role in the formation and stabilities of these complexes.

Attempts to react TeF_6 with nitrosyl fluoride failed to give any positive results.

Registry No. $CsTeF_7$, 51015-21-5; Rb_2TeF_8, 51015-22-6; $2CsF\cdot TeF_6$, 51015-23-7; $4CsF\cdot TeF_6$, 51021-60-4; CsF, 13400-13-0; RbF, 13446-74-7; 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 AsH_3 to generate product ions containing two and, on further reaction, three atoms af arsenic. In the process of condensation, one or two molecules of H_2 are expelled. The formation of AsH_4^+ occurs from $AsH_3\cdot^+$ which does not undergo condensation reactions to any significant extent. Where possible, thermochemical data have been determined, including the gas-phase acidity, $PA(AsH_2^-) = 360 \pm 10$ kcal/mol, and basicity, $PA(AsH_3) = 175 \pm 5$ kcal/mol, of AsH_3. Observation of gas-phase nucleophilic displacement reactions involving AsH_3 as a nucleophile have allowed limits to be placed on the basicity of AsH_3 toward a soft acid, CH_3^+. The implications of these results are discussed and the ion-molecule reactions of 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[4] 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,[4-6] and the observation of additional examples of recently reported ionic nucleophilic displacement reactions.[7-9] 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[10] trapped-ion experiments involving an examination of the variation of ion abundance with time at a fixed pressure.

With the exception of several reactions providing limits on the gas-phase acidity of arsine,[6] 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.[4,10-15] 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.[11] Spectral intensities used to derive rate constants and product distributions have been normalized by dividing by the square of ion mass.[4,11] 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.[4] Absolute rate constants were assigned by using as a standard the conversion of $AsH_3\cdot^+$ to AsH_4^+ (reaction 1) for which we have determined a rate constant of 5.6×10^{-10} cm^3 $molecule^{-1}$ sec^{-1} from data at 11 eV using the equations of Buttrill and Marshall.[15] 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.[10] 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.[16]

Arsine was generated *in vacuo* by transferring concentrated hydrochloric acid onto excess zinc arsenide, Zn_3As_2.[17] Purification was achieved by transferring the evolved gas into a KOH solution followed by bulb-to-bulb fractionation at −80°. Mass spectrometric

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(1) Supported by National Research Council of Canada, 1970–present.

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(17) The authors gratefully acknowledge the gift of samples of Zn_3As_2 and $Mg_3P_2\cdot 2AlP$ from Rocky Mountain Research, Inc., Denver, Colo.

examination at 70 eV showed the arsine to contain less than 0.1% impurities and in particular no HCl or diarsine. Phosphine was similarly prepared by transferring water onto excess magnesium aluminum phosphide, $Mg_3P_2 \cdot 2AlP$.[17] All other chemicals were reagent grade commercial samples utilized as supplied except for degassing with freeze-pump-thaw cycles. Purities as ascertained by mass spectrometric analysis were acceptable.

Results

Positive Ion Chemistry of Arsine. Electron impact (70 eV) on AsH_3 at low pressure (10^{-6} Torr) yields a single-resonance spectrum with ion intensities of $AsH_3 \cdot^+$ (30%), AsH_2^+ (11%), $AsH \cdot^+$ (42%), and As^+ (16%) in agreement with the known mass spectrum of arsine.[18] As the AsH_3 pressure is raised, ion-molecule reactions occur to form AsH_4^+ in addition to condensation products containing two ($As_2 \cdot^+$, As_2H^+, $As_2H_2 \cdot^+$, $As_2H_3^+$) and three (As_3^+, $As_3H \cdot^+$) arsenic atoms. At the highest pressures employed (10^{-3} Torr), the ions remaining are AsH_4^+, As_3^+, and $As_3H \cdot^+$. The variation of ion abundance with pressure at 70 eV is illustrated in Figure 1.

Reaction pathways were investigated by two methods: (1) observing the variation of single-resonance intensities as a function of the ionizing electron energy (appearance potential method)[19] and (2) the icr technique of double resonance.[11] Both methods are capable of establishing reaction pathways. As previously noted, the appearance potential method also allows for the determination of relative reaction rates and product distributions.[4] For example, at 11 eV, $AsH_3 \cdot^+$ is the only ion formed by electron impact. As AsH_3 pressure is increased, only the product ion AsH_4^+ appears, indicating reaction 1. At 12 eV, the fragment ion

$$AsH_3 \cdot^+ + AsH_3 \rightarrow AsH_4^+ + AsH_2 \cdot \tag{1}$$

$AsH \cdot^+$ appears. With increasing AsH_3 pressure, this ion leads to the formation of the product ions $As_2 \cdot^+$ and $As_2H_2 \cdot^+$, indicating reactions 2 and 3. At 14 eV, the fragment ion

$$AsH \cdot^+ + AsH_3 \xrightarrow{91\%} As_2 \cdot^+ + 2H_2 \tag{2}$$

$$AsH \cdot^+ + AsH_3 \xrightarrow{9\%} As_2H_2 \cdot^+ + H_2 \tag{3}$$

AsH_2^+ appears. With increasing AsH_3 pressure, this ion leads to the production of As_2H^+ and $As_2H_3^+$, indicating reactions 4 and 5. Finally at 15 eV, As^+ appears and, with

$$AsH_2^+ + AsH_3 \xrightarrow{91\%} As_2H^+ + 2H_2 \tag{4}$$

$$AsH_2^+ + AsH_3 \xrightarrow{9\%} As_2H_3^+ + H_2 \tag{5}$$

increasing AsH_3 pressure, leads to an increase in the As_2H^+ intensity relative to the intensity of the other condensation products, identifying reaction 6.

