

Multinuclear NMR Studies of the Reactions of MeAsH₂ with Me₂AsNMe₂ and Me₂AsNMe₂·BH₃

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Abstract

The reactions of MeAsH₂ with Me₂AsNMe₂ and Me₂AsNMe₂·BH₃ have been carried out in toluene-d₈ solution as a function of temperature and time. The progress of the reactions was monitored by multinuclear (¹H, ¹¹B, and ¹³C) NMR spectroscopy over the temperature range of -80 and -10 °C. NMR spectral data analysis suggests the initial formation of an unstable intermediate, Me₂AsAs(H)Me, which undergoes multiple condensation reactions to give (MeAs)₅. The other products of the reactions are Me₂AsAsMe₂, Me₂AsH, MeAsH₂, Me₂NH or Me₂NH·BH₃ and uncharacterized, condensed, As-As bonded compounds. Several competitive exchange reactions involving compounds capable of exchanging H-, MeAs<, Me₂As-, and Me₂N- units influence the rate of reaction, as well as the product yields. The reactions involving >AsN</>NH, >AsN</>AsH, >AsN</>AsN<, >AsN</>AsAs<, >AsN</>(MeAs)₅, >AsAs</>AsH, >AsAs</>-AsH₂, >AsAs</>(MeAs)₅, (MeAs)₅/>AsH and (MeAs)₅/-AsH₂ systems have been examined to determine their relative significance in the reactions of MeAsH₂ with Me₂AsNMe₂ and its N-B bonded BH₃ adduct.

Introduction

Mechanistic studies of the reactions involved in the synthesis of As-As bonded compounds have received little attention in the literature [1–3]. The ¹H NMR spectroscopic investigations of the reactions of Me₂AsH with Me₂AsX (X = Cl, Br, I or CN) indicate the reversible nature of these reactions in producing Me₂AsAsMe₂ [1]. Some rapid exchange processes involving >AsH/HX and >AsX/>AsAs< systems also occur in the solution. Similar studies [2, 3] on the reactions of MeAsH₂ with MeAsX₂ (X = Cl, Br, or I) to yield (MeAs)₅ and As-As bonded polymers (chains and ladder structures) suggest the presence of several competing equilibria involving different com-

pounds in the reaction mixture. On the basis of a detailed ¹H NMR study [3], the reaction of MeAsH₂ with MeAsI₂ has been proposed to occur through formation of the unstable Me(H)AsAs(I)Me, which undergoes several condensation reactions with MeAsH₂, MeAsHI and MeAsI₂ to yield ladder polymers of the general formula (MeAs)_x and several other uncharacterized As-As bonded oligomers.

Recently, we found [4] that Me₂AsH reacts irreversibly with Me₂AsNMe₂ and its N-B bonded BH₃ adduct to give Me₂AsAsMe₂. The ¹H, ¹³C and/or ¹¹B NMR studies of these reactions suggest that the Me₂AsH/Me₂AsNMe₂ reaction proceeds faster initially, but the overall rate of reaction is slower than that of the Me₂AsH/Me₂AsNMe₂·BH₃ reaction. This is a consequence of the presence of mainly an >AsN</>NH exchange process in the Me₂AsH/Me₂AsNMe₂ system that is absent in the Me₂AsH/Me₂AsNMe₂·BH₃ system due to formation of Me₂NH·BH₃. In both systems, other exchange processes involving >AsAs</>AsH, >AsAs</>AsAs<, and/or >AsAs</>AsN< systems occur, but these are of minor importance in influencing the overall rate of formation of Me₂AsAsMe₂.

No reports are found in the literature concerning the reactions of primary arsines with dialkylamino-dialkylarsines. Therefore, we undertook a multinuclear NMR investigation of the reactions involving the >AsH₂/[>]AsN< system to elucidate their mechanisms and to characterize and determine the importance of any exchange reactions occurring in the reaction mixture. In this paper, we report a comprehensive NMR study of the reactions of MeAsH₂ with Me₂AsNMe₂ and Me₂AsNMe₂·BH₃. Furthermore, an NMR investigation of several independent reaction systems has been carried out to establish their relative significance in influencing the rate of formation of different As-As bonded compounds and product yields.

