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

Thesis by

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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 AsH₃ to generate product ions containing two and, on further reaction, three atoms of arsenic. In the process of condensation, one or two molecules of H₂ are expelled. The formation of AsH₄⁺ occurs from AsH₃⁺⁺ which does not undergo condensation reactions to any significant extent. Where possible, thermochemical data have been determined, including the gas phase acidity, PA(AsH₂⁻) = 356 ± 6 kcal/mole, and basicity, PA(AsH₃) = 175 ± 5 kcal/mole, of AsH₃. Observation of gas phase nucleophilic displacement reactions involving AsH₃ as a nucleophile have allowed limits to be placed on the basicity of AsH₃ toward a soft acid, CH₃⁺. The implications of these results are discussed and the ion-molecule reactions of AsH₃ 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 $\text{AsH}_3$, alone and in mixtures with other molecules have been investigated. Where possible, kinetic and thermochemical data have been determined, including the basicity of $\text{AsH}_3$ 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$_3$·$^+$ 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$_3$As$_2$ (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$_3$P$_2$·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 diphosphate. 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$_3$·$^+$ (30%); AsH$_2$·$^+$ (11%); AsH·$^+$ (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$_2$·$^+$, As$_2$H$^+$, As$_2$H$_2$·$^+$, and As$_2$H$_3$·$^+$) and three (As$_3^+$ and As$_3$H·$^+$) arsenic atoms. At the highest pressures employed ($10^{-3}$ torr), the ions remaining are AsH$_4^+$, As$_3^+$, and As$_3$H·$^+$. 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$_3$·$^+$ 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

$$\text{AsH}_3\cdot^+ + \text{AsH}_3 \rightarrow \text{AsH}_4^+ + \text{AsH}_2^\cdot$$

(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$_3$H$^+$ are summed.
fragment ion \( \text{AsH}^{+} \) appears. With increasing \( \text{AsH}_3 \) pressure, this ion leads to the formation of the product ions \( \text{As}_2^{+} \) and \( \text{As}_2\text{H}_2^{+} \), indicating reactions 2 and 3. At 14 eV, the fragment ion \( \text{AsH}_2^{+} \)

\[
\text{AsH}^{+} + \text{AsH}_3 \rightarrow \begin{cases} 
91\% & \rightarrow \text{As}_2^{+} + 2\text{H}_2 \\
9\% & \rightarrow \text{As}_2\text{H}_2^{+} + \text{H}_2
\end{cases}
\]

appears. With increasing \( \text{AsH}_3 \) pressure, this ion leads to the production of \( \text{As}_2\text{H}^{+} \) and \( \text{As}_2\text{H}_3^{+} \), indicating reactions 4 and 5.

\[
\text{AsH}_2^{+} + \text{AsH}_3 \rightarrow \begin{cases} 
91\% & \rightarrow \text{As}_2\text{H}^{+} + 2\text{H}_2 \\
9\% & \rightarrow \text{As}_2\text{H}_3^{+} + \text{H}_2
\end{cases}
\]

Finally at 15 eV, \( \text{As}^{+} \) appears and, with increasing \( \text{AsH}_3 \) pressure, leads to an increase in the \( \text{As}_2\text{H}^{+} \) intensity relative to the intensity of the other condensation products, identifying reaction 6.

\[
\text{As}^{+} + \text{AsH}_3 \rightarrow \text{As}_2\text{H}^{+} + \text{H}_2
\]

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 \( \text{As}_3^{+} \) and \( \text{As}_3\text{H}^{+} \). 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

<table>
<thead>
<tr>
<th>Reaction $^a$</th>
<th>$\Delta H^b$</th>
<th>Prod. Distr.$^c$</th>
<th>$k_i^d$</th>
<th>$\sum_i k_i^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$^+$ + AsH$_3$ $\rightarrow$ As$_2$H$^+$ + H$_2$</td>
<td>-33</td>
<td>1.00</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$</td>
<td>As$_2$H$^+$ + 2H$_2$</td>
<td>+24</td>
<td>0.91</td>
</tr>
<tr>
<td>$\rightarrow$ As$_2$H$_2$ + H$_2$</td>
<td>+17</td>
<td>0.09</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>AsH$_2^+$ + AsH$_3$</td>
<td>$\rightarrow$</td>
<td>As$_2$H$^+$ + 2H$_2$</td>
<td>-32</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$</td>
<td>As$_2$H$_3$ + H$_2$</td>
<td>-37</td>
<td>0.09</td>
</tr>
<tr>
<td>AsH$_3^+$ + AsH$_3$</td>
<td>$\rightarrow$</td>
<td>AsH$_4^+$ + AsH$_2$</td>
<td>-21</td>
<td>1.00</td>
</tr>
</tbody>
</table>

$^a$ Reactions shown.

