a basis for prediction of the ¹⁸O counterpart at 882 cm⁻¹ just below the observed value. Likewise the 725-cm⁻¹ band assigned to the AsO fundamental is above this fundamental for species 2, a relationship like that for the phosphorus species. The expected ¹⁸O shift (to 691 cm⁻¹) exceeds the observed value again suggesting slight mode mixing. The torsional mode also comes above those for species 2 and 3 again following the phosphorus species.

Photolysis Mechanism. The matrix photochemistry of the AsH₃-O₃ complex parallels that reported for the PH₃-O₃ complex³ although the present data is less extensive in part due to overlapping of product and precursor bands. The arsine-ozone interaction in the complex markedly increased the oscillator strength for ozone photodissociation by red light. The primary photolysis product, arsine oxide, is energized by approximately 115 kcal/mol, the energy of the As=O "double" bond,²⁵ Scheme The matrix can quench this internal energy and stabilize arsine I. oxide (1) or the energized arsine oxide can rearrange to *cis*-arsince acid(2) and *trans*-arsinous acid(3) or decompose to the HAsO intermediate species (4). Following the example of HPO, HAsO is expected to absorb visible light, which can activate reaction with O_2 in the matrix cage (from the initial O_3 photodecomposition process) to give metaarsenic acid (5) HOAsO₂.

It is interesting to note that the reaction of ground-state (³P) oxygen atoms from the discharge of O_2 produced only arsine oxide, but the ozone reaction with arsine during red photolysis gave both isomers of arsenous acid and arsine oxide. Gas-phase studies of ground state O and O_2 produced by red laser excitation reveal considerable excess translation energy for the O atoms.²⁰ This excess energy may aid in overcoming the large energy barrier expected²² between the arsine oxide first formed and the arsinous acid structural isomers. The substantially lower yield of deu-

⁽²¹⁾ Person, W. B.; Kwiatkowski, J. S.; Bartlett, R. T. J. Mol. Struct. 1987, 157, 237.

⁽²²⁾ Schmidt, M. W.; Yabushita, S.; Gordon, M. S. J. Phys. Chem. 1984, 88, 382.

⁽²³⁾ Uehara, H. Chem. Phys. Lett. 1981, 84, 539.

⁽²⁴⁾ O'Keefe, J.; Domenges, B.; Gibbs, G. V. J. Phys. Chem. 1985, 89, 2304.

⁽²⁵⁾ Wagman, D. D. et al. J. Phys. Chem. Ref. Data Suppl. 2 1982, 11.

teriated arsinous acid relative to arsine oxide as compared to comparable yields of H₃AsO and H₂AsOH, based on As-H stretching band intensities, attests a substantial kinetic isotope effect for the $[D_3AsO]^* \rightarrow D_2AsOD$ rearrangement.

Finally, the production of arsinous acid and not arsine oxide during reagent codeposition is of interest. The lack of phosphinous acid on codeposition in similar phosphine experiments shows that arsine is more reactive than phosphine. A collision complex of different structure than determined here for the relaxed AsH₃-O₃ complex (two equivalent O atoms) must be involved in the gasphase reaction. A possible arrangement has been suggested to rationalize the gas-phase chemiluminescence from this reaction.⁷

Conclusions

The codeposition of AsH₃ and O₃ in excess argon at 15 K has been used to synthesize new oxyhydrides of arsenic. This reaction gave a small yield of products identified as cis- and trans-arsinous acids, H₂AsOH, and a large yield of AsH₃-O₃ complex. This complex photolyzed efficiently with red light, where isolated ozone dissociates with very low probability, to give strong arsine oxide, H₃AsO, absorptions, increased arsinous acid, and an intermediate species tentatively identified as HAsO. Further irradiation in the blue and near-UV regions destroyed HAsO and produced new bands probably due to molecular arsenic acid, HOAsO₂, from the HAsO $+ O_2$ matrix cage reaction. The solid argon matrix is an effective medium for the synthesis of new reactive molecular oxyhydrides of arsenic for spectroscopic study. In these experiments the highly reactive molecules, arsine and ozone, are brought together in a 1 to 1 ratio and isolated in a cold environment, which dissipates the energy and controls the photochemical reaction. It is found that arsine is slightly more reactive with ozone than phosphine in these experiments.

Acknowledgment. We gratefully acknowledge financial support for this work from N.S.F. Grant CHE 85-16611.

Registry No. 1, 31219-53-1; ¹⁸O-1, 117942-13-9; d₃-1, 117942-14-0; d_3 -¹⁸O-1, 117942-15-1; 2,3, 25400-21-9; ¹⁸O-2, ¹⁸O-3, 117959-02-1; d_3 - $2, d_3$ -3, 117942-11-7; d_3 -¹⁸O-2, d-¹⁸O-3, 117942-12-8; 5, 10102-53-1; ¹⁸O₃-5, 117942-16-2; d-5, 117942-17-3; d-¹⁸O₃-5, 117942-18-4; AsH₃, 7784-42-1; O₃, 10028-15-6; AsH₂D, 13464-49-8; AsHD₂, 13464-50-1; AsD₃, 13464-51-2.

