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

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Master of Science

California Institute of Technology
Pasadena, California

1971

(Submitted May 28, 1971)

Acknowledgments

Financial support from a National Science Foundation Fellowship and a Graduate Teaching Assistantship is gratefully acknowledged.

It is with pleasure that I acknowledge the guidance and support of my teacher and research advisor, Professor Jesse L. Beauchamp.

A special appreciation is expressed to Dr. David Holtz who helped with the experimental work, and who provided endless encouragement and inspiration.

Thanks are due to Mr. Terry McMahon for use of his computer program for calculating reaction rate constants, and for helpful discussions, along with Messrs. Peter Miasek, Doug Ridge, and John Weigel.

Finally, I express a sincere thankyou to Miss Sharon Vedrode for an excellent job of typing the thesis.

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Abstract

The ion-molecule reactions of arsine, both pure 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 the ion-molecule reactions for both positive and, to a lesser extent, negative ions. Arsine fragment ions condense with neutral 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 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, $PA(AsH_2^-) = 356 \pm 6$ kcal/mole, and basicity, $PA(AsH_3) = 175 \pm 5$ kcal/mole, 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 of the gas phase ion chemistry of the group V hydrides to include arsine. To accomplish these objectives, the gas phase ion-molecule reactions of AsH_3, alone and in mixtures with other molecules have been investigated. Where possible, kinetic and thermochemical data have been determined, including the basicity of AsH_3 toward both a hard acid (proton) and a soft acid (methyl cation), as well as the gas phase acidity of arsine. Of particular interest is the observation of periodic trends in thermochemical properties noted for other hydrides (1, 2), and the observation of additional examples of the recently reported ionic nucleophilic displacement reaction (3).

Experimental

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail (4-10). 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. Spectral intensities used to derive rate constant and product distribution data have been normalized by dividing by the square of ion mass. Relative rate constants and product distributions for reactions observed in arsine were determined by the variation of electron energy method described previously (1). 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 (11).

Arsine was generated *in vacuo* by transferring concentrated hydrochloric acid onto excess zinc arsenide, Zn_3As_2 (12). Purification was achieved by transferring the evolved gas into a KOH solution followed by bulb-to-bulb fractionation at -80°. Mass spectrometric examination at 70 eV showed the arsine to contain less than 0.1% impurities and in particular no HCl or diarsine. Phosphine was generated similarly by transferring water onto excess magnesium aluminum phosphide, $Mg_3P_2\cdot 2AlP$ (12). Purification was achieved by bulb-to-bulb fractionation at -80°. Mass spectrometric examination at 70 eV showed the phosphine to contain less than 0.1% impurities and in particular no water or diphosphine. 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

Reactions in Arsine

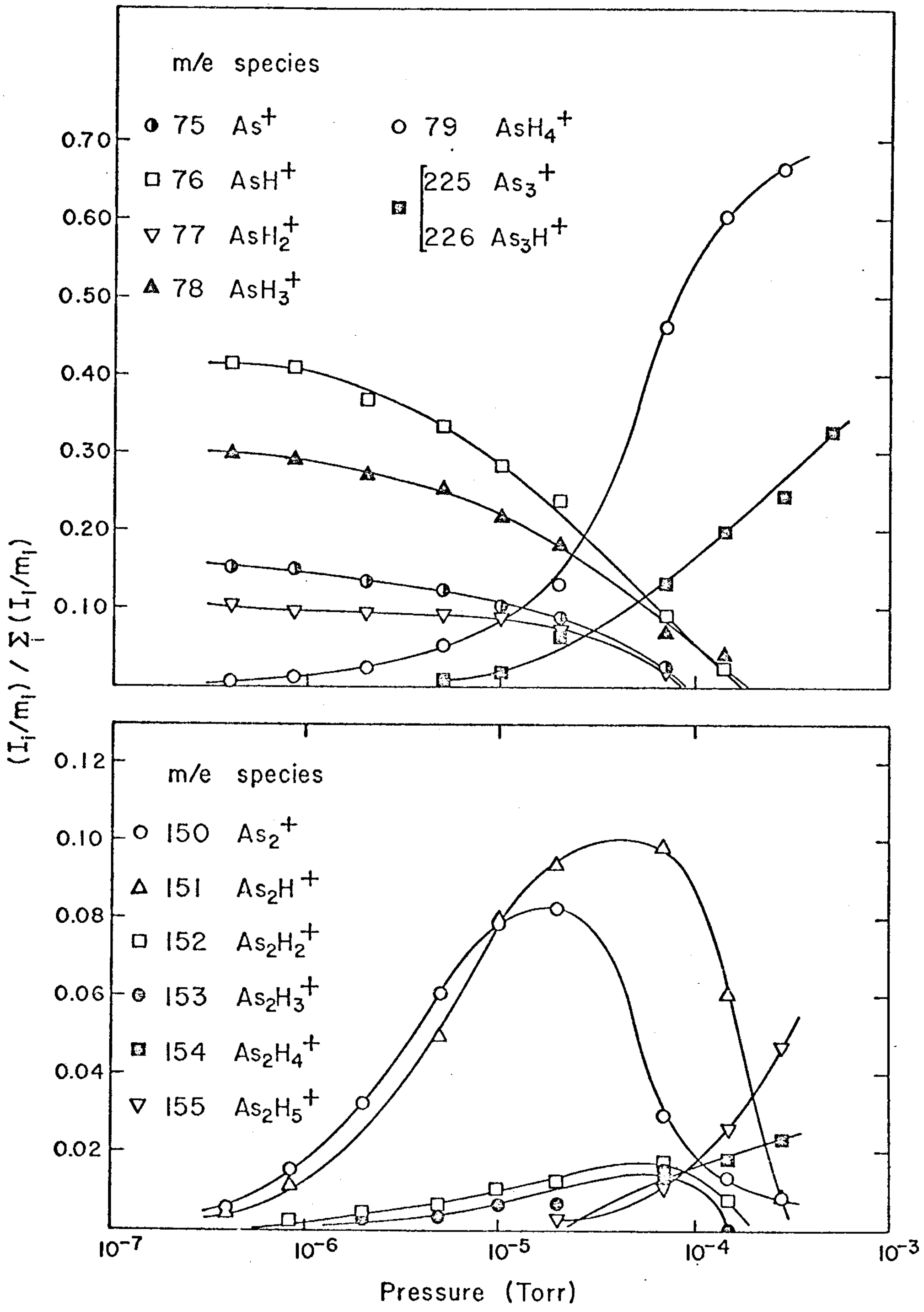
Electron impact (70 eV) on AsH_3 at low pressure (10^{-6} torr) yields a single resonance spectrum with ion intensities of $AsH_3\cdot^+$ (30%); AsH_2^+ (11%); $AsH\cdot^+$ (42%); and As^+ (16%) in agreement with the known mass spectrum of arsine (13). As the AsH_3 pressure is raised, ion-molecule reactions occur to form AsH_4^+ in addition to condensation products containing two ($As_2\cdot^+$, As_2H^+, $As_2H_2\cdot^+$, and $As_2H_3^+$) and three (As_3^+ and $As_3H\cdot^+$) 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) (14), and (2) the icr technique of double resonance (15). 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 (1). 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

