

**Alkali Fluorotellurates(VI)**

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The reactions of tellurium hexafluoride with cesium fluoride or rubidium fluoride go nearly to completion if the alkali fluorides are suspended in the inert solvent,  $C_6F_6$ . With cesium fluoride a limiting composition of  $CsF \cdot TeF_6$  is approached, while rubidium fluoride gives compounds of composition  $2RbF \cdot TeF_6$ . Thermogravimetric analyses of the products show various inflection points indicating the existence of intermediate products stable at higher temperatures. Complete decomposition of the complexes is not achieved up to the melting points of the alkali fluorides, except in some cases under prolonged pumping. The infrared and Raman spectra of the materials have been tentatively interpreted in terms of  $D_{3h}$  and  $D_{4d}$  structures for the  $TeF_7^-$  and  $TeF_8^{2-}$  anions, respectively.

**Introduction**

The reactions of tellurium hexafluoride with some of the alkali fluorides have been reported previously.<sup>1</sup> In that study fluorotellurates of limiting composition  $2MF \cdot TeF_6$  were prepared by heating the alkali fluorides with excess  $TeF_6$  at 250° and cooling the reaction mixture to room temperature over a period of 24 hr. Cesium fluoride gave a product of this nominal composition containing no starting material. Although products of empirical composition  $2RbF \cdot 0.52TeF_6$  and  $2KF \cdot 0.32TeF_6$  were reported, these contained RbF or KF indicating incomplete reaction or hydrolysis of the reaction products in the handling and preparation for X-ray analyses. The method used by Muetterties would isolate only species stable at high temperatures. Although attempts were made to obtain others stable at lower temperatures by prolonged cooling periods, the nature of solid-gas reactions militates against complete reaction. A salt of composition  $AgTeF_7$  has been reported<sup>2</sup> to form upon reaction of AgF with solutions of HF containing tellurium metal oxidized by chlorine trifluoride.

We have reinvestigated these reactions with the purpose of obtaining fluorotellurates stable at lower temperatures and determining their stabilities as a function of temperature and cation.

**Experimental Section**

**Materials.** Cesium and rubidium fluoride were prepared by repeated treatment of the hydroxides (obtained from Koch-Light Laboratories, 99.9% minimum purity) with 48% HF and final dehydration and dehydrofluorination by heating to the melting point. The cooled melt was ground to a fine powder and stored in the dry-box until use. Analysis of weighed portions of the alkali fluorides with an Orion fluoride ion electrode showed the absence of bound HF. X-Ray powder patterns showed no lines other than those of the alkali fluoride. Potassium fluoride from several different sources was used (see Table I).

Tellurium hexafluoride was prepared by the fluorination of tellurium powder (Fluka, pure) with excess fluorine in a high-pressure Monel reactor. The  $TeF_6$  was purified by repeated low-temperature distillations. Infrared spectra and vapor pressure measurements attested to its purity.

Hexafluorobenzene was obtained from the Pierce Chemical Co. Pretreatment with  $TeF_6$  showed that no reaction occurred. The  $C_6F_6$  was purified by repeated freezing, pumping, and thawing cycles and transferred to a thoroughly outgassed graduated glass storage vessel.

**Procedure.** Reactions were carried out in 25-ml glass erlenmeyer flasks connected *via* 1/4-in. Kovar-glass seals and Swagelock fittings

to 1/4-in. Monel Whitey valves. The glass reactors contained glass-enclosed magnetic stirring bars. Manipulation of volatile gases or liquids was carried out in a vacuum system previously described.<sup>3</sup> Empty preweighed reactors were loaded with alkali fluoride in a dry-box and well degassed and reweighed to determine the weight of starting material. About 2–3 ml of  $C_6F_6$  was distilled into the reaction vessel, and enough  $TeF_6$  to give a final pressure of 2–3 atm was added. The reaction mixture was stirred on a magnetic stirrer-hot plate in a paraffin bath maintained at about 90°. At approximately daily intervals the reaction was interrupted and checked for  $TeF_6$  uptake by tensimetric measurements in the calibrated manifold. In all cases the mixture was first cooled to –195° and opened to the manifold to check for the presence of noncondensable gases. None were ever detected, showing that neither decomposition nor air leakage into the vessel had occurred. The  $TeF_6$  was separated from  $C_6F_6$  by pumping on the reaction mixture maintained in a chloroform slush (–63.5°). The pressure of  $TeF_6$  above the solid was kept approximately constant by adding suitable amounts of  $TeF_6$  as it was consumed during the course of the reaction.