$$As^+ + AsH_3 \rightarrow As_2H^+ + H_2 \tag{6}$$

Due to line broadening and poor resolution, it was not possible experimentally to determine the precursor ions to the formation of the tertiary product ions As_3^+ and $As_3H \cdot^+$. Reactions 7 and 8, involving the prominent secondary ions,

$$As_2 \cdot^+ + AsH_3 \rightarrow As_3H \cdot^+ + H_2 \tag{7}$$

$$As_2H^+ + AsH_3 \rightarrow As_3^+ + 2H_2 \tag{8}$$

most likely account for the generation of these species, however.[20]

The formation of protonated arsine, AsH_4^+, deserves further comment. As noted above, $AsH_3 \cdot^+$ is the only ion formed by electron impact at 11 eV, reacting with AsH_3 to form only AsH_4^+. The ratio of the intensity of AsH_4^+ to $AsH_3 \cdot^+$ remains constant to within ±5% when the electron energy is varied between 11 and 70 eV, and at a pressure such that the conversion of primary to secondary ions is low. This suggests that AsH_4^+ is formed solely *via* reaction 1 and is not generated to any extent as a *secondary* ion by any of the remaining AsH_3 fragment ions. Furthermore, it is unlikely that charge-exchange processes such as the generalized reaction 9 are important, as this would lead to a decrease in the

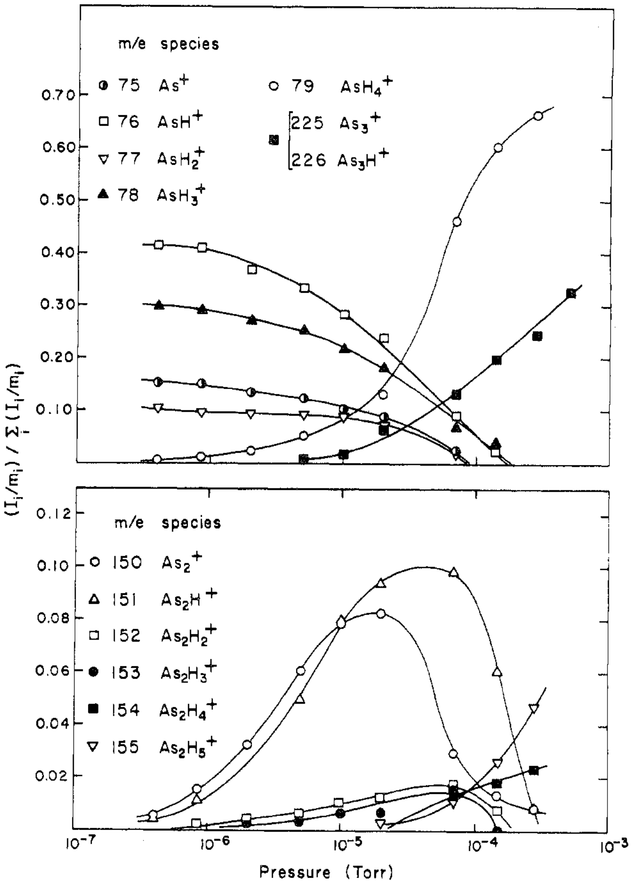

Figure 1. Variation of ion abundance with pressure for AsH_3 at 70 eV. The tertiary ions As_3^+ and As_3H^+ were poorly resolved in single-resonance spectra at high pressures. Their intensities are reported as an approximate sum.

$$AsH_n^+ + AsH_3 \rightarrow AsH_3 \cdot^+ + AsH_n \quad (n = 0\text{-}2) \tag{9}$$

ratio of AsH_4^+ to $AsH_3 \cdot^+$ with increasing electron energy.

The general reaction scheme proposed above is consistent with the observed variation of ion abundance with pressure (Figure 1) and is further corroborated by the variation of ion abundance with time (Figure 2).[10] The minor ions $As_2H_2^+$ and $As_2H_3^+$ were detected but could not be accurately measured due to the unavoidable lower sensitivity associated with the trapped ion mode of operation.[10] The decay of the four primary ions is illustrated in Figure 3, where the slopes are a measure of the total disappearance rate constant for each ion.[10] There is no appreciable upward curvature to any of the decay curves. Consistent with the proposed reaction scheme, this suggests that none of the primary ions are them-

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(20) At the highest pressures employed (3 × 10^{-4} Torr), $As_2H_4^+$ and $As_2H_5^+$ were noted (~4% of total ionization). These species may have been due to a minor diarsine impurity, either introduced with the sample or formed in the icr apparatus. AsH_3 is known to be thermally unstable.

Table I. Summary of Enthalpy Changes, Product Distributions, and Rate Constants for the Principal Ion-Molecule Reactions of Arsine

Reaction[a]	ΔH^b	Prod distr[c]	$k_i^{d,e}$	$\Sigma_i k_i^d$	$k_d^{d,f}$
$As^+ + AsH_3 \rightarrow As_2H^+ + H_2$	−33	1.00	4.9	4.9	10.0
$\rightarrow As_2\cdot^+ + 2H_2$	+24[g]	0.91	6.6		
$AsH\cdot^+ + AsH_3$				7.3	8.7
$\rightarrow As_2H_2^+ + H_2$	+17[g]	0.09	0.7		
$\rightarrow As_2H^+ + 2H_2$	−32	0.91	5.7		
$AsH_2^+ + AsH_3$				6.3	5.1
$\rightarrow As_2H_3^+ + H_2$	−37	0.09	0.6		
$AsH_3\cdot^+ + AsH_3 \rightarrow AsH_4^+ + AsH_2\cdot$	−21	1.00	5.6	5.6	5.1

[a] All reactions listed gave a negative double-resonance response, indicating $dk/dE < 0$. [b] Values in kcal/mol. Large errors may be present in these values owing to poorly known heats of formation for many relevant ions. Thermochemical data from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. G. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance of Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [c] Total product distribution normalized to unity for each reactant ion. [d] Units are 10^{-10} cm^3 molecule^{-1} sec^{-1}. [e] The k_i are rate constants appropriate to the individual reaction channels obtained as outlined in the text. [f] Disappearance rate constants for primary ions, determined in trapped-ion experiments. [g] It is unlikely that these reactions are endothermic in view of the rather large thermal reaction rate constants for these processes.