$$AsH_3\cdot^+ + AsH_3 \rightarrow AsH_4^+ + AsH_2\cdot \qquad (1)$$

Figure 1 Variation of ion single-resonance intensities with pressure for AsH_3 at 70 eV; (top) major ions, (bottom) minor ions. The intensities of the tertiary ions, As_3^+ and As_3H^+ are summed.

4b


m/e species
◑ 75 As^+
□ 76 AsH^+
▽ 77 AsH_2^+
▲ 78 AsH_3^+
○ 79 AsH_4^+
▣ 225 As_3^+
226 As_3H^+
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.12
0.10
0.08
0.06
0.04
0.02
m/e species
○ 150 As_2^+
△ 151 As_2H^+
□ 152 $As_2H_2^+$
⊙ 153 $As_2H_3^+$
▣ 154 $As_2H_4^+$
▽ 155 $As_2H_5^+$
$(I_i/m_i) / \sum_i (I_i/m_i)$
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
Pressure (Torr)

fragment ion $\mathrm{AsH}^{\cdot+}$ appears. With increasing $\mathrm{AsH_3}$ pressure, this ion leads to the formation of the product ions $\mathrm{As_2}^{\cdot+}$ and $\mathrm{As_2H_2}^{\cdot+}$, indicating reactions 2 and 3. At 14 eV, the fragment ion $\mathrm{AsH_2}^{+}$

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

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

appears. With increasing $\mathrm{AsH_3}$ pressure, this ion leads to the production of $\mathrm{As_2H}^{+}$ and $\mathrm{As_2H_3}^{+}$, indicating reactions 4 and 5.

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

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

Finally at 15 eV, As^{+} appears and, with increasing $\mathrm{AsH_3}$ pressure, leads to an increase in the $\mathrm{As_2H}^{+}$ intensity relative to the intensity of the other condensation products, identifying reaction 6.

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

Due to line broadening and poor resolution, it was not possible to experimentally determine the precursor ions to the formation of the tertiary product ions $\mathrm{As_3}^{+}$ and $\mathrm{As_3H}^{\cdot+}$. Reactions 7 and 8, involving the prominent secondary ions, most likely account for the generation of these species, however.

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

Reaction[a]	ΔH[b]	Prod. Distr.[c]	k_i[d]	$\sum_i k_i$[d]
$As^+ + AsH_3 \rightarrow As_2H^+ + H_2$	-33	1.00	3.2	3.2
$AsH\cdot^+ + AsH_3 \rightarrow As_2\cdot^+ + 2H_2$	+24	0.91	2.5	2.7
$\rightarrow As_2H_2\cdot^+ + H_2$	+17	0.09	0.2	
$AsH_2^+ + AsH_3 \rightarrow As_2H^+ + 2H_2$	-32	0.91	4.2	4.6
$\rightarrow As_2H_3^+ + H_2$	-37	0.09	0.4	
$AsH_3\cdot^+ + AsH_3 \rightarrow AsH_4^+ + AsH_2\cdot$	-21	1.00	5.6	5.6

[a] All reactions listed gave a negative double resonance response, indicating $dk/dE < 0$.