Experimental

Standard high vacuum line techniques and a Vacuum Atmospheres Model HE-43 Dri-lab equipped

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with a Model HE-493 Dri-Train were used for storing and handling of all compounds. Me_2NH (Matheson Gas Products) was dried over sodium metal and was distilled in the vacuum line prior to use. THF-d_8 , toluene- d_8 and Me_4Si were purchased from Aldrich chemical company and were stored over molecular sieves. Diborane(6) [5], $\text{Me}_2\text{AsNMe}_2$ (108 °C) [6], $\text{Me}_2\text{AsAsMe}_2$ (60 °C/25 torr) [7], $(\text{MeAs})_5$ (178 °C/15 torr) [8], Me_2AsH (36 °C) [9], Me_2AsCl (106 °C) [10], MeAsH_2 [11], $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$ [12], $\text{Et}_2\text{AsNEt}_2$ (58 °C/8 torr) [13], and $\text{Me}_2\text{AsNEt}_2$ (80.5 °C/90 torr) [14] were synthesized by previously reported methods. $\text{Et}_2\text{AsNMe}_2$ (132 °C/549 torr) was synthesized by the reaction of Et_2AsI with Me_2NH by a method [6] analogous to that reported for $\text{Me}_2\text{AsNMe}_2$. The purity of all compounds was checked by NMR spectroscopy prior to use.

^1H , ^{11}B , and ^{13}C NMR spectra were recorded on a Nicolet 300 MHz multinuclear FT NMR spectrometer operating at 300.1, 96.3 and 75.4 MHz, respectively. Chemical shift values for the ^{11}B resonance were measured relative to $\text{BF}_3\cdot\text{OEt}_2$, high field shift being negative. ^1H and ^{13}C NMR chemical shifts were measured with respect to tetramethylsilane as an internal reference. All NMR spectra were obtained in toluene- d_8 as the solvent. All the reactions were protected from exposure to light to minimize photochemical side reactions involving $(\text{MeAs})_5$. The integration of the peaks in the ^1H NMR spectra of a sample was done with respect to the constant integration value of TMS throughout a study. See spectral data below for all NMR assignments.

Reactions of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2$, $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$, $\text{Me}_2\text{AsAsMe}_2$ or $(\text{MeAs})_5$; $(\text{MeAs})_5$ with Me_2NH , Me_2AsH , $\text{Me}_2\text{AsAsMe}_2$ or $\text{Me}_2\text{AsNMe}_2$; and $\text{Et}_2\text{AsNEt}_2$ with $\text{Me}_2\text{AsNMe}_2$

The reactions of MeAsH_2 with equimolar amounts of $\text{Me}_2\text{AsNMe}_2$ (2.0 mmol), $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$ (2.0 mmol), $\text{Me}_2\text{AsAsMe}_2$ (1.0 mmol) or $(\text{MeAs})_5$ (1.0 mmol); $(\text{MeAs})_5$ with stoichiometric amounts of Me_2NH (1.0 mmol), Me_2AsH (1.0 mmol), $\text{Me}_2\text{AsAsMe}_2$ (1.0 mmol) or $\text{Me}_2\text{AsNMe}_2$ (1.0 mmol); and $\text{Et}_2\text{AsNEt}_2$ (1.0 mmol) with $\text{Me}_2\text{AsNMe}_2$ (1.0 mmol) were carried out in toluene- d_8 using the following procedure. A stoichiometric amount of the less volatile compound dissolved in enough toluene- d_8 to maintain a constant 4 ml total solution volume and a drop of TMS were added to an NMR tube (10 mm \times 22.5 cm, pyrex) equipped with a greaseless vacuum stopcock. The tube was degassed using standard vacuum line techniques. An equimolar amount of the more volatile compound was condensed at -196 °C into the NMR tube. The tube was sealed, agitated gently at -95 °C (toluene slush), and inserted into the precooled (-90 °C) probe of the NMR spectrometer. Each reaction was then followed

at the selected temperature intervals over a range of -80 to -10 °C by recording ^1H , ^{13}C and, where appropriate, ^{11}B NMR spectra as a function of time. The studies were restricted to a maximum temperature of -10 °C due to the low boiling point of Me_2NH and the instability of $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$ [12].