$^b$ Enthalpy changes in kcal mol$^{-1}$.

$^c$ Product distribution.

$^d$ Rate constants in cm$^3$ molecule$^{-1}$ s$^{-1}$. 


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


Total product distribution normalized to unity for each reactant ion.

Units are $\times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. 
\[
\begin{align*}
\text{As}_2^+ + \text{AsH}_3 & \rightarrow \text{As}_3^+ + \text{H}_2 \quad (7) \\
\text{As}_2\text{H}^+ + \text{AsH}_3 & \rightarrow \text{As}_3^+ + 2\text{H}_2 \quad (8)
\end{align*}
\]

The formation of protonated arsine, \(\text{AsH}_4^+\), deserves further comment. As noted above, \(\text{AsH}_3^+\) is the only ion formed by electron impact at 11 eV, reacting with \(\text{AsH}_3\) to form only \(\text{AsH}_4^+\). The ratio of the intensity of \(\text{AsH}_4^+\) to \(\text{AsH}_3^+\) 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 \(\text{AsH}_4^+\) is formed solely via reaction 1 and is not generated to any extent as a secondary ion by any of the remaining \(\text{AsH}_3\) 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

\[
\text{AsH}_n^+ + \text{AsH}_3 \rightarrow \text{AsH}_3^+ + \text{AsH}_n
\quad (9)
\]

in the ratio of \(\text{AsH}_4^+\) to \(\text{AsH}_3^+\) with increasing electron energy.

**Basicity of Arsine**

The ion chemistry occurring in mixtures of \(\text{AsH}_3\) with select molecules was investigated to determine the gas phase basicity of arsine. Such molecules included \(\text{PH}_3\), \(\text{H}_2\text{S}\), \(\text{CH}_3\text{CH}=\text{CH}_2\), \(\text{CH}_3\text{OH}\), and \(\text{CH}_3\text{Cl}\).
Arsine and Phosphine

The variation with pressure of the single resonance intensities for a 1.6:1 mixture of \( \text{AsH}_3 \) and \( \text{PH}_3 \) 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 \( \text{AsH}_3^+ \) and \( \text{PH}_3^+ \) react to form the protonated species \( \text{AsH}_4^+ \) and \( \text{PH}_4^+ \). At still higher pressures, \( \text{AsH}_4^+ \) is observed to decline in favor of \( \text{PH}_4^+ \), which is the only ion present at \( 2 \times 10^{-4} \) 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

\[
\text{AsH}_4^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{AsH}_3
\]  

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 \( \text{H}_2\text{S} \) and \( \text{AsH}_3 \) at 11 eV and \( 10^{-6} \) torr yields only the parent ions \( \text{H}_2\text{S}^+ \) and \( \text{AsH}_3^+ \). 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 \( \text{H}_3\text{S}^+ \) and \( \text{AsH}_4^+ \). The single resonance intensity of \( \text{H}_3\text{S}^+ \) passes through a maximum and decreases while that of \( \text{AsH}_4^+ \) continues to increase, \( \text{AsH}_4^+ \) being the only remaining ion
Figure 2  Variation of ion single-resonance intensities for a 1.6:1 mixture of AsH₃ and PH₃ at 11 eV.
Table II. Summary of Proton Transfer and Nucleophilic Displacement Reactions Observed in Mixtures of Arsine with Various Molecules