[b] Values in kcal/mole. 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 Potentials, and Heats of Formation of Gaseous Positive Ions," NSRFS-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 $\times 10^{-10}$ cm^3 $molecule^{-1}$ sec^{-1}.

$$As_2^{\cdot +} + AsH_3 \rightarrow As_3H^{\cdot +} + H_2 \qquad (7)$$

$$As_2H^+ + AsH_3 \rightarrow As_3^+ + 2H_2 \qquad (8)$$

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

$$AsH_n^+ + AsH_3 \rightarrow AsH_3^{\cdot +} + AsH_n \qquad (9)$$

$$n = 0,\ 1,\ 2$$

in the ratio of AsH_4^+ to $AsH_3^{\cdot +}$ with increasing electron energy.

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 2. 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

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

concluded that the proton affinity (PA) of phosphine is greater than that of arsine.

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 2 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

Figure 2 Variation of ion single-resonance intensities for a 1.6:1 mixture of AsH_3 and PH_3 at 11 eV.

10b

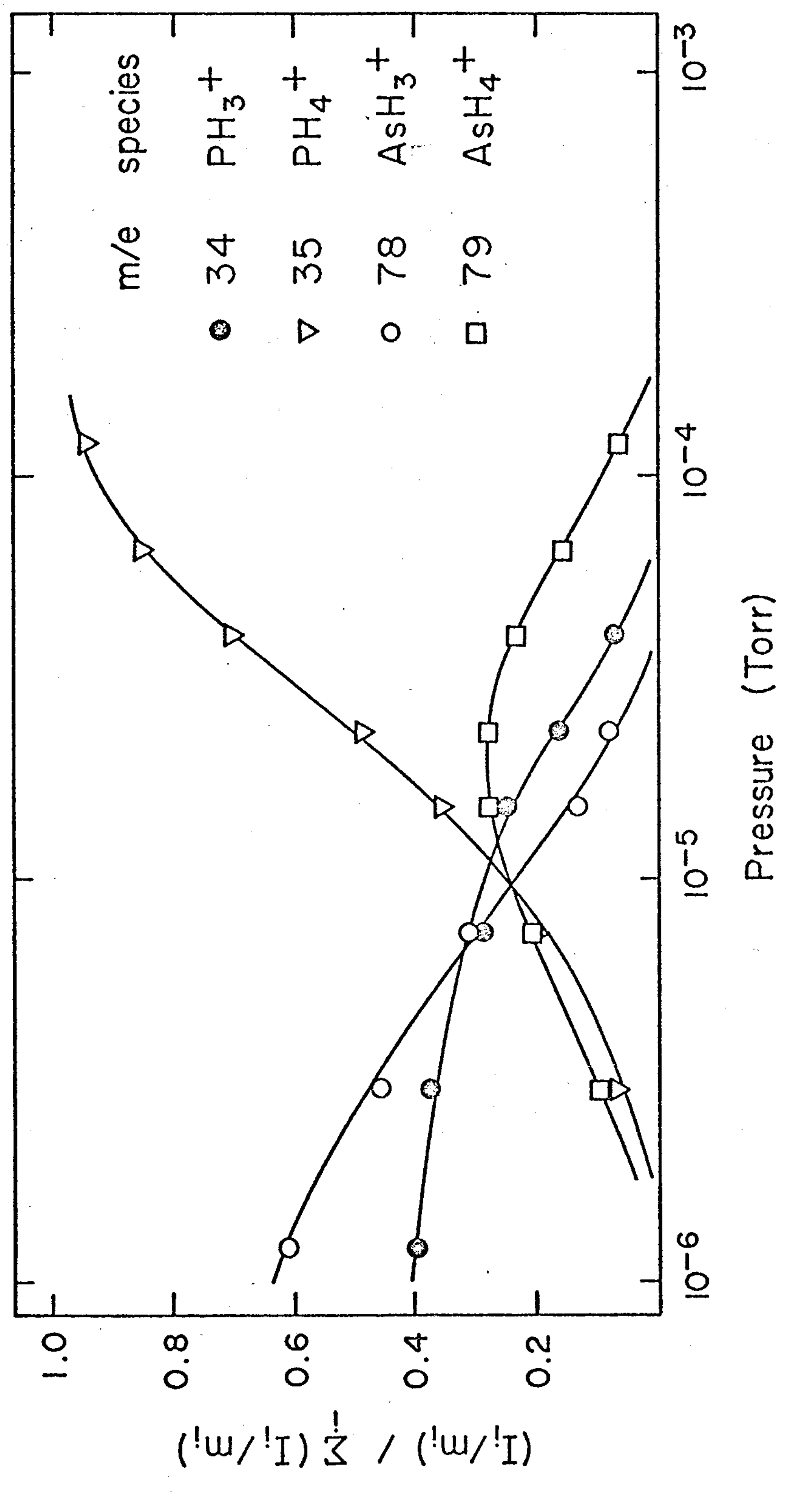

$(I_i/m_i) \, / \, \sum_i (I_i/m_i)$
1.0
0.8
0.6
0.4
0.2
10^{-6}
10^{-5}
10^{-4}
10^{-3}
Pressure (Torr)
m/e species
● 34 PH_3^+
▽ 35 PH_4^+
○ 78 AsH_3^+
□ 79 AsH_4^+