Reactions were accompanied by large volume increases of the solids. When no further  $TeF_6$  uptake was detected, the  $TeF_6$  and  $C_6F_6$  were separately distilled off under reduced pressure at ambient temperature until constant weight was obtained. The extent of conversion of alkali fluoride to fluorotellurate was obtained from the increase in weight of starting material which was assumed to be due solely to combined  $TeF_6$ . In all cases the reaction course was also checked by PVT measurements of  $TeF_6$  consumed, and these agreed with the weight gains within limits of error. These comparisons precluded the possibility that weight gains or pressure uptakes were due to lighter gases such as HF or  $SiF_4$  or unknown heavier gas impurities.

**Apparatus.** Thermogravimetric analyses of the samples were carried out on a semimicroscale on a Mettler Thermoanalyzer in a dry nitrogen flow. At certain stages isothermal runs were made and resulting products analyzed by X-ray powder photographs or Raman spectroscopy.

All manipulations of the solids such as transfer from reaction vessels, loading of capillaries or tga crucibles were carried out in a Vacuum-Atmospheres Corp. Dri-Lab with a dry nitrogen atmosphere of less than 1 ppm water content.

Infrared spectra were run on KBr disks using a Perkin-Elmer Model 457 spectrophotometer over the range 250–4000  $cm^{-1}$ .

Raman spectra were obtained on powdered samples contained in sealed capillaries. Instrumentation consisted of a Spex 1401 monochromator, a Spex 1419A Sample Illuminator, and a Spectra Physics Model 164  $Kr^+$  laser supplying about 60-mW power at the sample. (Certain commercial instruments are identified in this paper to specify completely the experimental procedure. In no case does such identification imply a recommendation or endorsement by the institutions sponsoring this research.)

**Results and Discussion**

In attempts to repeat Muetterties' results,<sup>1</sup> preliminary studies were carried out by treating the alkali fluoride with large excesses of  $TeF_6$  at 250° in thin-walled nickel weighing cans. Although reactions were obtained, the results were erratic and the reaction products were not easily recoverable

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Table I. Preparation of Alkali Fluorotellurates

Starting material	Reacn time, days	Initial wt of MF, g	Wt gain of TeF <sub>6</sub> , g	TeF <sub>6</sub> consumed from PVT measurements, mmol	Mole ratios MF:TeF <sub>6</sub>		Remarks
					From wt gain	From pressure	
CsF	3	0.6080	0.7735	3.09	1.25	1.30	No CsF in final products
	5	0.5465	0.7645	3.19	1.14	1.13	
	5	0.5105	0.7300	3.00	1.11	1.12	
RbF	7	0.1322	0.1564	0.563	1.96	2.25	No RbF in final products
	9	0.4648	0.5273	2.13	2.04	2.09	
	7	0.5813	0.6485	2.64	2.07	2.10	
KF	3	0.2279		0			KF Baker & Adamson reagent grade KF from decompn of Baker & Adamson reagent grade KF·2H <sub>2</sub> O KF from decompn of Reidel-de Haen KHF <sub>2</sub> , pure
	4	0.2578	0.0183	0.021			
	5	0.1321		0.054			

from the containers. It was apparent that the heat of reaction caused the reaction products to sinter, resulting in slow and incomplete reactions. Subsequent reactions were carried out by reacting TeF<sub>6</sub> with alkali fluorides suspended in the inert liquid, C<sub>6</sub>F<sub>6</sub>, with constant stirring. Such a technique had previously been shown to be successful in the preparation of analogous complexes with uranium hexafluoride.<sup>4</sup>

Results of the reactions with alkali fluorides are shown in Table I. Although complete reaction was never attained with cesium fluoride it is apparent that a limiting composition of CsF·TeF<sub>6</sub> is approached. Subsequent thermogravimetric analyses show that this compound is unstable at room temperature, as weight loss occurs already at ambient temperature, albeit rather slowly. The reaction does not proceed at a measurable rate at room temperature, apparently a minimum activation energy being required. X-Ray powder diffraction patterns indicate that no alkali fluoride starting material is present in the product. The powder pattern of the products, although not extremely complicated, could not be indexed, however. All products isolated were white fluffy solids.

