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Multinuclear NMR Studies of the Reactions of $MeAsH_2$ with Me_2AsNMe_2 and $Me_2AsNMe_2 \cdot BH_3$

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Abstract

The reactions of $MeAsH_2$ with Me_2AsNMe_2 and $Me_2AsNMe_2 \cdot BH_3$ have been carried out in toluene-d_8 solution as a function of temperature and time. The progress of the reactions was monitored by multinuclear (^1H, ^{11}B, and ^{13}C) NMR spectroscopy over the temperature range of −80 and −10 °C. NMR spectral data analysis suggests the initial formation of an unstable intermediate, $Me_2AsAs(H)Me$, which undergoes multiple condensation reactions to give $(MeAs)_5$. The other products of the reactions are $Me_2AsAsMe_2$, Me_2AsH, $MeAsH_2$, Me_2NH or $Me_2NH \cdot BH_3$ and uncharacterized, condensed, As–As bonded compounds. Several competitive exchange reactions involving compounds capable of exchanging H–, MeAs<, Me_2As–, and Me_2N– 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</–AsH_2, >AsAs</$(MeAs)_5$, $(MeAs)_5$/>AsH and $(MeAs)_5$/–AsH_2 systems have been examined to determine their relative significance in the reactions of $MeAsH_2$ with Me_2AsNMe_2 and its N–B bonded BH_3 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 Me_2AsH with Me_2AsX (X = Cl, Br, I or CN) indicate the reversible nature of these reactions in producing $Me_2AsAsMe_2$ [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 $MeAsH_2$ with $MeAsX_2$ (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 compounds in the reaction mixture. On the basis of a detailed ^1H NMR study [3], the reaction of $MeAsH_2$ with $MeAsI_2$ has been proposed to occur through formation of the unstable Me(H)AsAs(I)Me, which undergoes several condensation reactions with $MeAsH_2$, MeAsHI and $MeAsI_2$ to yield ladder polymers of the general formula $(MeAs)_x$ and several other uncharacterized As–As bonded oligomers.

Recently, we found [4] that Me_2AsH reacts irreversibly with Me_2AsNMe_2 and its N–B bonded BH_3 adduct to give $Me_2AsAsMe_2$. The ^1H, ^{13}C and/or ^{11}B NMR studies of these reactions suggest that the Me_2AsH/Me_2AsNMe_2 reaction proceeds faster initially, but the overall rate of reaction is slower than that of the $Me_2AsH/Me_2AsNMe_2 \cdot BH_3$ reaction. This is a consequence of the presence of mainly an >AsN</>NH exchange process in the Me_2AsH/Me_2AsNMe_2 system that is absent in the Me_2AsH/$Me_2AsNMe_2 \cdot BH_3$ system due to formation of $Me_2NH \cdot BH_3$. 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 $Me_2AsAsMe_2$.

No reports are found in the literature concerning the reactions of primary arsines with dialkylaminodialkylarsines. Therefore, we undertook a multinuclear NMR investigation of the reactions involving the >AsH_2/>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 $MeAsH_2$ with Me_2AsNMe_2 and $Me_2AsNMe_2 \cdot BH_3$. 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], Me_2AsNMe_2 (108 °C) [6], $Me_2AsAsMe_2$ (60 °C/25 torr) [7], $(MeAs)_5$ (178 °C/15 torr) [8], Me_2AsH (36 °C) [9], Me_2AsCl (106 °C) [10], $MeAsH_2$ [11], $Me_2As\overline{NMe_2}\cdot BH_3$ [12], Et_2AsNEt_2 (58 °C/8 torr) [13], and Me_2AsNEt_2 (80.5 °C/90 torr) [14] were synthesized by previously reported methods. Et_2AsNMe_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 Me_2AsNMe_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 $BF_3\cdot OEt_2$, 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 $(MeAs)_5$. 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 Me_2AsNMe_2, $Me_2As\overline{NMe_2}\cdot BH_3$, $Me_2AsAsMe_2$ or $(MeAs)_5$; $(MeAs)_5$ with Me_2NH, Me_2AsH, $Me_2AsAsMe_2$ or Me_2AsNMe_2; and Et_2AsNEt_2 with Me_2AsNMe_2

The reactions of $MeAsH_2$ with equimolar amounts of Me_2AsNMe_2 (2.0 mmol), $Me_2As\overline{NMe_2}\cdot BH_3$ (2.0 mmol), $Me_2AsAsMe_2$ (1.0 mmol) or $(MeAs)_5$ (1.0 mmol); $(MeAs)_5$ with stoichiometric amounts of Me_2NH (1.0 mmol), Me_2AsH (1.0 mmol), $Me_2AsAsMe_2$ (1.0 mmol) or Me_2AsNMe_2 (1.0 mmol); and Et_2AsNEt_2 (1.0 mmol) with Me_2AsNMe_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 X 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 $Me_2As\overline{NMe_2}\cdot BH_3$ [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