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

Reaction	$\frac{dk}{dE}$[a]	Thermochemical Inferences[b]
$AsH_4^+ + PH_3 \rightarrow PH_4^+ + AsH_3$	–	$PA(AsH_3) \leqslant 185$[c]
$H_3S^+ + AsH_3 \rightarrow AsH_4^+ + H_2S$	–	$PA(AsH_3) \geqslant 170$[d]
$AsH_4^+ + C_3H_6$[h] $\rightarrow C_3H_7^+ + AsH_3$	–	$PA(AsH_3) \leqslant 179$[e]
$CH_3ClH^+ + AsH_3 \rightarrow AsH_4^+ + CH_3Cl$	–	$PA(AsH_3) \geqslant 160$[f]
$CH_3ClH^+ + CH_3Cl \rightarrow (CH_3)_2Cl^+ + HCl$	–	$MCA(CH_3Cl) \geqslant MCA(HCl)$
$AsH_4^+ + CH_3OH \rightarrow CH_3OH_2^+ + AsH_3$	–	$PA(AsH_3) \leqslant 181$[g]
$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O$	–	$MCA(CH_3OH) \geqslant MCA(H_2O)$
$CH_3OH_2^+ + AsH_3 \rightarrow CH_3AsH_3^+ + H_2O$	–	$MCA(AsH_3) \geqslant MCA(H_2O)$

[a] The reverse reaction was investigated in each case and was found not to occur.

[b] Values given in kcal/mole.

[c] Reference 41.

[d] Reference 37.

Table II Continued.

[e] Reference 38.

[f] Reference 18.

[g] References 39 and 40.

[h] $CH_3CH=CH_2$.

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), suggest the occurrence of reaction 12. Double resonance experiments confirm this reaction in the direction shown. Hence PA($CH_3CH{=}CH_2$) $\geqslant$ PA(AsH_3).