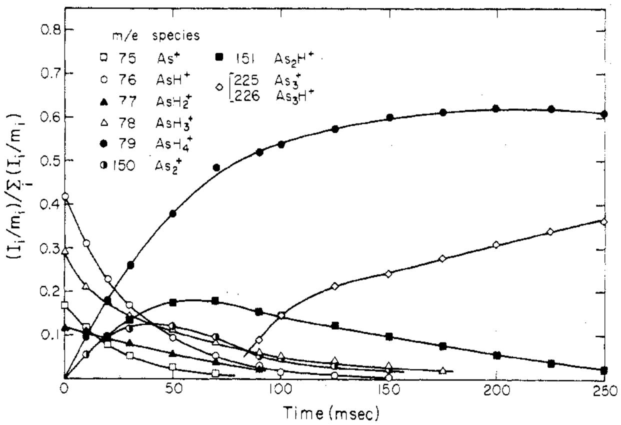

Figure 2. Variation of ion abundance with time for AsH_3 at 70 eV and 1.9×10^{-6} Torr. The intensities of the ions As_3^+ and As_3H^+ are reported as an approximate sum.

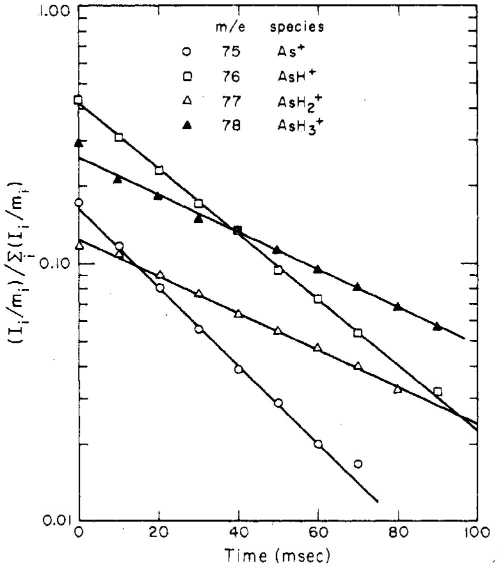

Figure 3. Variation of log (relative ion abundance) with time for the four primary ions in AsH_3 at 70 eV and 1.9×10^{-6} Torr. The slope of the line for each ion yields the total disappearance rate constant for that species.

selves products of reactions involving other primary ions. The total disappearance rate constants are compared in Table I with the summed rate constants for individual reaction channels of each of the primary ions. The agreement is quite good with the exception of As^+ where the disappearance rate constant is twice the rate constant for the single observed reaction channel. This suggests some additional process which we were unable to identify. The fact that As^+ has the highest appearance potential and lowest abundance make its reaction products difficult to monitor, particularly if it contributes to any of the several major primary ions.

Basicity of Arsine. The ion chemistry occurring in mixtures of AsH_3 with select molecules was investigated to determine the gas-phase basicity of arsine. Such molecules included PH_3, H_2S, $CH_3CH{=}CH_2$, CH_3OH, and CH_3Cl.

Arsine and Phosphine. The variation with pressure of the single-resonance intensities for a 1.6:1 mixture of AsH_3 and PH_3 at an electron energy (11 eV) such that only the parent ions are generated at low pressure is illustrated in Figure 4. With increasing pressure, the parent ions $AsH_3\cdot^+$ and $PH_3\cdot^+$ react to form the protonated species AsH_4^+ and PH_4^+. At still higher pressures, AsH_4^+ is observed to decline in favor of PH_4^+, which is the only ion present at 2×10^{-4} Torr. These observations suggest and double-resonance experiments (Table II) confirm that reaction 10 proceeds only in the direction indicated. For reasons discussed below, it may be concluded that the proton affinity (PA) of phosphine is greater than that of arsine.

$$AsH_4^+ + PH_3 \rightarrow PH_4^+ + AsH_3 \qquad (10)$$

Arsine and Hydrogen Sulfide. Electron impact on a 5.5:1 mixture of H_2S and AsH_3 at 11 eV and 10^{-6} Torr yields only the parent ions $H_2S\cdot^+$ and $AsH_3\cdot^+$. The ion chemistry of this mixture is qualitatively similar to that illustrated in Figure 4 for arsine and phosphine. Thus with increasing pressure, the parent ions react to form the protonated species H_3S^+ and AsH_4^+. The single-resonance intensity of H_3S^+ passes through a maximum and decreases while that of AsH_4^+ continues to increase, AsH_4^+ being the only remaining ion at 4×10^{-4} Torr. Double-resonance experiments confirm that reaction 11 is exothermic in the direction indicated, leading to the conclusion that $PA(AsH_3) \geqslant PA(H_2S)$.

$$H_3S^+ + AsH_3 \rightarrow AsH_4^+ + H_2S \qquad (11)$$

Arsine and Propene. In a manner similar to that described for the mixtures above, examination of the variation of single-resonance intensities with pressure for a 2.7:1 mixture of $CH_3CH{=}CH_2$ and AsH_3 under conditions such that only the parent ions $C_3H_6\cdot^+$ and $AsH_3\cdot^+$ are initially present (11 eV),

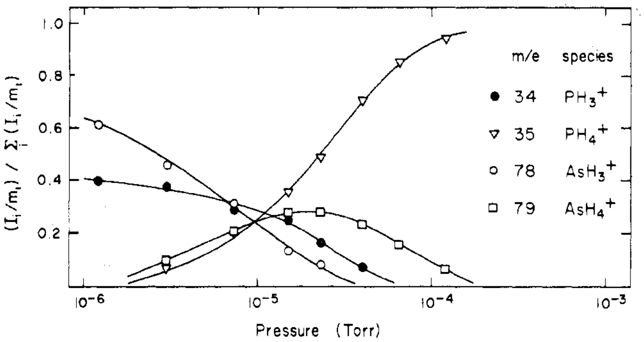

Figure 4. Variation of ion abundance with pressure for a 1.6:1 mixture of AsH_3 and PH_3 at 11 eV.