The following is a list of NMR spectral data (values in ppm) independently determined in this laboratory at -10 °C in toluene- d_8 solution on prepurified or synthesized compounds identified in the reaction mixtures.

^1H Spectral Data

$(\text{MeAs})_5$: 1.54, 1.50 and 1.48. $\text{Me}_2\text{AsAsMe}_2$: 0.96. $\text{Me}_2\text{AsNMe}_2$: 0.79 (Me_2As) and 2.42 (Me_2N). $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$: 0.82 (Me_2As) and 2.09 (Me_2N). $\text{Et}_2\text{AsNEt}_2$: 1.00 ($\text{CH}_3\text{CH}_2\text{N}$, t, $^3J(\text{HH}) = 7.1$), 2.86 ($\text{CH}_3\text{CH}_2\text{N}$, q), and 1.04–1.48 ($\text{CH}_3\text{CH}_2\text{As}$, m). $\text{Et}_2\text{AsNMe}_2$: 1.01–1.52 ($\text{CH}_3\text{CH}_2\text{As}$, m), and 2.55 (Me_2N). $\text{Me}_2\text{AsNEt}_2$: 0.85 (Me_2As), 0.97 ($\text{CH}_3\text{CH}_2\text{N}$, t, $^3J(\text{HH}) = 7.1$) and 2.80 ($\text{CH}_3\text{CH}_2\text{N}$, q). Me_2AsH : 0.77 (Me_2As , d, $^3J(\text{HH}) = 7.0$ Hz) and 2.39 (AsH , s). Me_2NH : 2.17. $\text{Me}_2\text{NH}\cdot\text{BH}_3$: 1.96 (Me_2N , d, $^3J(\text{HH}) = 5.7$ Hz) and 3.99 (NH , q). MeAsH_2 : 0.69 (MeAs , t, $^3J(\text{HH}) = 7.2$ Hz) and 1.96 (AsH_2 , q).

^{11}B Spectral Data

$\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$: -11.36 (q, $^1J(\text{B-H}) = 98.7$ Hz). $\text{Me}_2\text{NH}\cdot\text{BH}_3$: -14.05 (q, $^1J(\text{B-H}) = 97.7$ Hz).