Thermogravimetric analyses indicate that the product isolated at room temperature gives off TeF<sub>6</sub> in several stages. A typical thermogram is shown in Figure 1. The differential thermogram (dtg) shows several minima which do not all fit integral ratios of CsF to TeF<sub>6</sub>. Among them are two which correspond approximately to the compositions 2CsF·TeF<sub>6</sub> (135°) and 4CsF·TeF<sub>6</sub> (400°). Supporting evidence exists that the 2:1 and 4:1 compositions are significant. In Table II are given calculated and measured weight losses for several samples. Samples 1 and 3 were decomposed isothermally at room temperature and reached compositions approximating 2CsF·TeF<sub>6</sub>. These results confirm Muetterties' preparation of 2CsF·TeF<sub>6</sub> at 250°. Sample 4 was decomposed by pumping to constant weight at 120° and reached the composition 4CsF·TeF<sub>6</sub>. Decomposition pressures of TeF<sub>6</sub> in equilibrium with solid cesium fluorotellurate were measured at several temperatures. Some of these were  $p(80^\circ) = 13$  mm,  $p(90^\circ) = 29$  mm, and  $p(117^\circ) = 50$  mm. They do not conform to a Clausius-Clapeyron plot, indicating that several solid phases may have been present simultaneously. For sample 2 whose thermogram is given in Figure 1 the region up to 200° shows a complex dtg pattern which may be partially due to kinetic effects. Unfortunately X-ray powder patterns were of little help in elucidating the decomposition; because, except for the starting product, all of the intermediates appear to be amorphous.

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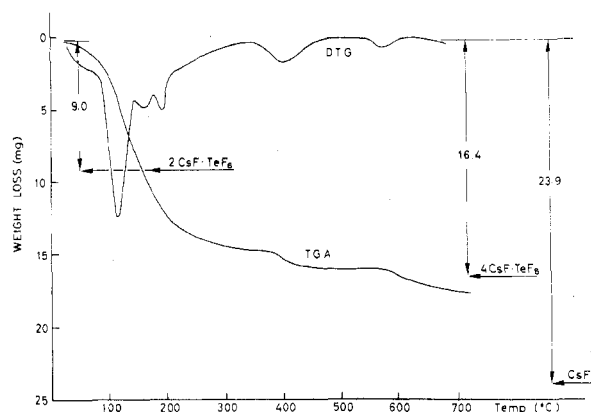


Figure 1. Thermogram of 1.25CsF·TeF<sub>6</sub>. Arrows and numbers indicate calculated weight loss steps (in mg) for intermediate compounds. Heating rate 8°/min in dry nitrogen flow of 7.5 l./hr at atmospheric pressure; initial weight of the sample 42.7 mg.

Table II. Decomposition Patterns of CsF-TeF<sub>6</sub> Complexes

Sample no.	Compn	Initial wt, mg	Wt losses to			
			2CsF·TeF <sub>6</sub>		4CsF·TeF <sub>6</sub>	
			Calcd	Measd	Calcd	Measd
1	1.20CsF·TeF <sub>6</sub>	57.4	13.1	14.4 <sup>a</sup>	22.9	21.9
2	1.25CsF·TeF <sub>6</sub>	42.7 <sup>b</sup>	9.0	(9.8) <sup>c</sup>	16.4	15.9
3	1.12CsF·TeF <sub>6</sub>	59.0	15.2	14.9 <sup>c</sup>	24.9	22.8
4	1.20CsF·TeF <sub>6</sub>	711.5 <sup>d</sup>			283.9	287.7 <sup>e</sup>

<sup>a</sup> Isothermal at ambient temperatures. <sup>b</sup> Figure 1. <sup>c</sup> At 160° dtg minimum. <sup>d</sup> Pumped to constant weight at 120° for 16 hr. <sup>e</sup> Confirmed by PVT measurement of evolved gas.

The tga runs were discontinued at 690°, because it was found that pure CsF itself begins to lose weight slowly near the melting point. It is obvious that at that temperature the residue still contains appreciable amounts of bound TeF<sub>6</sub>.