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

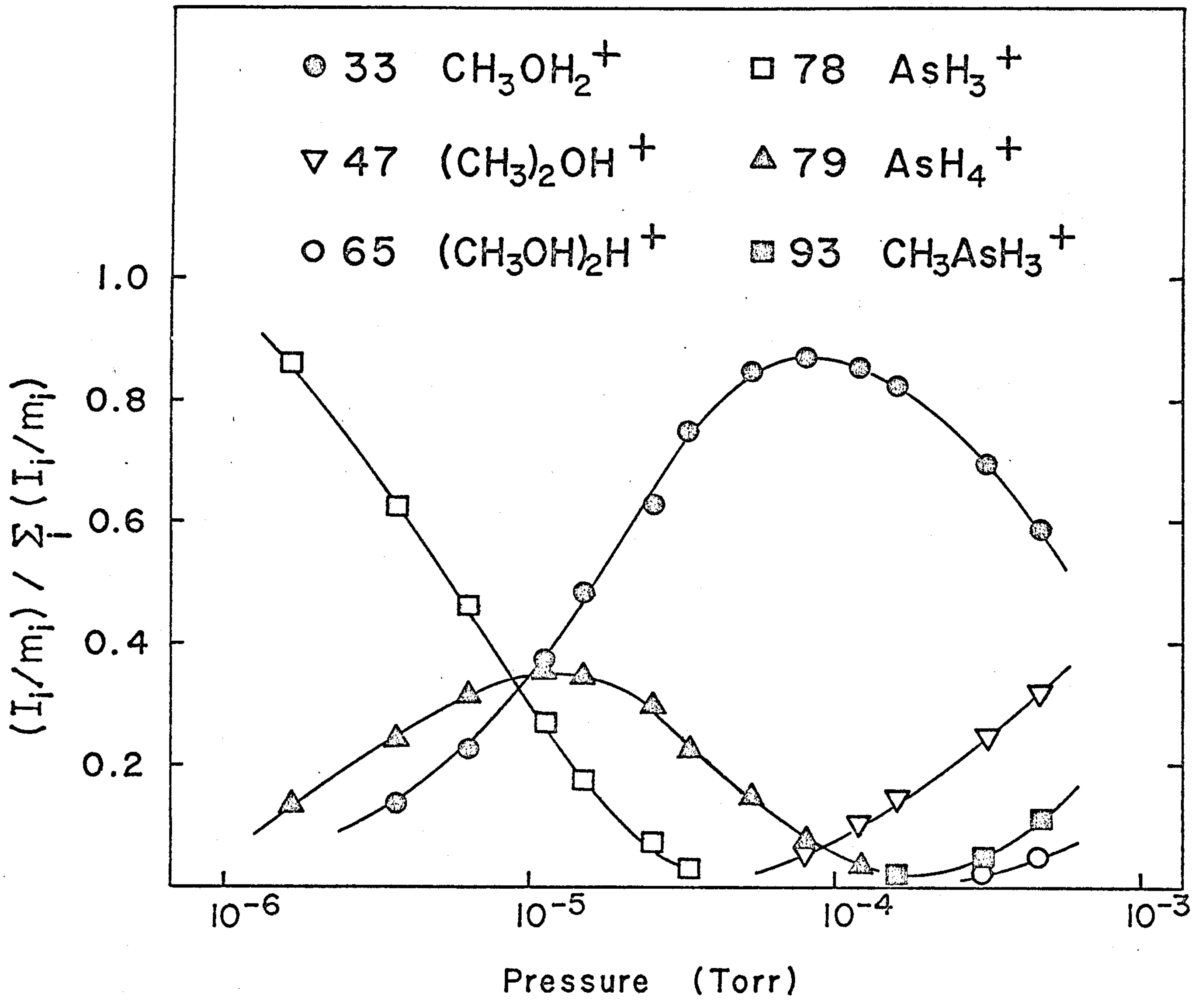
Arsine and Methanol

The variation of single resonance intensities with pressure, illustrated in Figure 3, 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

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

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

Figure 3 Variation of single-resonance intensities with pressure for a 3:1 mixture of AsH_3 and CH_3OH at 11 eV.


● 33 $CH_3OH_2^+$
▽ 47 $(CH_3)_2OH^+$
○ 65 $(CH_3OH)_2H^+$
□ 78 AsH_3^+
▲ 79 AsH_4^+
■ 93 $CH_3AsH_3^+$
1.0
0.8
0.6
0.4
0.2
$(I_i/m_i) / \sum_i (I_i/m_i)$
10^{-6}
10^{-5}
10^{-4}
10^{-3}
Pressure (Torr)

The formation of ions at m/e values corresponding to protonated dimethyl ether and protonated methyl arsine 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 (16)

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2OH^+ + H_2O \tag{14}$$

$$CH_3OH_2^+ + AsH_3 \rightarrow CH_3AsH_3^+ + H_2O \tag{15}$$

and more recently Henis (17) have reported the 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 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 confirm to proceed as shown. Hence we conclude that $PA(AsH_3) \geqslant PA(CH_3Cl)$.

$$CH_3ClH^+ + AsH_3 \rightarrow AsH_4^+ + CH_3Cl \tag{16}$$

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 dimethyl chloronium ion (18). Significantly, the analogous displacement reaction with AsH_3, reaction 18, is not observed.

$$CH_3ClH^+ + CH_3Cl \rightarrow (CH_3)_2Cl^+ + HCl \tag{17}$$

$$CH_3ClH^+ + AsH_3 \not\rightarrow CH_3AsH_3^+ + HCl \tag{18}$$

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. Line

$$As^- + AsH_3 \rightarrow As_2H^- + H_2 \tag{19}$$

broadening prevented further identification of these secondary ions and their precursors.

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, $C_2H_5O^-$. (19-21) 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 4 is the variation of single resonance

$$C_2H_5O^- + AsH_3 \rightarrow AsH_2^- + C_2H_5OH \tag{20}$$

$$C_2H_5O^- + H_2S \rightarrow HS^- + C_2H_5OH \tag{21}$$

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, 21 and 22 proceed as written and lead to the