Near-Infrared-Light-Induced Reaction of Singlet SO with Allene and Dimethylacetylene in a Rare Gas Matrix. Infrared Spectra of Two Novel Episulfoxides

Farid Salama and Heinz Frei*

Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720 (Received: June 2, 1988)

SO-allene and SO-dimethylacetylene pairs were prepared in solid Ar at 12 K in order to explore near-infrared-light-induced chemistry of SO(a¹ Δ) ($T_{00} = 5860 \text{ cm}^{-1}$) and SO(b¹ Σ^+) ($T_{00} = 10470 \text{ cm}^{-1}$). Sulfur monoxide was generated by pyrolysis of ethylene episulfoxide in the matrix gas deposition line. Fundamental absorptions of SO($X^3\Sigma^-$) were measured at 1138.7 cm⁻¹ (Ar), 1134.8 cm⁻¹ (Kr), and 1129.5 cm⁻¹ (Xe). Selective excitation of SO($^{1}\Delta$) and SO($^{1}\Sigma^{+}$) vibronic levels with CW dye laser or filtered tungsten source light led to chemical reaction, the first ever observed of singlet SO. Product analysis by FT-infrared spectroscopy revealed two novel three-membered ring molecules, allene episulfoxide and dimethylacetylene episulfoxide. The SO ${}^{1}\Sigma^{+}$, $1 \leftarrow {}^{3}\Sigma^{-}$, 0 vibronic transition was recorded by laser reaction excitation spectroscopy, and an absorption peak was found at 11 420 cm⁻¹ (Ar).

Introduction

Sulfur monoxide, a triplet ground-state radical, has two electronically excited singlet states in the near-infrared region, the $a^{1}\Delta$ state ($T_{00} = 5862 \text{ cm}^{-1}$)¹ and $b^{1}\Sigma^{+}$ state ($T_{00} = 10469 \text{ cm}^{-1}$).² While a few gas³ and solution-phase⁴ reactions of ground-state $SO(X^3\Sigma^-)$ have been reported, there are no reports at all on chemical reactions of singlet excited SO. We anticipate the chemistry of metastable singlet SO to be distinctly different from that of the ground-state triplet radical, in analogy to the case of molecular oxygen which has the same outer electron configuration. $O_2({}^1\Delta_s)$ is a very reactive species whose organic⁵ and inorganic⁶ chemistry differs strongly from that of the radical like $O_2({}^3\Sigma_g)$

ground-state species. The prospect of similar state-specific chemistry made it particularly interesting to explore near-infrared-light-initiated reactions of SO.

We began to search for the chemistry of singlet excited SO by exciting reactions with small unsaturated hydrocarbons, namely allene and dimethylacetylene. A cryogenic matrix offers an ideal environment to study singlet SO chemistry. First, consumption of SO through self-reaction is suppressed because of absence of diffusion. Second, the cryogenic technique allows us to trap unstable products that may arise from photoinduced reactions, and to determine their structure by infrared spectroscopy. Third, laser reaction excitation spectroscopy⁷⁻⁹ can be employed to search for singlet SO vibronic transitions which, to our best knowledge, have not been observed so far in absorption. We report here the first singlet SO chemistry in any phase, induced by direct, selective excitation of SO($^{1}\Delta$) and SO($^{1}\Sigma^{+}$) vibronic levels.

Experimental Section

Matrix samples of SO suspended in solid rare gases were prepared on a cold CsI window by pyrolysis of an SO precursor,

⁽¹⁾ Barnes, I.; Becker, K. H.; Fink, E. H. Chem. Phys. Lett. 1979, 67, 310. Bielefeld, M.; Elfers, G.; Fink, E. H.; Kruse, H.; Wildt, J.; Winter, R.; Zabel, F. J. Photochem. 1984, 25, 419.

⁽²⁾ Colin, R. Can. J. Phys. 1968, 46, 1539.

⁽³⁾ Clyne, M. A. A.; MacRobert, A. J. Int. J. Chem. Kinet. 1981, 13, 187. DeMore, W. B.; Margitan, J. J.; Molina, M. J.; Watson, R. T.; Golden, D. M. et al. Int. J. Chem. Kinet. 1985, 17, 1135.

⁴⁾ Dodson, R. M.; Sauers, R. F. Chem. Commun. 1967, 1189. Dodson,

R. M.; Nelson, J. P. Chem. Commun. 1969, 1159. Chow, Y. L.; Tam, J. N. S.; Blier, J. E.; Szmant, H. H. Chem. Commun. 1970, 1604. Chao, P.; Lemal,

D. M. J. Am. Chem. Soc. 1973, 95, 920; 1973, 95, 922.
 (5) Singlet O₂; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I-III.

⁽⁶⁾ Braathen, G.; Chou, P. T.; Frei, H. J. Phys. Chem., in press.

⁽⁷⁾ Frei, H.; Pimentel, G. C. J. Chem. Phys. 1983, 79, 3307.

⁽⁸⁾ Frei, H. J. Chem. Phys. 1984, 80, 5616.

⁽⁹⁾ Frei, H.; Pimentel, G. C. In Chemistry and Physics of Matrix Isolated Species; Andrews, L., Moskovits, M., Eds.; Elsevier: Amsterdam, 1989; p 139.