Table II. Summary of Proton Transfer and Nucleophilic Displacement Reactions Observed in Mixtures of Arsine with Various Molecules

Reaction[a]	Thermochemical inferences[b]
$AsH_4^+ + PH_3 \rightarrow PH_4^+ + AsH_3$	$PA(AsH_3) \leqslant 185$[c]
$H_3S^+ + AsH_3 \rightarrow AsH_4^+ + H_2S$	$PA(AsH_3) \geqslant 170$[c]
$AsH_4^+ + CH_3CHCH_2 \rightarrow C_3H_7^+ + AsH_3$	$PA(AsH_3) \leqslant 179$[d]
$CH_3ClH^+ + AsH_3 \rightarrow AsH_4^+ + CH_3Cl$	$PA(AsH_3) \geqslant 160$[e]
$CH_3ClH^+ + CH_3Cl \rightarrow (CH_3)_2Cl^+ + HCl$	$MCA(CH_3Cl) \geqslant MCA(HCl)$
$AsH_4^+ + CH_3OH \rightarrow CH_3OH_2^+ + AsH_3$	$PA(AsH_3) \leqslant 181$[f]
$CH_2OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O$	$MCA(CH_3OH) \geqslant MCA(H_2O)$
$CH_3OH_2^+ + AsH_3 \rightarrow CH_3AsH_3^+ + H_2O$	$MCA(AsH_3) \geqslant MCA(H_2O)$

[a] The reverse reaction was investigated in each case and was not found to occur; d*k*/d*E* was negative in all cases. [b] Values given in kcal/mol. [c] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969). [d] F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). [e] Reference 9. [f] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969); J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, **94**, 2638 (1972).

suggests the occurrence of reaction 12. Double-resonance

$$AsH_4^+ + C_3H_6 \rightarrow C_3H_7^+ + AsH_3 \qquad (12)$$

experiments confirm this reaction in the direction shown. Hence $PA(CH_3CH{=}CH_2) \geqslant PA(AsH_3)$.

Arsine and Methanol. The variation of single-resonance intensities with pressure, illustrated in Figure 5, for a 3:1 mixture of AsH_3 and CH_3OH under conditions where initially only $AsH_3\cdot^+$ is present (11 eV) suggests the occurrence of reaction 13. Double-resonance experiments con-

$$AsH_4^+ + CH_3OH \rightarrow CH_3OH_2^+ + AsH_3 \qquad (13)$$

firm that reaction 13 proceeds in the direction shown. We conclude that $PA(CH_3OH) \geqslant PA(AsH_3)$.

The formation of ions at *m/e* values corresponding to protonated dimethyl ether and protonated methylarsine is of particular interest. These ions, which represent 35 and 15%, respectively, of the total ions present at 8×10^{-4} Torr, are formed in the nucleophilic displacement reactions 14 and 15. Munson[21] and more recently Henis[22] have reported the

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \qquad (14)$$

$$CH_3OH_2^+ + AsH_3 \rightarrow CH_3AsH_3^+ + H_2O \qquad (15)$$

formation of protonated dimethyl ether in methanol.

Arsine and Methyl Chloride. Examination of the variation of single-resonance intensities with pressure for a 5:1 mixture

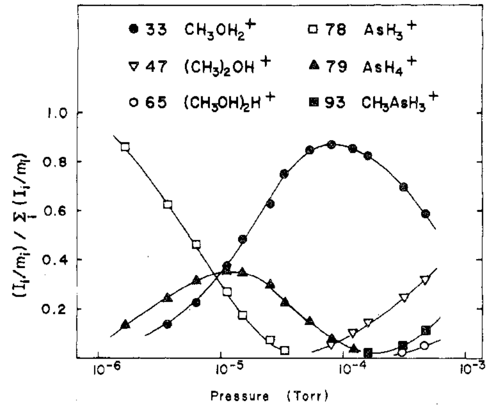

Figure 5. Variation of ion abundance with pressure for a 3:1 mixture of AsH_3 and CH_3OH at 11 eV.

of CH_3Cl and AsH_3 under conditions where only the parent ion of arsine is initially present (11 eV) shows that $AsH_3\cdot^+$ reacts with both neutrals to form the protonated species AsH_4^+ and CH_3ClH^+. At higher pressures evidence for reaction 16 is observed, which double-resonance experiments

$$CH_3ClH^+ + AsH_3 \rightarrow AsH_4^+ + CH_3Cl \qquad (16)$$

confirm to proceed as shown. Hence we conclude that $PA(AsH_3) \geqslant PA(CH_3Cl)$.

In agreement with previous studies of the positive ion-molecule chemistry of methyl chloride, CH_3ClH^+ is observed to react with CH_3Cl to undergo the nucleophilic displacement reaction 17 forming dimethylchloronium ion.[9] Signifi-

$$CH_3ClH^+ + CH_3Cl \rightarrow (CH_3)_2Cl^+ + HCl \qquad (17)$$

cantly, the analogous displacement reaction with AsH_3, reaction 18, is not observed.

$$CH_3ClH^+ + AsH_3 \not\rightarrow CH_3AsH_3^+ + HCl \qquad (18)$$

Negative Ion Chemistry of Arsine. Electron impact (6.3 eV) on AsH_3 at 4×10^{-5} Torr yields the negative ions As^- (10%), AsH^- (15%), and AsH_2^- (75%). The contribution to the total ionization by As^- and AsH^- decreases with increasing AsH_3 pressure while product ions containing two arsenic atoms appear in the negative ion single-resonance spectrum. Double-resonance experiments identified As^- as the precursor of the product ion As_2H^-, indicating reaction 19. AsH^- reacts to produce AsH_2^-, which is unreactive

$$As^- + AsH_3 \rightarrow As_2H^- + H_2 \qquad (19)$$

toward AsH_3.