^{13}C Spectral Data

$(\text{MeAs})_5$: 3.78, 5.23, and 6.81 ($^1J(\text{CH}) = 134.9$ Hz). $\text{Me}_2\text{AsAsMe}_2$: 5.94 ($^1J(\text{CH}) = 132.6$ Hz). $\text{Me}_2\text{AsNMe}_2$: 9.70 (Me_2As , $^1J(\text{CH}) = 130.6$ Hz, $^3J(\text{CH}) = 4.0$ Hz) and 41.92 (Me_2N , $^1J(\text{CH}) = 132.7$ Hz, $^3J(\text{CH}) = 5.3$ Hz). $\text{Me}_2\text{AsNMe}_2\cdot\text{BH}_3$: 12.63 (Me_2As , $^1J(\text{CH}) = 132.7$ Hz) and 47.76 (Me_2N , $^1J(\text{CH}) = 138.4$ Hz). $\text{Et}_2\text{AsNEt}_2$: 10.56 ($\text{CH}_3\text{CH}_2\text{As}$, $^1J(\text{CH}) = 126.4$), 20.84 ($\text{CH}_3\text{CH}_2\text{As}$, $^1J(\text{CH}) = 130.6$), 16.19 ($\text{CH}_3\text{CH}_2\text{N}$, $^1J(\text{CH}) = 124.9$, $^2J(\text{CH}) = 2.4$ Hz) and 44.49 ($\text{CH}_3\text{CH}_2\text{N}$, $^1J(\text{CH}) = 132.2$, $^2,^3J(\text{CH}) = 4.64$). $\text{Et}_2\text{AsNMe}_2$: 10.51 ($\text{CH}_3\text{CH}_2\text{As}$, $^1J(\text{CH}) = 126.4$), 19.50 ($\text{CH}_3\text{CH}_2\text{As}$, $^1J(\text{CH}) = 130.6$ Hz), and 42.58 (Me_2N , $^1J(\text{CH}) = 132.6$ Hz, $^3J(\text{CH}) = 5.2$ Hz). $\text{Me}_2\text{AsNEt}_2$: 11.99 (Me_2As , $^1J(\text{CH}) = 130.3$ Hz, $^3J = 4.0$ Hz), 15.51 ($\text{CH}_3\text{CH}_2\text{N}$, $^1J(\text{CH}) = 125.1$ Hz, $^2J(\text{CH}) = 2.4$ Hz), and 43.94 ($\text{CH}_3\text{CH}_2\text{N}$, $^1J(\text{CH}) = 132.2$ Hz, $^2,^3J = 4.7$ Hz). Me_2AsH : 1.43 ppm ($^1J(\text{CH}) = 132.5$ Hz, $^2,^3J(\text{CH}) = 3.0$ Hz). Me_2NH : 38.87 ($^1J(\text{CH}) = 131.9$ Hz and $^3J(\text{CH}) = 6.0$ Hz). $\text{Me}_2\text{NH}\cdot\text{BH}_3$: 43.82 ($^1J(\text{CH}) = 138.7$ Hz, $^2,^3J(\text{CH}) = 4.6$ Hz). MeAsH_2 : -8.74 ($^1J(\text{CH}) = 134.4$ Hz, $^2,^3J(\text{CH}) = 3.0$ Hz).

Results and Discussion

Reaction of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2$

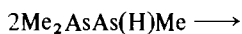
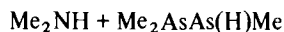
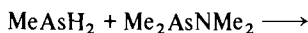
The ^1H and ^{13}C NMR spectra of an equimolar mixture of MeAsH_2 and $\text{Me}_2\text{AsNMe}_2$ in toluene- d_8

solution showed no reaction over the temperature range of -80 to -20 °C. After 20 min at -10 °C, low intensity peaks were observed due to Me_2NH , Me_2AsH , $\text{Me}_2\text{AsAsMe}_2$ and uncharacterized As–As bonded oligomeric compounds. The ^1H NMR peaks assigned to the Me_2N -moieties of $\text{Me}_2\text{AsNMe}_2$ and Me_2NH exhibited considerable line broadening associated with Me_2N group exchange [4, 15]. After $2\frac{1}{2}$ h, three low intensity peaks attributed to the polycyclic $(\text{MeAs})_5$ appeared in the ^1H NMR spectrum in an area ratio of 2:1:2 [16].

As the reaction progressed, the intensities of the ^1H and ^{13}C NMR peaks associated with $(\text{MeAs})_5$, $\text{Me}_2\text{AsAsMe}_2$, Me_2AsH and Me_2NH increased; the line width of the Me_2N ^1H NMR peak narrowed as more $\text{Me}_2\text{AsNMe}_2$ was consumed; and the intensities of the resonances assigned to $\text{Me}_2\text{AsNMe}_2$ and MeAsH_2 decreased. A disproportionate decrease in the intensities of the $\text{Me}_2\text{AsNMe}_2$ peaks in comparison to those of MeAsH_2 was noted. After 23 h, all of the $\text{Me}_2\text{AsNMe}_2$ was consumed.