Analogous results were obtained with rubidium fluoride, except that the stable species isolated at room temperature has the composition 2RbF·TeF<sub>6</sub>. A representative thermogram is given in Figure 2. Measured and calculated values of weight losses for intermediate steps are given in Table III. The dtg curve shows a striking similarity to that obtained in the cesium fluorotellurate decomposition. A complex pattern exists in the initial rapid decomposition period up to about 200°, one of whose minima (~215°) corresponds to the composition 4RbF·TeF<sub>6</sub>. It cannot be averred, however, that this confirms Muetterties' complex of composition 2RbF·0.52TeF<sub>6</sub> because the latter reportedly contained unreacted starting material. Another minimum at about 425° corresponds to the composition 6RbF·TeF<sub>6</sub>. This phase begins to decompose around 600°. Decompositions

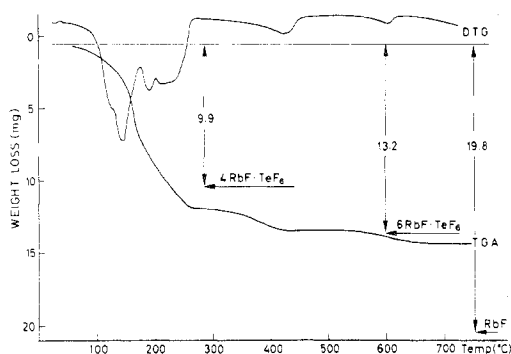


Figure 2. Thermogram of  $2\text{RbF}\cdot\text{TeF}_6$ . Heating rate  $8^\circ/\text{min}$ ; nitrogen flow 7.5 l./hr; initial weight of the sample 36.9 mg.

Table III. Decomposition Patterns of  $\text{RbF}\cdot\text{TeF}_6$  Complexes

Sam- ple- no.	Compn	Initial wt, mg	Wt losses to			
			$4\text{RbF}\cdot\text{TeF}_6$		$6\text{RbF}\cdot\text{TeF}_6$	
			Calcd	Measd	Calcd	Measd
1	$1.96\text{RbF}\cdot\text{TeF}_6$	36.9 <sup>a</sup>	9.9	11.4	13.2	13.0
2	$2.04\text{RbF}\cdot\text{TeF}_6$	134.9	36.2	39.1 <sup>b</sup>	48.2	48.4
3	$2.07\text{RbF}\cdot\text{TeF}_6$	1229.7	313.0		425.0	423.7 <sup>c</sup>

<sup>a</sup> Figure 2. <sup>b</sup> Isothermal at  $80^\circ$  in nitrogen atmosphere. <sup>c</sup> Isothermal at  $95^\circ$  after 38 hr under dynamic vacuum; confirmed by PVT measurement of evolved gases; further weight loss negligible.

were discontinued at  $750^\circ$  near the melting point of  $\text{RbF}$ . At this stage the residue still contained appreciable amounts of bound  $\text{TeF}_6$ . X-Ray powder patterns, however, showed only the presence of  $\text{RbF}$  indicating the other phase to be amorphous.

We have found that  $\text{KF}$  obtained from three different sources as shown in Table I does not give any reaction with  $\text{TeF}_6$  under the presently given conditions. Muetterties reported a nominal composition  $2\text{KF}\cdot 0.32\text{TeF}_6$ . His products contained unreacted  $\text{KF}$  which, however, may have resulted from hydrolysis of the product upon handling and preparation for X-ray analysis. The possibility that minimal reaction does occur at  $250^\circ$  cannot be ruled out. It is interesting that the stoichiometry  $2\text{KF}\cdot 0.32\text{TeF}_6$  corresponds to one of the intermediate compounds in the  $\text{RbF}$  system.

Infrared spectra have been obtained of  $1.12\text{CsF}\cdot\text{TeF}_6$  and  $2\text{RbF}\cdot\text{TeF}_6$ . The infrared spectra showed some degree of hydrolysis. Although the die was loaded in the drybox and transported to the press in a plastic bag, a short exposure to air had been necessary during disk preparation. Raman spectra of powders contained in sealed capillaries showed minimal hydrolysis, however. Raman spectra were obtained on  $1.12\text{CsF}\cdot\text{TeF}_6$  and  $2\text{RbF}\cdot\text{TeF}_6$ . The  $2\text{CsF}\cdot\text{TeF}_6$  sample prepared by isothermal heating of the former had significant oxyfluoride impurity as indicated by a line at about  $870\text{ cm}^{-1}$ .

Attempts to obtain a Raman spectrum of alkali fluorotellurate in a solution of anhydrous hydrogen fluoride failed. Such solutions showed only the presence of dissolved  $\text{TeF}_6$ . This is in accord with earlier observations<sup>1</sup> that the fluorotellurates display no stability outside the solid state but casts some doubts on the validity of the preparation<sup>2</sup> of  $\text{AgTeF}_7$  from a solution in  $\text{HF}$ .