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\frac{dk}{dE}$</th>
<th>Thermochemical Inferences $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AsH}_4^+ + \text{PH}_3 \rightarrow \text{PH}_4^+ + \text{AsH}_3$</td>
<td>$-$</td>
<td>$\text{PA(AsH}_3) \leq 185^c$</td>
</tr>
<tr>
<td>$\text{H}_3\text{S}^+ + \text{AsH}_3 \rightarrow \text{AsH}_4^+ + \text{H}_2\text{S}$</td>
<td>$-$</td>
<td>$\text{PA(AsH}_3) \geq 170^d$</td>
</tr>
<tr>
<td>$\text{AsH}_4^+ + \text{C}_3\text{H}_6^h \rightarrow \text{C}_3\text{H}_7^+ + \text{AsH}_3$</td>
<td>$-$</td>
<td>$\text{PA(AsH}_3) \leq 179^e$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{ClH}^+ + \text{AsH}_3 \rightarrow \text{AsH}_4^+ + \text{CH}_3\text{Cl}$</td>
<td>$-$</td>
<td>$\text{PA(AsH}_3) \geq 160^f$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{ClH}^+ + \text{CH}_3\text{Cl} \rightarrow (\text{CH}_3)_2\text{Cl}^+ + \text{HCl}$</td>
<td>$-$</td>
<td>$\text{MCA(CH}_3\text{Cl) \geq MCA(HCl)}$</td>
</tr>
<tr>
<td>$\text{AsH}_4^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2^+ + \text{AsH}_3$</td>
<td>$-$</td>
<td>$\text{PA(AsH}_3) \leq 181^g$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{OH}^+ + \text{H}_2\text{O}$</td>
<td>$-$</td>
<td>$\text{MCA(CH}_3\text{OH) \geq MCA(H}_2\text{O)}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH}_2^+ + \text{AsH}_3 \rightarrow \text{CH}_3\text{AsH}_3^+ + \text{H}_2\text{O}$</td>
<td>$-$</td>
<td>$\text{MCA(AsH}_3) \geq \text{MCA(H}_2\text{O)}$</td>
</tr>
</tbody>
</table>

$^a$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.

<table>
<thead>
<tr>
<th>Reference 38.</th>
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<td>Reference 18.</td>
</tr>
<tr>
<td>References 39 and 40.</td>
</tr>
<tr>
<td>$CH_3CH=CH_2$.</td>
</tr>
</tbody>
</table>
at $4 \times 10^{-4}$ torr. Double resonance experiments confirm that reaction 11 is exothermic in the direction indicated, leading to the conclusion that $\text{PA(AsH}_3\text{)} \geq \text{PA(H}_2\text{S)}$.

$$\text{H}_3\text{S}^+ + \text{AsH}_3 \rightarrow \text{AsH}_4^+ + \text{H}_2\text{S} \quad (11)$$

**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 $\text{CH}_3\text{CH}=\text{CH}_2$ and $\text{AsH}_3$ under conditions such that only the parent ions $\text{C}_3\text{H}_6^+$ and $\text{AsH}_3^+$ are initially present (11 eV), suggest the occurrence of reaction 12. Double resonance experiments confirm this reaction in the direction shown. Hence $\text{PA(CH}_3\text{CH}=\text{CH}_2\text{)} \geq \text{PA(AsH}_3\text{)}$.

$$\text{AsH}_4^+ + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_7^+ + \text{AsH}_3 \quad (12)$$

**Arsine and Methanol**

The variation of single resonance intensities with pressure, illustrated in Figure 3, for a 3:1 mixture of $\text{AsH}_3$ and $\text{CH}_3\text{OH}$ under conditions where initially only $\text{AsH}_3^+$ is present (11 eV) suggests the occurrence of reaction 13. Double resonance experiments confirm that reaction 13 proceeds in the direction shown. We conclude that $\text{PA(CH}_3\text{OH)} \geq \text{PA(AsH}_3\text{)}$.
Figure 3  Variation of single-resonance intensities with pressure for a 3:1 mixture of AsH₃ and CH₂OH at 11 eV.
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 $8 \times 10^{-4}$ torr, are formed in the nucleophilic displacement reactions 14 and 15. Munson (16)

$$\text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{OH}^+ + \text{H}_2\text{O} \quad (14)$$

$$\text{CH}_3\text{OH}_2^+ + \text{AsH}_3 \rightarrow \text{CH}_3\text{AsH}_3^+ + \text{H}_2\text{O} \quad (15)$$

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$_3$Cl and AsH$_3$ under conditions where only the parent ion of arsine is initially present (11 eV) shows that AsH$_3^{+}$ reacts with both neutrals to form the protonated species AsH$_4^+$ and CH$_3$ClH$^+$. At higher pressures evidence for reaction 16 is observed, which double resonance experiments confirm to proceed as shown. Hence we conclude that PA(AsH$_3$) $\geq$ PA(CH$_3$Cl).

$$\text{CH}_3\text{ClH}^+ + \text{AsH}_3 \rightarrow \text{AsH}_4^+ + \text{CH}_3\text{Cl} \quad (16)$$