$$AsH_2^- + H_2S \rightarrow HS^- + AsH_3 \tag{22}$$

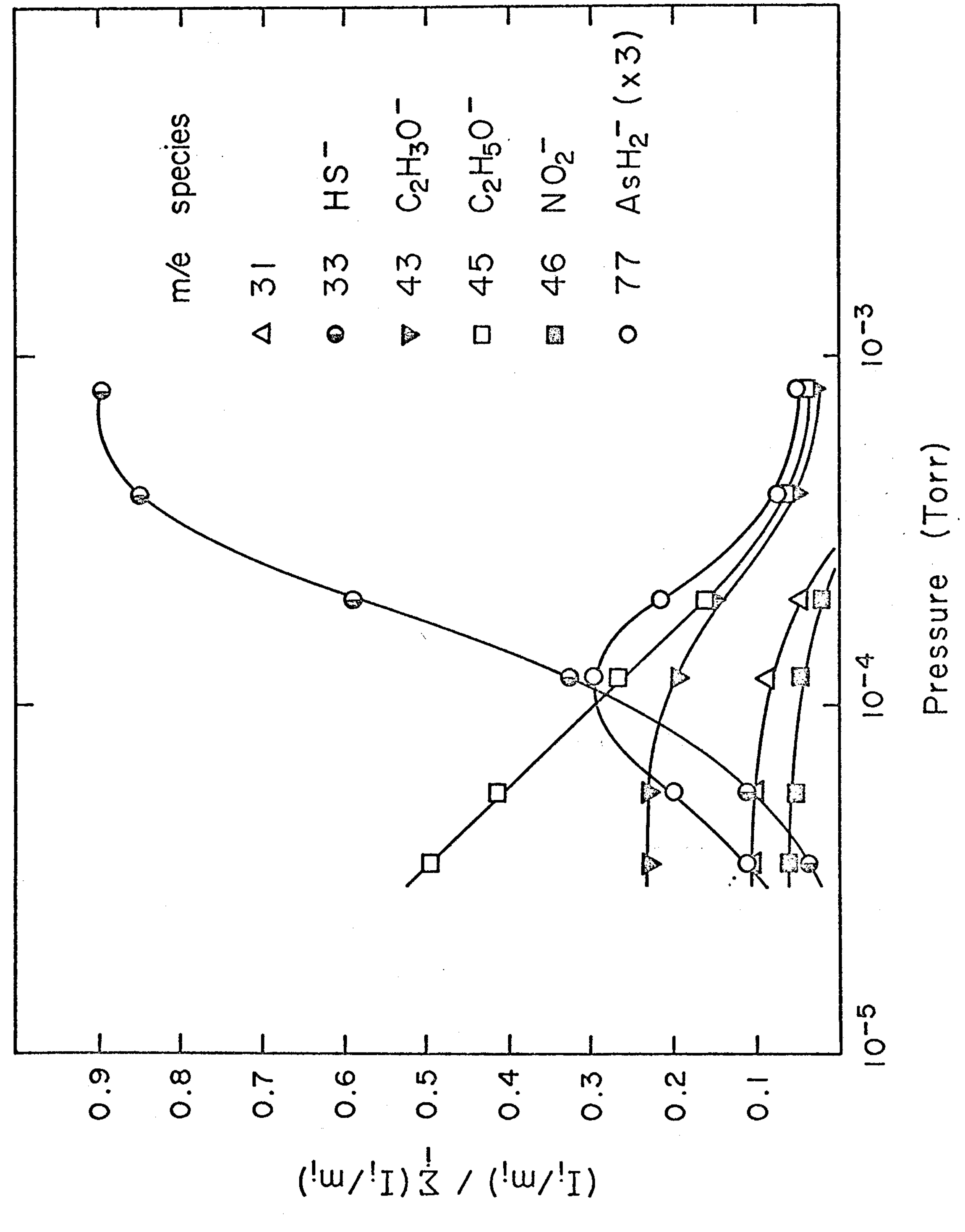
conclusion that $PA(C_2H_5O^-) \geqslant PA(AsH_2^-) \geqslant PA(HS^-)$.

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 to the displacement

$$C_2H_5O^- + C_2H_5ONO \rightarrow NO_2^- + (C_2H_5)_2O \tag{23}$$

$$C_2H_5O^- + C_2H_5OH \rightarrow C_2H_3O^- + H_2 + C_2H_5OH \tag{24}$$

Figure 4 Variation of single-resonance intensities with pressure for a 1:2 mixture of AsH_3 and H_2S at a fixed pressure (2×10^{-5} torr) of C_2H_5ONO and at 25 eV.


$(I_i/m_i) / \sum_i (I_i/m_i)$
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10^{-5}
10^{-4}
10^{-3}
Pressure (Torr)
m/e species
△ 31
● 33 HS^-
▼ 43 $C_2H_3O^-$
□ 45 $C_2H_5O^-$
■ 46 NO_2^-
○ 77 AsH_2^- (x3)

of NO_3^- from ethyl nitrate by $C_2H_5O^-$ observed by Buttrill and Kriemler (22). That C_2H_5OH is the neutral reactant in reaction 24 is strengthened by the observation of the same process in ethanol alone (23). 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

$$PH_2^- + AsH_3 \rightarrow AsH_2^- + PH_3 \tag{25}$$

the 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 (1). 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 (1), 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 (1). Fragment ions of NH_3 react with the neutral to generate $NH_3\cdot^+$ and NH_4^+ by charge exchange and proton transfer processes (24-29). Ionic condensation reactions are not prevalent.

The observed trends in reactivity of the group V hydrides can be attributed in part to the relative order of bond strengths, $D(N{-}H) \sim D(H{-}H) \gg D(P{-}H) > D(As{-}H)$. Condensation reactions which involve the expulsion of H_2 become increasingly favorable on an energetic basis in proceeding from ammonia to phosphine to arsine. Thus it is not surprising that arsine, which forms the weakest bond to hydrogen, participates in condensation reactions which involve loss of molecular hydrogen. An identical trend in reactivity, which can be similarly explained, is observed for the group VI hydrides H_2O, H_2S, and H_2Se (30-33, 2).

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. Since gas phase ion-molecule reactions are assumed to proceed with negligible activation energy (14, 34-36), the observation of a process such as reaction 26 is usually interpreted as indicating

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

that $PA(M_2) > PA(M_1)$. Thus from reactions 10-13, 16 reported above, which indicate $PA(CH_3Cl)$, $PA(H_2S) \leqslant PA(AsH_3) \leqslant PA(CH_3CH{=}CH_2)$, $PA(CH_3OH)$, $PA(PH_3)$, and the known values $PA(CH_3Cl) = 160$ kcal/mole (18), $PA(H_2S) = 170$ kcal/mole (37), $PA(CH_3CH{=}CH_2) = 179$ kcal/mole (38), $PA(CH_3OH) = 181$ kcal/mole (39, 40), and $PA(PH_3) = 185$ kcal/mole (39, 41), an estimate of $PA(AsH_3) = 175 \pm 5$ kcal/mole is derived, corresponding to $\Delta H_f(AsH_4^+) = 207 \pm 5$ kcal/mole.