A summary of the frequencies in the infrared and Raman spectra is given in Table IV. Despite the difficulties in assigning a structure using only solid-phase samples, it is tempting to do so in these cases, particularly since solution spectra are not available. As one can see from Table IV,  $1.12\text{CsF}\cdot\text{TeF}_6$  has five Raman lines and four infrared absorption bands. These results are quite similar to those of  $\text{IF}_7$ <sup>5</sup> and indicate

Table IV. Raman and Infrared Frequencies of Fluorotellurates ( $\text{cm}^{-1}$ )

$1.12\text{CsF}\cdot\text{TeF}_6$		$2\text{RbF}\cdot\text{TeF}_6$	
Raman	Ir	Raman	Ir
	725 s		645 s
652 vs		597 vs	
	620 vs		587 s
593 s		569 s	
455 s			555 s
	380 s	475 vw	
305 m		425 w	
	275 s	395 m	
122 w			385 s
			330 w
		205 w	
		185 w	
		145 w	

a  $D_{5h}$  structure for the  $\text{TeF}_7^-$  ion. While this assignment must be regarded as rather tentative, it is thought to be significant that there are no coincidences between infrared and Raman frequencies, which would be required for other possible symmetries with the exception of  $D_{7h}$  which has been rejected for the other heptafluorides,  $\text{ReF}_7$  and  $\text{IF}_7$ .<sup>5</sup> In any event there are two more observed Raman frequencies than would be expected for  $D_{7h}$  symmetry.

Spectra of eight-coordinated species have been studied by Hartman and Miller.<sup>6</sup> They have shown that the  $\text{TaF}_8^{3-}$  ion probably has an Archimedean antiprism structure,  $D_{4d}$ . This structure requires three stretching modes and four deformation modes in the Raman spectrum and two stretching modes and three deformation modes in the infrared spectrum with no coincidences between them. The Raman spectrum of  $2\text{RbF}\cdot\text{TeF}_6$  exhibits three lines in the stretching region and five lines which probably are deformation modes. There are several lines between the exciting line and  $105\text{ cm}^{-1}$  which probably are lattice modes. The infrared spectrum has three absorption bands in the stretching region and two bands in the bending region. Only two stretching modes are expected for  $D_{4d}$  symmetry. In the infrared spectra significant hydrolysis was found, so that some of the bands in the stretching region may be due to  $\text{Te-F}$  modes of an oxyfluoride. It should again be noted that there are no coincidences between the infrared and Raman spectra. The number of vibrations observed exceed those expected on the basis of octahedral symmetry,  $O_h$ , but are not enough to correspond to symmetry  $D_{2d}$ . Therefore a  $D_{4d}$  symmetry is tentatively proposed for the  $\text{TeF}_8^{2-}$  ion.

The results of this study confirm the utility of the technique<sup>4</sup> of dispersing the solid alkali fluorides in an inert liquid in order to overcome the problem of sintering. The reaction causes refluxing of the liquid, thus carrying away the heat of reaction. This, combined with constant stirring, maintains the solid in a finely divided state and enables reactions to be carried out at lower temperatures. We have thus been able to isolate the new compounds  $\text{CsTeF}_7$  and  $\text{Rb}_2\text{TeF}_8$  as well as to obtain evidence for the existence of the intermediate phases  $2\text{CsF}\cdot\text{TeF}_6$ ,  $4\text{CsF}\cdot\text{TeF}_6$ ,  $4\text{RbF}\cdot\text{TeF}_6$ , and  $6\text{RbF}\cdot\text{TeF}_6$ .

A striking analogy thus exists in the stoichiometries of the  $\text{CsF}$  and  $\text{RbF}$  adducts obtained at room temperature to those obtained at intermediate stages in their decompositions. The size of the cations appears to play an important

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role in the formation and stabilities of these complexes.

Attempts to react  $\text{TeF}_6$  with nitrosyl fluoride failed to give any positive results.

Registry No.  $\text{CsTeF}_7$ , 51015-21-5;  $\text{Rb}_2\text{TeF}_8$ , 51015-22-6;  $2\text{CsF} \cdot \text{TeF}_6$ , 51015-23-7;  $4\text{CsF} \cdot \text{TeF}_6$ , 51021-60-4;  $\text{CsF}$ , 13400-13-0;  $\text{RbF}$ , 13446-74-7;  $\text{TeF}_6$ , 7783-80-4.