In agreement with previous studies of the positive ion-molecule chemistry of methyl chloride, CH$_3$ClH$^+$ is observed to react with CH$_3$Cl to undergo the nucleophilic displacement reaction
17 forming dimethyl chloronium ion (18). Significantly, the analogous displacement reaction with AsH₃, reaction 18, is not observed.

\[
\text{CH}_3\text{ClH}^+ + \text{CH}_3\text{Cl} \rightarrow (\text{CH}_3)_2\text{Cl}^+ + \text{HCl}
\]  

(17)

\[
\text{CH}_3\text{ClH}^+ + \text{AsH}_3 \rightleftharpoons \text{CH}_3\text{AsH}_3^+ + \text{HCl}
\]  

(18)

**Negative Ion Chemistry of Arsine**

Electron impact (6.3 eV) on AsH₃ at 4 × 10⁻⁵ torr yields the negative ions As⁻ (10%), AsH⁻ (15%), and AsH₂⁻ (75%). The contribution to the total ionization by As⁻ and AsH⁻ decreases with increasing AsH₃ 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 As₂H⁻, indicating reaction 19. Line

\[
\text{As}^- + \text{AsH}_3 \rightarrow \text{As}_2\text{H}^- + \text{H}_2
\]  

(19)

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

**Acidity of Arsine**

The investigation of the negative ion chemistry of AsH₃ in mixtures with PH₃, H₂S, and C₂H₅ONO was undertaken to determine the gas phase acidity of AsH₃.
Arsine and Hydrogen Sulfide

The negative ions $\text{AsH}_2^-$ and $\text{HS}^-$ in a 1:2 mixture of $\text{AsH}_3$ and $\text{H}_2\text{S}$ were produced chemically via proton transfer reactions. The negative ion single resonance spectrum of ethyl nitrite, $\text{C}_2\text{H}_5\text{ONO}$, at 25 eV shows abundant ethoxide ion, $\text{C}_2\text{H}_5\text{O}^-$. (19-21) Both arsine and hydrogen sulfide readily transfer a proton to $\text{C}_2\text{H}_5\text{O}^-$ forming $\text{AsH}_2^-$ and $\text{HS}^-$ in accordance with reactions 20 and 21. Illustrated in Figure 4 is the variation of single resonance

$$\text{C}_2\text{H}_5\text{O}^- + \text{AsH}_3 \rightarrow \text{AsH}_2^- + \text{C}_2\text{H}_5\text{OH} \quad (20)$$

$$\text{C}_2\text{H}_5\text{O}^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{C}_2\text{H}_5\text{OH} \quad (21)$$

intensities with increasing partial pressure of $\text{AsH}_3$ and $\text{H}_2\text{S}$ at a fixed pressure of ethyl nitrite. At high pressure, $\text{AsH}_2^-$ declines in favor of $\text{HS}^-$. Double resonance experiments (Table V) confirm that reactions 20, 21 and 22 proceed as written and lead to the

$$\text{AsH}_2^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{AsH}_3 \quad (22)$$

conclusion that $\text{PA}(\text{C}_2\text{H}_5\text{O}^-) \geq \text{PA}(\text{AsH}_2^-) \geq \text{PA}(\text{HS}^-)$.

Two other ions present in the negative ion single resonance spectrum of this mixture, $\text{NO}_2^-$ and $\text{C}_2\text{H}_5\text{O}^-$, are formed via reactions 23 and 24. Reaction 23 is analogous to the displacement

$$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{ONO} \rightarrow \text{NO}_2^- + (\text{C}_2\text{H}_5)_2\text{O} \quad (23)$$

$$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_3\text{O}^- + \text{H}_2 + \text{C}_2\text{H}_5\text{OH} \quad (24)$$
Figure 4  Variation of single-resonance intensities with pressure for a 1:2 mixture of AsH$_3$ and H$_2$S at a fixed pressure (2 \times 10^{-5} \text{ torr}) of C$_2$H$_5$ONO and at 25 eV.
of NO$_3^-$ from ethyl nitrate by C$_2$H$_5$O$^-$ observed by Buttrill and Kriemler (22). That C$_2$H$_5$OH 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$_2$S will transfer a proton to C$_2$H$_5$O$^-$ while AsH$_3$ does not (Table V). This suggests that PA(AsH$_2^-$) $\geq$ PA(C$_2$H$_5$O$^-$) $\geq$ 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 $3 \times 10^{-6}$ torr include AsH$_2^-$, PH$_2^-$, and minor contributions from As$^-$ and AsH$^-$. At the highest pressure employed, $3 \times 10^{-4}$ torr, AsH$_2^-$ increases relative to PH$_2^-$. Double resonance experiments confirm reaction 25 as written and permit