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

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

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

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/mole.

[b] Calculated from equation 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).

[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.

the increase of 20-30 kcal/mole has been noted previously in other systems (41). 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 a parallel decrease in the proton and hydrogen affinities of the group V hydrides upon proceeding down the group in the periodic table.

Nucleophilic Displacement Reactions

We have recently shown that the nucleophilic displacement reaction generalized in reaction 28 occurs provided two criteria are met: (1) the reaction is exothermic or thermoneutral; and

$$YH_n + CH_3XH_m^+ \rightarrow CH_3Y_n^+ + XH_m \qquad (28)$$

(2) proton transfer from the substrate to the nucleophile is endothermic, i.e., $PA(CH_3XH_{m-1}) \geq PA(YH_n)$ (3). Reaction processes observed in mixtures of AsH_3 with CH_3OH and CH_3Cl serve to illustrate these principles.

As noted above, protonated methyl arsine, $CH_3AsH_3^+$, is formed via reaction 15 as AsH_3 reacts with $CH_3OH_2^+$ to displace

Table IV. Thermochemical Properties of the Group V Hydrides[a]

MH	IP(MH)[b]	PA(MH)	HA(MH^+)[f]	D(M—H)
NH_3	10.15	207[c]	128	109[g]
PH_3	9.98	185[d]	102	84[h]
AsH_3	10.03	175[e]	92	72[i]

[a] Except for ionization potentials, all values are given in kcal/mole.

[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 39.

[d] Reference 41.

[e] This work.

[f] Calculated from equation 27.

[g] S. W. Benson and H. E. O'Neil, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRFS-NBS 21, U. S. Government Printing Office, Washington, D.C., 1970, p. 35.

[h] T. McAllister and F. P. Lossing, J. Phys. Chem., **73**, 2996 (1969).

[i] Calculated in the text.

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/mole (42). 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 (3). 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

$$M + CH_3^+ \rightarrow MCH_3^+; \quad MCA(M) = -\Delta H \qquad (29)$$

data indicate that the following will be the order in which nucleophilic displacements occur (3) (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/mole (3).

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 (43). The threshold energy determined for this

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

Mixture	Reaction	$\frac{dk}{dE}$[a]	Thermochemical[b] Inference
$AsH_3—PH_3$	$PH_2 + AsH_3 \overset{\rightarrow}{\not\leftrightarrow} AsH_2^- + PH_3$	$\mp$	$PA(AsH_2^-) \leqslant 362^c$
	$C_2H_5O^- + AsH_3 \rightarrow AsH_2^- + C_2H_5OH$	-	$PA(AsH_2^-) \leqslant 376^d$
	$C_2H_5O^- + H_2S \rightarrow HS^- + C_2H_5OH$	-	$PA(HS^-) \leqslant PA(C_2H_5O^-)$
$AsH_3—H_2S$ $- C_2H_5ONO$ $(+ C_2H_5OH)$	$C_2H_3O^- + H_2S \rightarrow HS^- + C_2H_4O$	-	$PA(C_2H_3O^-) \geqslant 350^e$
	$C_2H_5O^- + C_2H_5ONO \rightarrow NO_2^- + (C_2H_5)_2O$	-	
	$C_2H_5O^- + C_2H_5OH \rightarrow C_2H_3O^- + H_2 + C_2H_5OH$	-	
	$AsH_2^- + H_2S \overset{\rightarrow}{\not\leftrightarrow} HS^- + AsH_3$	$\mp$	$PA(AsH_2^-) \geqslant 350^e$

[a] Unless otherwise indicated, the reverse reaction was investigated by double resonance experiments and found not to occur.

[b] All values given in kcal/mole.

Table V Continued.

[c] Reference 41.

[d] Reference 45.

[e] Reference 44.

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

process, $E_t = 2.0 \pm 0.1$ eV (43), can be employed to estimate the proton affinity of AsH_2^- through the thermochemical cycle of equation 31. Using IP(H•) = 313 kcal/mole and equation 31,

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

$PA(AsH_2^-)$, the gas phase acidity of arsine, is estimated to be 359 ± 3 kcal/mole. 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/mole (44), $PA(PH_2^-) = 362$ kcal/mole (1), and $PA(C_2H_5O^-) = 376$ kcal/mole (45), the value 356 ± 6 kcal/mole may be assigned to $PA(AsH_2^-)$, consistent with the value derived from equation 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•), as shown in the thermochemical cycle 32. Brauman and Eyler have recently determined $EA(AsH_2\cdot)$ to be 29 kcal/mole from photodetachment studies (46, 47). Using this value and equation 33, $D(H_2As{-}H)$ is calculated to be 72 kcal/mole. This value, not unexpectedly, is slightly higher than the average As—H bond energy in AsH_3 (70.9 kcal/mole) (48).

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

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

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.