Acidity of Arsine. The investigation of the negative ion chemistry of AsH_3 in mixtures with PH_3, H_2S, and C_2H_5ONO was undertaken to determine the gas-phase acidity of AsH_3.

Arsine and Hydrogen Sulfide. The negative ions AsH_2^- and HS^- in a 1:2 mixture of AsH_3 and H_2S were produced chemically *via* proton-transfer reactions. The negative ion single-resonance spectrum of ethyl nitrite, C_2H_5ONO, at 25 eV shows abundant ethoxide ion, $C_2H_5O^-$.[23-25] Both arsine and hydrogen sulfide readily transfer a proton to $C_2H_5O^-$ forming AsH_2^- and HS^- in accordance with reactions 20 and 21. Illustrated in Figure 6 is the variation of single-

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(21) M. S. B. Munson, *J. Amer. Chem. Soc.*, 87, 5313 (1965).

(22) J. Henis, *J. Amer. Chem. Soc.*, 90, 844 (1968).

(23) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, 42, 1632 (1971).

(24) K. Jaeger and A. Henglein, *Z. Naturforsch. A*, 22, 700 (1967), reported a large cross section for the formation of $C_2H_5O^-$ from C_2H_5ONO.

(25) The sample of ethyl nitrite contained ~10% ethanol.

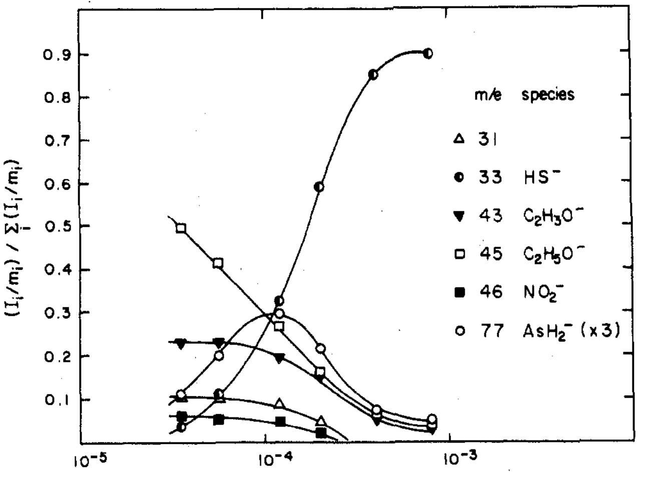

Figure 6. Variation of ion abundance with pressure for a 1:2 mixture of AsH_3 and H_2S at a fixed pressure (2×10^{-5} Torr) of C_2H_5-ONO and 25 eV.

$$C_2H_5O^- + AsH_3 \rightarrow AsH_2^- + C_2H_5OH \qquad (20)$$

$$C_2H_5O^- + H_2S \rightarrow HS^- + C_2H_5OH \qquad (21)$$

resonance intensities with increasing partial pressure of AsH_3 and H_2S at a fixed pressure of ethyl nitrite. At high pressure, AsH_2^- declines in favor of HS^-. Double-resonance experiments (Table V) confirm that reactions 20-22 proceed as

$$AsH_2^- + H_2S \rightarrow HS^- + AsH_3 \qquad (22)$$

written and lead to the conclusion that $PA(C_2H_5O^-) \geq PA(AsH_2^-) \geq PA(HS^-)$.

Two other ions present in the negative ion single-resonance spectrum of this mixture, NO_2^- and $C_2H_3O^-$, are formed *via* reactions 23 and 24. Reaction 23 is analogous

$$C_2H_5O^- + C_2H_5ONO \rightarrow NO_2^- + (C_2H_5)_2O \qquad (23)$$

$$C_2H_5O^- + C_2H_5OH \rightarrow C_2H_3O^- + H_2 + C_2H_5OH \qquad (24)$$

to the displacement of NO_3^- from ethyl nitrate by $C_2H_5O^-$ observed by Kriemler and Buttrill.[26] That C_2H_5OH is the neutral reactant in reaction 24 is strengthened by the observation of the same process in ethanol alone.[27] It was found by double-resonance experiments that H_2S will transfer a proton to $C_2H_3O^-$ while AsH_3 does not (Table V). This suggests that $PA(AsH_2^-) \geq PA(C_2H_3O^-) \geq PA(HS^-)$.

Arsine and Phosphine. The negative ions observed in the single-resonance spectrum of a 1:2 mixture of AsH_3 and PH_3 at an electron energy of 6.3 eV and a pressure of 3×10^{-6} Torr include AsH_2^-, PH_2^-, and minor contributions from As^- and AsH^-. At the highest pressure employed, 3×10^{-4} Torr, AsH_2^- increases relative to PH_2^-. Double-resonance experiments confirm reaction 25 as written and permit the

$$PH_2^- + AsH_3 \rightarrow AsH_2^- + PH_3 \qquad (25)$$

conclusion that $PA(PH_2^-) \geq PA(AsH_2^-)$.