$$\text{PH}_2^- + \text{AsH}_3 \rightarrow \text{AsH}_2^- + \text{PH}_3$$  \hspace{1cm} (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 $8 \times 10^{-5}$ 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$^+$ with PH$_3$ (1), however, hydrogen atom loss is not observed even when the reactant is a radical ion such as AsH$^+$.

As previously noted, the ion-molecule reactions of the first row congeners, ammonia, stand in contrast to both phosphine and arsine (1). Fragment ions of NH$_3$ react with the neutral to generate NH$_3^+$ 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) ~ 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$_2$O, H$_2$S, and H$_2$Se (30-33, 2).
Basicity of Arsine

The enthalpy change for the gas phase reaction $\text{M}^+ + \text{H}^+ \rightarrow \text{M} + \text{H}^+$ 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

$$\text{M}_1\text{H}^+ + \text{M}_2 \rightarrow \text{M}_2\text{H}^+ + \text{M}_1$$

(26)

that $\text{PA(M}_2) > \text{PA(M}_1)$. Thus from reactions 10-13, 16 reported above, which indicate $\text{PA(CH}_3\text{Cl)}$, $\text{PA(H}_2\text{S)} \leq \text{PA(AsH}_3) \leq \text{PA(CH}_3\text{CH=CH}_2)$, $\text{PA(CH}_3\text{OH)}$, $\text{PA(PH}_3)$, and the known values $\text{PA(CH}_3\text{Cl)} = 160 \text{ kcal/mole (18), PA(H}_2\text{S)} = 170 \text{ kcal/mole (37), PA(CH}_3\text{CH=CH}_2) = 179 \text{ kcal/mole (38), PA(CH}_3\text{OH)} = 181 \text{ kcal/mole (39, 40), and PA(PH}_3) = 185 \text{ kcal/mole (39, 41), an estimate of PA(AsH}_3) = 175 \pm 5 \text{ kcal/mole is derived, corresponding to } \Delta H_f^\circ (\text{AsH}_4^+) = 207 \pm 5 \text{ kcal/mole.}$

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, $\text{HA(M}^+)$, is simply the

$$\text{PA(M)} - \text{HA(M}^+) = \text{IP(H}^+ - \text{IP(M)}$$

(27)

$\text{H-M}^+$ 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

<table>
<thead>
<tr>
<th>Ion</th>
<th>Hydrogen Affinity&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Neutral</th>
<th>Bond Strength</th>
<th>Δf</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>128</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>104&lt;sup&gt;c&lt;/sup&gt;</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>PH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>102</td>
<td>SiH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>94&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>77&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>AsH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>92</td>
<td>GeH&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td>69&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> All values in kcal/mole.

<sup>b</sup> Calculated from equation 27.


<sup>f</sup> 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 iso-electronic 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 NH₃, PH₃, and AsH₃, 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.

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

\[ \text{YH}_n + \text{CH}_3\text{XH}_m^+ \rightarrow \text{CH}_3\text{Y}_n^+ + \text{XH}_m \]

(28)

(2) proton transfer from the substrate to the nucleophile is endothermic, i.e., \( \text{PA(\text{CH}_3\text{XH}_{m-1})} \geq \text{PA(\text{YH}_n)} \) (3). Reaction processes observed in mixtures of AsH₃ with CH₃OH and CH₃Cl serve to illustrate these principles.

As noted above, protonated methyl arsine, CH₃AsH₃⁺, is formed via reaction 15 as AsH₃ reacts with CH₃OH₂⁺ to displace
Table IV. Thermochemical Properties of the Group V Hydrides\(^a\)

<table>
<thead>
<tr>
<th>MH</th>
<th>IP(MH)(^b)</th>
<th>PA(MH)</th>
<th>HA(MH(^+))(^f)</th>
<th>D(M–H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_3)</td>
<td>10.15</td>
<td>207(^c)</td>
<td>128</td>
<td>109(^g)</td>
</tr>
<tr>
<td>PH(_3)</td>
<td>9.98</td>
<td>185(^d)</td>
<td>102</td>
<td>84(^h)</td>
</tr>
<tr>
<td>AsH(_3)</td>
<td>10.03</td>
<td>175(^e)</td>
<td>92</td>
<td>72(^i)</td>
</tr>
</tbody>
</table>

\(^a\)Except for ionization potentials, all values are given in kcal/mole.