With additional time, the ^1H and ^{13}C NMR spectra showed a significant decrease in the intensities of the peaks assigned to $\text{Me}_2\text{AsAsMe}_2$ and MeAsH_2 with a concomitant increase in the intensities of the $(\text{MeAs})_5$ and Me_2AsH resonances. After 32 h, the ^1H and ^{13}C NMR spectra indicated that the overall reaction achieves equilibrium. Very low intensity peaks $\delta_{\text{C}} = -3.69, 0.38, 7.08, 7.19, 7.57$ and 8.78 ppm and $\delta_{\text{H}} = 0.91, 0.93, 0.95, 1.02, 1.05$ and 1.07 ppm may be attributed to MeAs groups in uncharacterized As–As bonded oligomers. The ^1H NMR intensity data at equilibrium indicate the presence of 86% characterized compounds [6% MeAsH_2 , 22% Me_2AsH , 5% $\text{Me}_2\text{AsAsMe}_2$, 5% $(\text{MeAs})_5$ and 48% Me_2NH] and 14% uncharacterized As–As bonded oligomers.

The above results coupled with previous data reported by Rheingold *et al.*, on the $\text{MeAsH}_2/\text{MeAsI}_2$ system [3] suggest that the overall reaction of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2$ to give $(\text{MeAs})_5$ is complex and involves a series of condensation reactions and competing exchange equilibria. We propose that via the formation of a concerted, four-centered activated intermediate [3, 17] initially the As–N and As–H bonds cleave and Me_2NH and the unstable intermediate, $\text{Me}_2\text{AsAs}(\text{H})\text{Me}$, form. The latter then undergoes a facile exchange to yield the symmetrical diarsines, $\text{Me}_2\text{AsAsMe}_2$ and $\text{Me}(\text{H})\text{AsAs}(\text{H})\text{Me}$.



Subsequent condensation and exchange reactions give

Me_2AsH and the $\text{Me}(\text{H})\text{As}(\text{AsMe})_x\text{As}(\text{H})\text{Me}$ species, which cyclize via MeAsH_2 elimination to $(\text{MeAs})_5$.

This formation of $\text{Me}(\text{H})\text{AsAs}(\text{H})\text{Me}$ and $\text{Me}(\text{H})\text{As}(\text{AsMe})_x\text{As}(\text{H})\text{Me}$ is analogous to that of $\text{Me}(\text{H})\text{AsAs}(\text{I})\text{Me}$ and $\text{Me}(\text{H})\text{As}(\text{AsMe})_x\text{As}(\text{I})\text{Me}$ as proposed [3] in the $\text{MeAsH}_2/\text{MeAsI}_2$ system. Several competing exchange equilibria that involve reactants, different intermediate species, and products (discussed below) influence the relative rates of consumption of $\text{Me}_2\text{AsNMe}_2$, $\text{Me}_2\text{AsAsMe}_2$, MeAsH_2 , and Me_2AsH at different stages of $(\text{MeAs})_5$ formation; the stoichiometric ratios of the products; and the Me_2N -moiety spectral line width.

Reaction of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$

The ^1H , ^{11}B , and ^{13}C NMR spectra of an equimolar mixture of MeAsH_2 and $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ in toluene- d_8 solution also showed no reaction over the -80 to -20 °C temperature range. After 30 min at -10 °C, very low intensity NMR peaks assignable to $\text{Me}_2\text{NH} \cdot \text{BH}_3$, $\text{Me}_2\text{AsAsMe}_2$, Me_2AsH and uncharacterized As–As bonded compounds were observed in the spectra. The reaction proceeded very slowly with time. After 4 h, the ^1H and ^{13}C NMR spectra indicated complete consumption of $\text{Me}_2\text{AsAsMe}_2$. The $\text{Me}_2\text{AsAsMe}_2$ peak then reappeared after $17\frac{1}{2}$ h and the presence of new resonances assignable to $(\text{MeAs})_5$ was observed.

No significant spectral changes were noted after 40 h when all the $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ was consumed. The ^1H NMR intensity data indicate the presence of 86% characterized [9% MeAsH_2 , 23% Me_2AsH , 3% $\text{Me}_2\text{AsAsMe}_2$, 3% $(\text{MeAs})_5$ and 48% $\text{Me}_2\text{NH} \cdot \text{BH}_3$] and 14% uncharacterized compounds in the reaction mixture. The ^1H and ^{13}C NMR spectra of the latter consisted of numerous weak resonances at δ_{H} and δ_{C} values previously noted in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ reaction and assigned to As–As bonded oligomers.