Discussion

Positive Ion Reactions in Arsine. The ion-molecule reactions of arsine are qualitatively similar to those of its group V congener, phosphine.[4] Thus, at 70 eV and at pressures above 10^{-6} Torr, condensation reactions generate ions containing two and three atoms of arsenic. Such reaction products make up more than 50% of the total ionization observed at 8×10^{-5} Torr. From the summary of reactions in Table I, it is evident that fragment ions derived from AsH_3 most commonly react with the parent neutral to form an intermediate complex from which occurs the subsequent rapid expulsion of one or two molecules of hydrogen. In contrast to the condensation reactions of $PH\cdot^+$ with PH_3,[5] however, hydrogen atom loss is not observed even when the reactant is a radical ion such as $AsH\cdot^+$. As previously noted, the ion-molecule reactions of the first-row congener, ammonia, stand in contrast to both phosphine and arsine.[4] Fragment ions of NH_3 react with the neutral to generate $NH_3\cdot^+$ and NH_4^+ by charge-exchange and proton-transfer processes.[28-34] Ionic condensation reactions are not prevalent. An identical trend in reactivity is observed for the group VI hydrides H_2O, H_2S, and H_2Se.[5,35-38]

Basicity of Arsine. The enthalpy change for the gas-phase reaction $MH^+ \rightarrow M + H^+$ defines the proton affinity (PA) of the species, M, and provides a quantitative measure of intrinsic basicity.[4-6,11] Since gas-phase ion-molecule reactions are assumed to proceed with negligible activation energy,[19,39-41] the observation of a process such as reaction 26 is usually interpreted as indicating that $PA(M_2) > PA(M_1)$.

$$M_1H^+ + M_2 \rightarrow M_2H^+ + M_1 \qquad (26)$$

Thus from reactions 10-13 and 16 reported above, which indicate $PA(CH_3Cl), PA(H_2S) \leq PA(AsH_3) \leq PA(CH_3CH{=}CH_2), PA(CH_3OH), PA(PH_3)$, and the known values $PA(CH_3Cl) = 160$ kcal/mol,[9] $PA(H_2S) = 170$ kcal/mol,[42] $PA(CH_3CH{=}CH_2) = 179$ kcal/mol,[43] $PA(CH_3OH) = 181$ kcal/mol,[44,45] and $PA(PH_3) = 185$ kcal/mol,[44,46] an estimate of $PA(AsH_3) = 175 \pm 5$ kcal/mol is derived, corresponding to $\Delta H_f(AsH_4^+) = 207 \pm 5$ kcal/mol.

The proton and hydrogen affinities of a molecule and its corresponding ion are interrelated by ionization potentials as shown in eq 27. The hydrogen affinity, $HA(M^+)$, is

$$PA(M) - HA(M^+) = IP(H\cdot) - IP(M) \qquad (27)$$

simply the $H\text{-}M^+$ bond strength. A comparison of the hydrogen affinities of the group V hydrides to the bond

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strengths of isoelectronic group IV neutrals is presented in Table III. As expected, the M-H bond strengths increase upon proceeding to the isoelectronic ion; the increase of 20-30 kcal/mol has been noted previously in other systems.[46] Parallel decreases in bond strengths for the isoelectronic neutral species are also noted in proceeding from the first to the second to the third row of the periodic table.

The ionization potentials, proton affinities, hydrogen affinities, and bond dissociation energies for the group V hydrides are summarized in Table IV. *Owing to the similarity in the ionization potentials of NH_3, PH_3, and AsH_3, a constant difference exists between their proton and hydrogen affinities.* Hence, there is a parallel decrease in the proton and hydrogen affinities of the group V hydrides upon proceeding down the group in the periodic table. A more complete discussion of periodic trends in gas-phase basicities of simple hydrides, based in part on these results, is presented in a recent review.[11]

Nucleophilic Displacement Reactions. We have shown[7-9] that the nucleophilic displacement reaction generalized in reaction 28 occurs provided two criteria are met: (1) the

$$YH_n + CH_3XH_m^+ \rightarrow CH_3YH_n^+ + XH_m \qquad (28)$$

reaction is exothermic or thermoneutral and (2) proton transfer from the substrate to the nucleophile is endothermic, *i.e.*, $PA(CH_3XH_{m-1}) \geqslant PA(YH_n)$. Reaction processes observed in mixtures of AsH_3 with CH_3OH and CH_3Cl serve to illustrate these principles.

As noted above, protonated methylarsine, $CH_3AsH_3^+$, is formed *via* reaction 15 as AsH_3 reacts with $CH_3OH_2^+$ to displace H_2O. Proton transfer from the substrate ($CH_3OH_2^+$) to the nucleophile (AsH_3) does not occur since $PA(CH_3OH) > PA(AsH_3)$. In contrast, in a mixture of CH_3Cl and AsH_3, the analogous nucleophilic displacement, reaction 18, does not proceed to produce $CH_3AsH_3^+$ even though the process is estimated to be exothermic by 37 kcal/mol.[47] Instead, since $PA(AsH_3) > PA(CH_3Cl)$, only the exothermic proton-transfer reaction 16 is observed.

The relative effectiveness of nucleophiles in undergoing reaction 28 has been quantified.[7,8] A useful thermochemical quantity to employ is the methyl cation affinity (MCA), defined as the negative of the enthalpy change for attaching a methyl cation to a neutral M as depicted in the general reaction 29. Available data indicate that the following will

$$M + CH_3^+ \rightarrow MCH_3^+ \qquad (29)$$

be the order in which nucleophilic displacements occur[7,8] (decreasing methyl cation affinity): $NH_3 > CO > H_2S > CH_3OH > CH_2O > HI > H_2O > HBr > HCl > N_2 > HF$. Observation of reaction 15 implies that $MCA(AsH_3) > MCA(H_2O) = 66$ kcal/mol.[7,8]

Table III. Bond Strengths of Some Isoelectronic Species[a]

Ion	Hydrogen affinity[b]	Neutral	Bond strength	Δ[f]
NH_4^+	128	CH_4	104[c]	24
			99[e]	29
PH_4^+	102	SiH_4	94[d]	8
			77[e]	25
AsH_4^+	92	GeH_4	69[e]	23

[a] All values in kcal/mol. [b] Homolytic bond dissociation energies (*e.g.*, for $NH_4^+ \rightarrow NH_3^+ + H$), calculated from eq 27. [c] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [d] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **84**, 4441 (1962). The SiH_3-H bond dissociation energy reported in this article is most likely too high. [e] Average bond energy; data from S. R. Gunn and L. G. Green, *J. Phys. Chem.*, 65, 779 (1961). [f] Difference in bond strengths for isoelectronic species.