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## Acidity, Basicity, and Ion-Molecule Reactions of Arsine in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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The ion-molecule reactions of arsine, both in pure form and in binary mixtures with several other molecules, have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and rate constants have been determined for ion-molecule reactions of both positive and, to a lesser extent, negative ions. Rate constants are determined by examining variation of ion abundance with both pressure and time, the latter experiments utilizing trapped ion techniques. Arsine fragment ions condense with neutral  $\text{AsH}_3$  to generate product ions containing two and, on further reaction, three atoms of arsenic. In the process of condensation, one or two molecules of  $\text{H}_2$  are expelled. The formation of  $\text{AsH}_4^+$  occurs from  $\text{AsH}_3^+$  which does not undergo condensation reactions to any significant extent. Where possible, thermochemical data have been determined, including the gas-phase acidity,  $\text{PA}(\text{AsH}_2^-) = 360 \pm 10$  kcal/mol, and basicity,  $\text{PA}(\text{AsH}_2) = 175 \pm 5$  kcal/mol, of  $\text{AsH}_3$ . Observation of gas-phase nucleophilic displacement reactions involving  $\text{AsH}_3$  as a nucleophile have allowed limits to be placed on the basicity of  $\text{AsH}_3$  toward a soft acid,  $\text{CH}_3^+$ . The implications of these results are discussed and the ion-molecule reactions of  $\text{AsH}_3$  are compared with those of other hydrides.

### Introduction

In order to provide a more complete understanding of the factors important in determining the intrinsic properties and reactivity of simple hydrides, we have extended our study<sup>4</sup> of the gas phase ion chemistry of the group V hydrides to include arsine. These studies are a necessary prelude to investigations of substituent effects on the properties and reactions of organic and inorganic ions and neutrals containing arsenic. To accomplish these objectives, the gas-phase ion-molecule reactions of arsine, alone and in mixtures with other molecules have been investigated. Where possible, kinetic and thermochemical data have been determined, including the gas-phase acidity and basicity of arsine. Of particular interest is the observation of periodic trends in thermochemical properties noted for other hydrides,<sup>4-6</sup> and the observation of additional examples of recently reported ionic nucleophilic displacement reactions.<sup>7-9</sup> Rate constants obtained in the present study were determined using the more usual technique of examining the variation of ion abundance with pressure in conjunction with recently developed<sup>10</sup> trapped-ion experiments involving an examination of the variation of ion abundance with time at a fixed pressure.

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With the exception of several reactions providing limits on the gas-phase acidity of arsine,<sup>6</sup> the ion chemistry of this species has not previously been investigated.

### Experimental Section

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.<sup>4,10-15</sup> In examining the variation of ion abundance with pressure, spectral intensities reported in tables and figures have been corrected to ion abundance by dividing the measured icr single resonance peak heights by ion mass.<sup>11</sup> Spectral intensities used to derive rate constants and product distributions have been normalized by dividing by the square of ion mass.<sup>4,11</sup> Reaction rate constants were derived using two complementary methods. Relative rate constants and product distributions for reactions observed in arsine were determined by the variation of electron energy method described previously.<sup>4</sup> Absolute rate constants were assigned by using as a standard the conversion of  $\text{AsH}_3^+$  to  $\text{AsH}_2^+$  (reaction 1) for which we have determined a rate constant of  $5.6 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> from data at 11 eV using the equations of Buttrill and Marshall.<sup>15</sup> These data are correlated with total disappearance rate constants for the primary ions generated in arsine. The latter were determined using trapped ion techniques recently developed in our laboratory.<sup>10</sup> The control unit for a Varian V-5900 icr spectrometer has been redesigned to incorporate pulse circuitry for performing trapped ion experiments. This circuitry, which allows for switching between trapped ion and normal drift modes of operation, will be described in detail elsewhere.<sup>16</sup>

Arsine was generated *in vacuo* by transferring concentrated hydrochloric acid onto excess zinc arsenide,  $\text{Zn}_3\text{As}_2$ .<sup>17</sup> Purification was achieved by transferring the evolved gas into a KOH solution followed by bulb-to-bulb fractionation at  $-80^\circ$ . Mass spectrometric

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(17) The authors gratefully acknowledge the gift of samples of  $\text{Zn}_3\text{As}_2$  and  $\text{Mg}_3\text{P}_2 \cdot 2\text{AlP}$  from Rocky Mountain Research, Inc., Denver, Colo.