These results suggest that the reaction of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ yields $\text{Me}_2\text{NH} \cdot \text{BH}_3$ and all the arsenic-containing products observed in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ reaction. The absence of line broadening in the ^1H NMR spectrum of the peaks associated with Me_2N -moieties suggests that exchange involving Me_2N - groups does not occur in this system, since Me_2NH is preferentially bound to BH_3 [4]. Also the slower consumption of $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ relative to that of $\text{Me}_2\text{AsNMe}_2$ in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ system is undoubtedly a consequence of the lowered basicity of the nitrogen atom in the N–B adduct [4].

The stoichiometric ratio of the products obtained for both the studied systems is essentially the same at equilibrium. However, a comparison of the ratio at the point of consumption of $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ or $\text{Me}_2\text{AsNMe}_2$ indicates a significantly lower $\text{Me}_2\text{AsH}:\text{Me}_2\text{AsAsMe}_2$ ratio for the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ system than for the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ system.

This suggests that the bonding of the BH_3 to the nitrogen atom in $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ also diminishes the relative significance of exchange processes (see discussion below) that involved $\text{Me}_2\text{AsNMe}_2$ in the previously studied system.

Characterization of Exchange Processes

Previously established [4] exchange processes involving the >AsN</>NH , >AsAs</>AsH , >AsAs</>AsAs< , and >AsN</>AsAs< systems undoubtedly occur in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ system, since $\text{Me}_2\text{AsAsMe}_2$ and Me_2AsH are present as reaction products. All except >AsN</>NH and >AsN</>AsAs< processes are also present in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ system. Several additional exchange processes involving $(\text{MeAs})_5$ and MeAsH_2 with $\text{Me}_2\text{AsNMe}_2$, $\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$, Me_2NH and Me_2AsH could possibly also be important in influencing the rate of reaction as well as the relative product yields. Therefore, we investigated independently these possible exchange reactions. In each case, a 1:1 mole ratio of potential reactants was studied under the same conditions as in the $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2$ and $\text{MeAsH}_2/\text{Me}_2\text{AsNMe}_2 \cdot \text{BH}_3$ systems. The results are summarized below.

The NMR spectral data of an equimolar mixture of $(\text{MeAs})_5$ and Me_2NH and of $(\text{MeAs})_5$ and MeAsH_2 indicated no reaction over the temperature range of -80 to -10 °C.

$(\text{MeAs})_5$ undergoes exchange with $\text{Me}_2\text{AsAsMe}_2$ at -80 °C to yield $\text{Me}_2\text{As}(\text{AsMe})_x\text{AsMe}_2$ compounds. At -10 °C, the reaction reached equilibrium in 7 days. The NMR intensity data indicate the presence of 74% characterized [38% $(\text{MeAs})_5$, and 36% $\text{Me}_2\text{AsAsMe}_2$] and 26% uncharacterized species in the reaction mixture. These results are in agreement with those of Knoll *et al.* [18] suggesting the formation of equilibrium mixtures of different As-As bonded compounds in which $\text{Me}_2\text{AsAsMe}_2$ and $(\text{MeAs})_5$ predominate because of the relatively large value of the pertinent ring-chain equilibrium constants.

$(\text{MeAs})_5$ reacted slowly with Me_2AsH at -10 °C to yield $\text{Me}_2\text{AsAsMe}_2$, MeAsH_2 and uncharacterized As-As bonded oligomeric species. The intensity data at equilibrium (44 h) indicate the presence of 84% characterized [29% Me_2AsH , 41% $(\text{MeAs})_5$, 5% $\text{Me}_2\text{AsAsMe}_2$, and 9% MeAsH_2] and 16% uncharacterized compounds in solution.