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	109[b]	17[d]	405[c]
PH_3	84[b]	35[e]	362[e]
AsH_3	72[c]	29[d]	356[f]

[a] All values are given in kcal/mole.

[b] See Table IV.

[c] Calculated from equation 33 employing IP(H·) = 313 kcal/mole.

[d] Reference 46.

[e] Reference 1.

[f] This work.

References

(1) David Holtz, J. L. Beauchamp, and J. R. Eyler, J. Amer. Chem. Soc., **92**, 7045 (1970).

(2) D. Dixon, D. Holtz, and J. L. Beauchamp, Inorg. Chem., submitted for publication.

(3) David Holtz, J. L. Beauchamp, Shelia D. Woodgate, J. Amer. Chem. Soc., **92**, 7484 (1970).

(4) J. D. Baldeschwieler, Science, **159**, 263 (1968).

(5) J. L. Beauchamp and R. C. Dunbar, J. Amer. Chem. Soc., **92**, 1477 (1970).

(6) S. E. Buttrill, Jr., J. Chem. Phys., **50**, 4125 (1969).

(7) J. L. Beauchamp and S. E. Buttrill, ibid., **48**, 1783 (1968).

(8) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, J. Amer. Chem. Soc., **89**, 4569 (1967).

(9) J. L. Beauchamp and D. P. Ridge, J. Chem. Phys., submitted for publication.

(10) J. L. Beauchamp, Thesis, Harvard University, 1968.

(11) A. G. Marshall and S. E. Buttrill, J. Chem. Phys., **52**, 2752 (1970).

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

(13) A. Cornu and R. Massot, Compilation of Mass Spectral Data, Heyden and Son Limited, London (1966).

(14) J. L. Franklin, J. Chem. Educ., **40**, 288 (1963).

(15) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, J. Chem. Phys., **45**, 1062 (1966).

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

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

(18) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, J. Amer. Chem. Soc., submitted for publication.

(19) T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instr., in press.

(20) K. Jaeger and A. Henglein, Z. Naturforsch., A, **22**, 700 (1967), report a large cross section for the formation of $C_2H_5O^-$ from C_2H_5ONO. We thank Dr. M. A. Haney for suggesting the procedure which greatly enhanced the negative ion intensities of HS^- and AsH_2^- over that obtainable by electron impact on H_2S and AsH_3.

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

(22) Peter Kriemler and S. E. Buttrill, Jr., J. Amer. Chem. Soc., **92**, 1123 (1970).

(23) J. L. Beauchamp, unpublished results.

(24) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, J. Chem. Phys., **39**, 1599 (1963).

(25) C. E. Melton, ibid., **45**, 4414 (1966).

(26) A. G. Harrison and J. C. J. Thynne, Trans. Faraday Soc., **62**, 2804 (1966).

(27) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, Can. J. Chem., **45**, 3107 (1967).

(28) K. R. Ryan, J. Chem. Phys., **53**, 3844 (1970).

(29) R. A. Fluegge and D. A. Landman, *ibid.*, **54**, 1576 (1971).

(30) A. G. Harrison, J. C. J. Thynne, *Trans. Faraday Soc.*, **62**, 2468 (1966).

(31) K. R. Ryan, *J. Chem. Phys.*, **52**, 6009 (1970).

(32) W. E. W. Ruska and J. L. Franklin, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 221 (1969).

(33) W. T. Huntress, unpublished work.

(34) A. Cassuto, *Advan. Mass Spectrom.*, **2**, 296 (1963).

(35) V. L. Tal'roze, *Pure Appl. Chem.*, **5**, 455 (1962).

(36) F. W. Lampe, J. L. Franklin, and F. K. Field, *Progr. React. Kinet.*, **1**, 67 (1961).

(37) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969).

(38) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

(39) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).

(40) J. L. Beauchamp, unpublished results.

(41) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

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

(43) Von H. Ebinghaus, K. Kraus, W. Müller-Duysing, and H. Neuert, *Z. Naturforsch.*, A, **19**, 732 (1964).

(44) Calculated from equation 32 employing EA(HS•) = 53 kcal/mole, R. S. Berry, Chem. Rev., **69**, 533 (1969); and D(HS—H) = 90 kcal/mole, J. A. Kerr, Chem. Rev., **66**, 465 (1966).

(45) Calculated from equation 32 employing EA($C_2H_5O\cdot$) = 39 kcal/mole, J. M. Williams and W. H. Hamill, J. Chem. Phys. **49**, 4467 (1968); and D(C_2H_5O—H) = 102 kcal/mole, J. A. Kerr, Chem. Rev., **66**, 465 (1966).

(46) J. J. Brauman and J. R. Eyler, ACS National Meeting, 1971.

(47) J. J. Brauman and K. C. Smyth, J. Amer. Chem. Soc., **91**, 7778 (1969).

(48) The average As—H bond energy in AsH_3 was calculated employing ΔH_f (AsH_3) = 15.9 kcal/mole, ΔH_f (As) = 72.3 kcal/mole, and $\Delta H_f(H\cdot)$ = 52.1 kcal/mole. Thermochemical data were taken from footnote 6 in Table I.