Table IV. Thermochemical Quantities Related to the Basicities of the Group V Hydrides[a]

M	IP(M)[b]	PA(M)	$HA(M^+)$[f]
NH_3	10.15	207[c]	128
PH_3	9.98	185[d]	102
AsH_3	10.03	175[e]	92

[a] Except for ionization potentials, all values are given in kcal/mol. [b] Ionization potentials given in eV; data from J. L. Franklin and J. G. Dillard; H. M. Rosenstock, J. T. Herron, and K. Draxl; and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [c] Reference 44. [d] Reference 46. [e] This work. [f] Calculated from eq 27.

$$\begin{tikzcd}
e^- + AsH_3 \arrow[rr, "PA(AsH_2^-)"] \arrow[dr, "E_t"'] & & AsH_2^- + H^+ + e^- \\
& AsH_2^- + H\cdot \arrow[ur, "IP(H\cdot)"'] &
\end{tikzcd} \qquad (31)$$

Acidity of Arsine. The proton affinity of the anion, M^-, is both a definition and measure of the gas-phase acidity of the species MH. The anion, AsH_2^-, can be produced by the dissociative electron-capture reaction 30.[48] The thres-

$$e^- + AsH_3 \rightarrow AsH_2^- + H\cdot \qquad (30)$$

hold energy determined for this process, $E_t = 2.0 \pm 0.1$ eV,[48] can be employed to estimate the proton affinity of AsH_2^- through the thermochemical cycle of eq 31. Using $IP(H\cdot) = 313$ kcal/mol and eq 31, $PA(AsH_2^-)$, the gas-phase acidity of arsine, is estimated to be 359 ± 3 kcal/mol. Proton transfer reactions which provide useful limits for $PA(AsH_2^-)$ are summarized in Table V. From reactions 20, 22, and 25 reported above, we conclude that $PA(HS^-) \leqslant PA(AsH_2^-) \leqslant PA(PH_2^-)$, $PA(C_2H_5O^-)$. Using the values $PA(HS^-) = 350$ kcal/mol,[49] $PA(PH_2^-) = 369$ kcal/mol,[50] and $PA(C_2H_5O^-) = 376$ kcal/mol,[51] the value 360 ± 10 kcal/mol may be assigned to $PA(AsH_2^-)$, consistent with the value derived from eq 31.

The acidity of a species MH is related to the bond dissociation energy, D(M-H), and the electron affinity of the radical, $EA(M\cdot)$, as shown in the thermochemical cycle of eq 32.

$$\begin{tikzcd}
MH \arrow[r, "PA(M^-)"] \arrow[d, "D(M-H)"'] & M^- + H^+ \\
M\cdot + H\cdot \arrow[r, "IP(H\cdot)"'] & M\cdot + H^+ + e^- \arrow[u, "-EA(M\cdot)"']
\end{tikzcd} \qquad (32)$$

Smyth and Brauman have recently determined $EA(AsH_2\cdot)$ to be 29 kcal/mol from photodetachment studies.[52] Using this

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(47) Reaction 18 is calculated to be 37 kcal/mol exothermic using the authors' estimates of $\Delta H_f(CH_3AsH_2) = 12$ kcal/mol and $PA(CH_3AsH_2) = 190$ kcal/mol, corresponding to $\Delta H_f(CH_3AsH_3^+) = 188$ kcal/mol.

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(49) Calculated from eq 32 employing $EA(HS\cdot) = 53$ kcal/mol (R. S. Berry, *Chem. Rev.*, 69, 533 (1969)) and $D(HS\text{-}H) = 90$ kcal/mol (J. A. Kerr, *Chem. Rev.*, 66, 465 (1966)).

(50) Calculated from eq 32 employing $EA(PH_2) = 28.8$ kcal/mol (K. C. Smyth and J. L. Brauman, *J. Chem. Phys.*, 56, 1132 (1972)) and $D(PH_2\text{-}H) = 83.9$ kcal/mol (T. McAllister and F. P. Lossing, *J. Phys. Chem.*, 73, 2996 (1969)).

(51) Calculated from eq 32 employing $EA(C_2H_5O\cdot) = 39$ kcal/mol (J. M. Williams and W. H. Hamill, *J. Chem. Phys.*, 49, 4467 (1968)) and $D(C_2H_5O\text{-}H) = 102$ kcal/mol (J. A. Kerr, *Chem. Rev.*, 66, 465 (1966)).

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Table V. Negative Ion-Molecule Reactions Observed in Arsine Mixtures

Mixture	Reaction	d*k*/d*E*[a]	Thermochemical inferences[b]
AsH_3-PH_3	$PH_2^- + AsH_3 \underset{\not\leftarrow}{\rightarrow} AsH_2^- + PH_3$	∓	$PA(AsH_2^-) \leqslant 369$[c]
	$C_2H_5O^- + AsH_3 \rightarrow AsH_2^- + C_2H_5OH$	–	$PA(AsH_2^-) \leqslant 376$[d]
	$C_2H_5O^- + H_2S \rightarrow HS^- + C_2H_5OH$	–	$PA(HS^-) \leqslant 376$[d]
AsH_3-H_2S-C_2H_5ONO (+C_2H_5OH)	$C_2H_3O^- + H_2S \rightarrow HS^- + C_2H_4O$	–	$PA(C_2H_3O^-) \geqslant 350$[e]
	$C_2H_5O^- + C_2H_5ONO \rightarrow NO_2^- + (C_2H_5)_2O$	–	
	$C_2H_5O^- + C_2H_5OH \rightarrow C_2H_3O^- + H_2 + C_2H_5OH$	–	
	$AsH_2^- + H_2S \underset{\not\leftarrow}{\rightarrow} HS^- + AsH_3$	∓	$PA(AsH_2^-) \geqslant 350$[e]