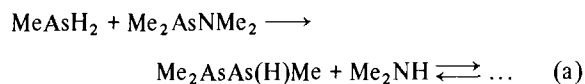
The reaction involving $(\text{MeAs})_5$ and $\text{Me}_2\text{AsNMe}_2$ occurred slowly at -10 °C to produce $\text{Me}_2\text{AsAsMe}_2$, As-As bonded oligomers and unidentified products containing the Me_2N - moiety. At equilibrium (4 days), the intensity data indicate the presence of 81% characterized compounds [10% $\text{Me}_2\text{AsAsMe}_2$, 32% $\text{Me}_2\text{AsNMe}_2$, and 39% $(\text{MeAs})_5$] and 19% uncharacterized species in the reaction mixture.

MeAsH_2 reacted with $\text{Me}_2\text{AsAsMe}_2$ at -80 °C to produce Me_2AsH and As-As bonded oligomers.

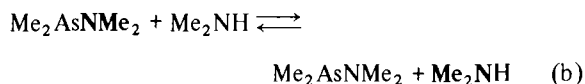
Decoupling of the quartet at $\delta_{\text{H}} = 2.05$ ppm (>AsH) collapsed the $\delta_{\text{H}} = 0.94$ ppm doublet (MeAs<). This suggests the presence of a terminal $\text{Me}(\text{H})\text{As}$ - moiety in an oligomeric compound. At -40 °C, this quartet disappeared with the concomitant appearance of the peaks associated with $(\text{MeAs})_5$. The intensity data at equilibrium (24 h, -10 °C) indicate the presence of 88% characterized [10% MeAsH_2 , 61% Me_2AsH , 10% $\text{Me}_2\text{AsAsMe}_2$ and 7% $(\text{MeAs})_5$] and 12% uncharacterized species in the reaction mixture.

In order to examine the possibility of self exchange of the Me_2As - moiety in $\text{Me}_2\text{AsNMe}_2$, we investigated the reaction of $\text{Me}_2\text{AsNMe}_2$ with $\text{Et}_2\text{AsNEt}_2$. A slow reaction occurred at -80 °C to yield $\text{Me}_2\text{AsNEt}_2$ and $\text{Et}_2\text{AsNMe}_2$. The intensity data (-10 °C) indicate the presence of 23% each of $\text{Et}_2\text{AsNMe}_2$ and $\text{Me}_2\text{AsNEt}_2$ and 27% each of $\text{Me}_2\text{AsNMe}_2$ and $\text{Et}_2\text{AsNEt}_2$ in solution at equilibrium.

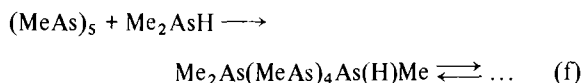
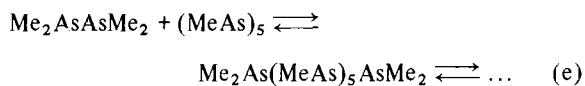
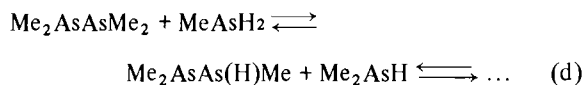
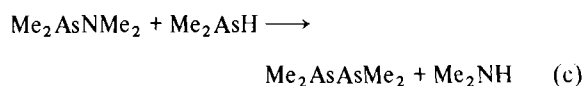
Our studies on the reaction of MeAsH_2 with $\text{Me}_2\text{AsNMe}_2$, (a),



suggest that the exchange process (b)

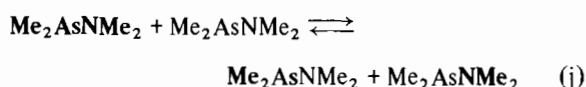
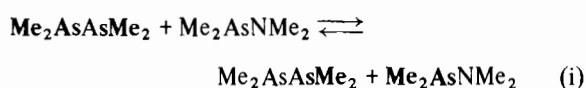
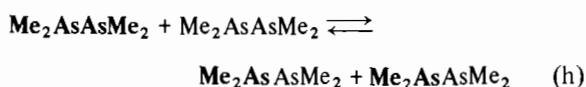
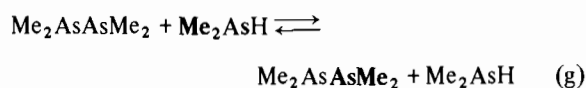


is of prime importance in slowing down the rate of reaction when significant concentrations of $\text{Me}_2\text{AsNMe}_2$ and Me_2NH are present [4]. Processes (c), (d), (e) and (f)