\(^c\)Reference 39.

\(^d\)Reference 41.

\(^e\)This work.

\(^f\)Calculated from equation 27.


\(^i\)Calculated in the text.
H₂O. Proton transfer from the substrate (CH₃OH₂⁺) to the nucleophile (AsH₃) does not occur since PA(CH₃OH) > PA(AsH₃). In contrast, in a mixture of CH₃Cl and AsH₃, the analogous nucleophilic displacement, reaction 18, does not proceed to produce CH₃AsH₃⁺ even though the process is estimated to be exothermic by 37 kcal/mole (42). Instead, since PA(AsH₃) > PA(CH₃Cl), 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

\[ M + CH₃⁺ \rightarrow MCH₃⁺; \text{ MCA}(M) = -\Delta H \tag{29} \]

data indicate that the following will be the order in which nucleophilic displacements occur (3) (decreasing methyl cation affinity): NH₃ > CO > H₂S > CH₃OH > CH₂O > HI > H₂O > HBr > HCl > N₂ > HF. Observation of reaction 15 implies that MCA(AsH₃) > MCA(H₂O) = 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, AsH₂⁻, can be produced by the dissociative electron capture reaction 30 (43). The threshold energy determined for this
<table>
<thead>
<tr>
<th>Mixture</th>
<th>Reaction</th>
<th>$\frac{dk}{dE}$</th>
<th>Thermochemical Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AsH$_3$ - PH$_3$</td>
<td>$\text{PH}_2 + \text{AsH}_3 \rightarrow \text{AsH}_2^- + \text{PH}_3$</td>
<td>$\dagger$</td>
<td>PA(AsH$_2^-$) $\leq$ 362$^c$</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{O}^- + \text{AsH}_3 \rightarrow \text{AsH}_2^- + \text{C}_2\text{H}_5\text{OH}$</td>
<td>$-$</td>
<td>PA(AsH$_2^-$) $\leq$ 376$^d$</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{O}^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{C}_2\text{H}_5\text{OH}$</td>
<td>$-$</td>
<td>PA(HS$^-$) $\leq$ PA(C$_2$H$_5$O$^-$)</td>
</tr>
<tr>
<td>AsH$_3$ - H$_2$S - C$_2$H$_5$ONO (+ C$_2$H$_5$OH)</td>
<td>$\text{C}_2\text{H}_3\text{O}^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{C}_2\text{H}_4\text{O}$</td>
<td>$-$</td>
<td>PA(C$_2$H$_3$O$^-$) $\geq$ 350$^e$</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{ONO} \rightarrow \text{NO}_2^- + (\text{C}_2\text{H}_5)_2\text{O}$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_2\text{H}_5\text{O}^- + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_3\text{O}^- + \text{H}_2 + \text{C}_2\text{H}_5\text{OH}$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td></td>
<td>$\text{AsH}_2^- + \text{H}_2\text{S} \rightarrow \text{HS}^- + \text{AsH}_3$</td>
<td>$\dagger$</td>
<td>PA(AsH$_2^-$) $\geq$ 350$^e$</td>
</tr>
</tbody>
</table>

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

$^b$All values given in kcal/mole.
\begin{equation}
\text{e} + \text{AsH}_3 \rightarrow \text{AsH}_2^- + \text{H}^+ \tag{30}
\end{equation}

process, \(E_t = 2.0 \pm 0.1 \text{ eV (43)}\), can be employed to estimate
the proton affinity of \(\text{AsH}_2^-\) through the thermochemical cycle of
equation 31. Using \(\text{IP(H}^-) = 313 \text{ kcal/mole}\) and equation 31,

\begin{align*}
\text{e} + \text{AsH}_3 & \xrightarrow{\text{PA(AsH}_2^-)} \text{AsH}_2^- + \text{H}^+ + \text{e} \\
\text{PA(AsH}_2^-), \text{ the gas phase acidity of arsenic, is estimated to be} & \text{359} \pm 3 \text{ kcal/mole. From reactions 20, 22, and 25 reported} \\
\text{above, we conclude that } & \text{PA(HS}^-) \ll \text{PA(AsH}_2^-) \ll \text{PA(PH}_2^-), \\
\text{PA(C}_2\text{H}_5\text{O}^-), \text{ Using the values } & \text{PA(HS}^-) = 350 \text{ kcal/mole (44),} \\
\text{PA(PH}_2^-) = 362 \text{ kcal/mole (1), and PA(C}_2\text{H}_5\text{O}^-) = 376 \text{ kcal/mole} & \text{(45), the value 356} \pm 6 \text{ kcal/mole may be assigned to PA(AsH}_2^-,} \\
\text{consistent with the value derived from equation 31.} & \\