[a] Unless otherwise indicated, the reverse reaction was investigated by double-resonance experiments and found not to occur. [b] All values given in kcal/mol. [c] Reference 50. [d] Reference 51. [e] Reference 49.

value and eq 33, $D(H_2As\text{-}H)$ is calculated to be 79 kcal/mol.

$$PA(M^-) = D(M\text{-}H) + IP(H\cdot) - EA(M\cdot) \qquad (33)$$

This value, not unexpectedly, is somewhat higher than the average As-H bond energy in AsH_3 (71.2 kcal/mol).[53]

Table VI summarizes D(M-H), EA(M·), and PA(M⁻) for the first three group V hydrides. In proceeding from NH_3 to PH_3 to AsH_3, the gas-phase acidities are seen to increase monotonically while the bond dissociation energies decrease. However, the electron affinities of the radical species are not constant and do not follow any recognizable trend. Hence, both D(M-H) and EA(M·) appear to be important in establishing the trend in acidities observed for the group V hydrides.[6,11]

Table VI. Some Thermochemical Quantities Related to the Acidities of the Group V Hydrides[a]

MH	D(M-H)	EA(M·)	PA(M⁻)
NH_3	107[b]	17[b,e]	405[b]
PH_3	84[c]	29[f]	369[f]
AsH_3	79[d]	29[e]	360[g]

[a] All values are given in kcal/mol. [b] D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, *J. Chem. Phys.*, 59, 77 (1973). [c] T. McAllister and F. P. Lossing, *J. Phys. Chem.*, 73, 2996 (1969). [d] See text for discussion. The average bond energy is 71 kcal/mol.[53] [e] Reference 52. [f] Reference 50. [g] This work.

Registry No. AsH_3, 7784-42-1; PH_3, 7803-51-2; H_2S, 7783-06-4; CH_3CHCH_2, 115-07-1; CH_3OH, 67-56-1; CH_3Cl, 74-87-3; C_2H_5ONO, 109-95-5.

[53] The average As-H bond energy in AsH_3 (71.2 kcal/mol) was calculated employing $\Delta H_f(AsH_3)$ = 14.6 kcal/mol, $\Delta H_f(As)$ = 72.3 kcal/mol, and $\Delta H_f(H\cdot)$ = 52.1 kcal/mol (S. R. Gunn, *Inorg. Chem.*, 11, 796 (1972)).

Notes

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Preparation and Characterization of Vinyldifluorophosphine

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Recently there has been considerable interest in the basicity toward borane of certain phosphines.[1-3] Of particular interest is the report by Foester and Cohn[4] that PF_2CH_3 is a relatively strong base. Thus as one moves across the periodic chart ($PF_2CH_3 \rightarrow PF_2N(CH_3)_2 \rightarrow PF_2OCH_3 \rightarrow PF_3$), basicity decreases following electronegativity. Past arguments for the high basicity of $PF_2N(CH_3)_2$ were based on basicity enhancement of the phosphorus by the formation of a dative π bond between the nitrogen electron pair and the vacant orbitals of the phosphorus.[16] This effect would be absent in PF_2CH_3; therefore basicity parameters may require revision.

A comparison of the basicity of alkene- and alkynylphosphines to alkylphosphines could help clarify the role of π bonding and electronegativity in phosphorus basicity. Toward this goal we wish to report the preparation and characterization of vinyldifluorophosphine and its borane adduct.

Experimental Section

General Techniques. All volatile materials were handled in high-vacuum manifolds with interconnecting U traps.[5] Infrared spectra were measured on a Perkin-Elmer 137 NaCl spectrophotometer and on a Perkin-Elmer 421 grating spectrophotometer using a 10-cm gas cell with KBr windows. Mass spectra were obtained on a Varian M66 (70 eV), while ^{19}F nmr spectra were traced on a Varian T-60 operating at 56.4 MHz and on a Varian Associates HR-100 nmr spectrometer operating at 94.1 MHz. ^{11}B nmr spectra were recorded on a Varian XL-100 operating at 32.1 MHz. Proton nmr spectra were determined with a Jeol MN-100 operating at 100 MHz. Internal TMS and external $CFCl_3$ and $B(C_2H_5)_3$ served as references for ^1H, ^{19}F, and ^{11}B spectra, respectively, unless noted otherwise.

Material. Commercial B_2H_6 (Callery), HBr (Matheson), ZnF_2 (Ozark-Mahoning), $P(OCH_2CH{=}CH_2)_3$ (City Chemical Corp.), and $(CH_2{=}CH)_2Hg$ (Orgmet, Inc.) were used without further purification. PF_2Br[6] was prepared by literature methods.

Synthesis of $PF_2CH{=}CH_2$. A 15.5-mmol sample of PF_2Br was condensed at −196° on 20.0 mmol (~2.55 g) of $(CH_2{=}CH)_2Hg$ in a 500-cm³ reaction vessel with a removable tube. The mixture was warmed to room temperature where the formation of yellow-white solids indicated immediate reaction. The reaction vessel was shaken for 8 hr and then allowed to sit at ambient temperature for 12 hr. The volatile contents of the bulb were led through traps at −105, −135, and 196°. The −105° trap held an unidentified liquid (possibly excess $(CH_2{=}CH)_2Hg$), while the −196° trap contained 6.52 mmol of PF_3, identified by ir. The −135° trap contained 4.7 mmol of $PF_2CH{=}CH_2$ for a yield based on consumed PF_2Br of 27%.

Care must be taken to avoid using excess PF_2Br as the separation of $PF_2CH{=}CH_2$ and PF_2Br is extremely difficult. Under the reac-

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