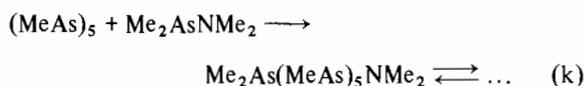


are very significant in increasing the rate of consumption of starting materials and in influencing the relative yields of the products. The faster rate of consumption of $\text{Me}_2\text{AsNMe}_2$ as compared to that of MeAsH_2 in the reaction mixture can be attributed to the occurrence of competitive reactions of MeAsH_2 and Me_2AsH (produced in the reaction mixture) with $\text{Me}_2\text{AsNMe}_2$, processes (a) and (c), respectively. Reaction (c) should be favored over (a), since the

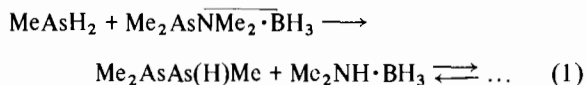
As—H bond strength is lower in Me₂AsH than in MeAsH₂ [19]. Thus, Me₂AsNMe₂ is consumed in reactions (a) and (c); while some of the MeAsH₂ remains unreacted. The reactions represented by equations (g), (h), (i), and (j), undoubtedly occur



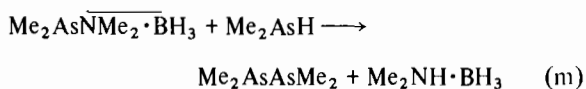
in the reaction mixture. Due to the indistinguishability of reactants and products in these processes, they could not be independently studied using our NMR techniques. Reaction (k) is of no significance under the conditions of the studied reactions.



In the reaction of MeAsH₂ with Me₂AsNMe₂·BH₃, (1),



bonding of BH₃ to Me₂NH and Me₂AsNMe₂ eliminates the occurrence of processes (b), (i), (j) and (k). Those reactions represented by (d), (e), (f), (g), (h), and (m) occur in



the MeAsH₂/Me₂AsNMe₂·BH₃ system and influence the rate of reaction and the relative product yields. Since the reaction of MeAsH₂ with Me₂AsAsMe₂, (d), is more facile than that with Me₂AsNMe₂·BH₃, (1), the Me₂AsAsMe₂ initially produced in the MeAsH₂/Me₂AsNMe₂·BH₃ system is consumed within 4 h at -10 °C. Once the concentration of the MeAsH₂ is sufficiently low and that of the Me₂AsH produced from reactions (d) and (1) sufficiently high, a net

formation of Me₂AsAsMe₂ from competing reactions (m) and (d) is observed. At the point of consumption of the As—N bonded starting material, the Me₂AsH:Me₂AsAsMe₂ stoichiometric ratio was noted to be significantly lower in the MeAsH₂/Me₂AsNMe₂·BH₃ system than in the MeAsH₂/Me₂AsNMe₂ system. This difference in stoichiometric ratios appears to be a consequence of the slower rate of consumption of Me₂AsH in process (m) than in process (c).

In addition to the above delineated exchange processes, several other MeAs</Me₂As—/Me(H)As— moiety exchange reactions involving different oligomeric intermediate compounds are possible in the MeAsH₂/Me₂AsNMe₂ and MeAsH₂/Me₂AsNMe₂·BH₃ systems. These could not be studied independently, since the intermediate oligomers are unstable and unisolable. All the exchange reactions and the various steps that lead to oligomeric As—As bonded species probably involve the formation of a concerted, four-centered activated intermediate [3, 17] which undergoes bond dissociation and formation processes to give the different exchange products observed in the reaction mixtures.

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