\text{The acidity of a species MH is related to the bond disso-} \\
\text{ciation energy, } D(M-H), \text{ and the electron affinity of the radical,} \\
\text{EA(M}^-), \text{ as shown in the thermochemical cycle 32. Brauman} \\
\text{and Eyler have recently determined EA(AsH}_2^\cdot) \text{ to be 29 kcal/mole} \\
\text{from photodetachment studies (46, 47). Using this value and} \\
\text{equation 33, } D(\text{H}_2\text{As}-\text{H}) \text{ is calculated to be 72 kcal/mole. This} \\
\text{value, not unexpectedly, is slightly higher than the average As-H} \\
\text{bond energy in AsH}_3 (70.9 \text{ kcal/mole}) (48).}
\[
\text{MH} \xrightarrow{\text{PA}(\text{M}^-)} M^- + H^+ \\
\text{D}(\text{M-H}) \downarrow \text{D}(\text{M-H}) \quad \text{IP}(\text{H}^+) \quad \text{IP}(\text{H}^+) \\
M^- + H^+ \quad \text{M}^+ + H^+ + e \\
\text{PA}(\text{M}^-) = \text{D}(\text{M-H}) + \text{IP}(\text{H}^+) - \text{EA}(\text{M}^+). \quad (32)
\]

Table VI summarizes D(M-H), EA(M·), and PA(M−) for the first three group V hydrides. In proceeding from NH₃ to PH₃ to AsH₃, 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\textsuperscript{a}

<table>
<thead>
<tr>
<th>MH</th>
<th>D(M–H)</th>
<th>EA(M•)</th>
<th>PA(M⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{3}</td>
<td>109\textsuperscript{b}</td>
<td>17\textsuperscript{d}</td>
<td>405\textsuperscript{c}</td>
</tr>
<tr>
<td>PH\textsubscript{3}</td>
<td>84\textsuperscript{b}</td>
<td>35\textsuperscript{e}</td>
<td>362\textsuperscript{e}</td>
</tr>
<tr>
<td>AsH\textsubscript{3}</td>
<td>72\textsuperscript{c}</td>
<td>29\textsuperscript{d}</td>
<td>356\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All values are given in kcal/mole.
\textsuperscript{b} See Table IV.
\textsuperscript{c} Calculated from equation 33 employing IP(H•) = 313 kcal/mole.
\textsuperscript{d} Reference 46.
\textsuperscript{e} Reference 1.
\textsuperscript{f} This work.
References


(12) The authors gratefully acknowledge the gift of samples of Zn₃As₂ and Mg₃P₂·2AlP from Rocky Mountain Research, Inc., Denver, Colorado.


(20) K. Jaeger and A. Henglein, Z. Naturforsch., A, 22, 700 (1967), report a large cross section for the formation of 
C$_2$H$_5$O$^-$ from C$_2$H$_5$ONO. 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$_2$S and AsH$_3$.
(21) The sample of ethyl nitrite contained ~ 10% ethanol.
(23) J. L. Beauchamp, unpublished results.


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


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


(42) Reaction 18 is calculated to be 37 kcal/mole exothermic using the authors' estimates of $\Delta H_f (\text{CH}_3\text{AsH}_2) = 12$ kcal/mole and $\text{PA}(\text{CH}_3\text{AsH}_2) = 190$ kcal/mole, corresponding to $\Delta H_f (\text{CH}_3\text{AsH}_3^+) = 188$ kcal/mole.


(48) The average As–H bond energy in AsH$_3$ was calculated employing $\Delta H_f(\text{AsH}_3) = 15.9$ kcal/mole, $\Delta H_f(\text{As}) = 72.3$ kcal/mole, and $\Delta H_f(\text{H}\cdot) = 52.1$ kcal/mole. Thermochemical data were taken from footnote 6 in Table I.