$(MeAs)_5$: 1.54, 1.50 and 1.48. $Me_2AsAsMe_2$: 0.96. Me_2AsNMe_2: 0.79 (Me_2As) and 2.42 (Me_2N). $Me_2As\overline{NMe_2}\cdot BH_3$: 0.82 ($Me_2As$) and 2.09 ($Me_2N$). Et_2AsNEt_2: 1.00 ($\mathbf{CH_3}CH_2N$, t, $^3J(HH) = 7.1$), 2.86 ($CH_3\mathbf{CH_2}N$, q), and 1.04–1.48 ($\mathbf{CH_3CH_2}As$, m). Et_2AsNMe_2: 1.01–1.52 (CH_3CH_2As, m), and 2.55 (Me_2N). Me_2AsNEt_2: 0.85 (Me_2As), 0.97 ($\mathbf{CH_3}CH_2N$, t, $^3J(HH) = 7.1$) and 2.80 ($CH_3\mathbf{CH_2}N$, q). Me_2AsH: 0.77 (Me_2As, d, $^3J(HH) = 7.0$ Hz) and 2.39 (AsH, s). Me_2NH: 2.17. $Me_2NH\cdot BH_3$: 1.96 (Me_2N, d, $^3J(HH) = 5.7$ Hz) and 3.99 (NH, q). $MeAsH_2$: 0.69 (MeAs, t, $^3J(HH) = 7.2$ Hz) and 1.96 (AsH_2, q).

^{11}B Spectral Data

$Me_2As\overline{NMe_2}\cdot BH_3$: −11.36 (q, $^1J(B–H) = 98.7$ Hz). $Me_2NH\cdot BH_3$: −14.05 (q, $^1J(B–H) = 97.7$ Hz).

^{13}C Spectral Data

$(MeAs)_5$: 3.78, 5.23, and 6.81 ($^1J(CH) = 134.9$ Hz). $Me_2AsAsMe_2$: 5.94 ($^1J(CH) = 132.6$ Hz). Me_2AsNMe_2: 9.70 (Me_2As, $^1J(CH) = 130.6$ Hz, $^3J(CH) = 4.0$ Hz) and 41.92 (Me_2N, $^1J(CH) = 132.7$ Hz, $^3J(CH) = 5.3$ Hz). $Me_2As\overline{NMe_2}\cdot BH_3$: 12.63 ($Me_2As$, $^1J(CH) = 132.7$ Hz) and 47.76 (Me_2N, $^1J(CH) = 138.4$ Hz). Et_2AsNEt_2: 10.56 ($\mathbf{CH_3}CH_2As$, $^1J(CH) = 126.4$), 20.84 ($CH_3\mathbf{CH_2}As$, $^1J(CH) = 130.6$), 16.19 ($\mathbf{CH_3}CH_2N$, $^1J(CH) = 124.9$, $^2J(CH) = 2.4$ Hz) and 44.49 ($CH_3\mathbf{CH_2}N$, $^1J(CH) = 132.2$, $^{2,3}J(CH) = 4.64$). Et_2AsNMe_2: 10.51 ($\mathbf{CH_3}CH_2As$, $^1J(CH) = 126.4$), 19.50 ($CH_3\mathbf{CH_2}As$, $^1J(CH) = 130.6$ Hz), and 42.58 (Me_2N, $^1J(CH) = 132.6$ Hz, $^3J(CH) = 5.2$ Hz). Me_2AsNEt_2: 11.99 (Me_2As, $^1J(CH) = 130.3$ Hz, $^3J = 4.0$ Hz), 15.51 ($\mathbf{CH_3}CH_2N$, $^1J(CH) = 125.1$ Hz, $^2J(CH) = 2.4$ Hz), and 43.94 ($CH_3\mathbf{CH_2}N$, $^1J(CH) = 132.2$ Hz, $^{2,3}J = 4.7$ Hz). Me_2AsH: 1.43 ppm ($^1J(CH) = 132.5$ Hz, $^{2,3}J(CH) = 3.0$ Hz). Me_2NH: 38.87 ($^1J(CH) = 131.9$ Hz and $^3J(CH) = 6.0$ Hz). $Me_2NH\cdot BH_3$: 43.82 ($^1J(CH) = 138.7$ Hz, $^{2,3}J(CH) = 4.6$ Hz). $MeAsH_2$: −8.74 ($^1J(CH) = 134.4$ Hz, $^{2,3}J(CH) = 3.0$ Hz).

Results and Discussion

Reaction of $MeAsH_2$ with Me_2AsNMe_2

The ^1H and ^{13}C NMR spectra of an equimolar mixture of $MeAsH_2$ and Me_2AsNMe_2 in toluene-d_8

solution showed no reaction over the temperature range of −80 to −20 ℃. After 20 min at −10 ℃, low intensity peaks were observed due to Me_2NH, Me_2AsH, $Me_2AsAsMe_2$ and uncharacterized As–As bonded oligomeric compounds. The ^1H NMR peaks assigned to the Me_2N-moieties of Me_2AsNMe_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 $(MeAs)_5$ 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 $(MeAs)_5$, $Me_2AsAsMe_2$, Me_2AsH and Me_2NH increased; the line width of the Me_2N ^1H NMR peak narrowed as more Me_2AsNMe_2 was consumed; and the intensities of the resonances assigned to Me_2AsNMe_2 and $MeAsH_2$ decreased. A disproportionate decrease in the intensities of the Me_2AsNMe_2 peaks in comparison to those of $MeAsH_2$ was noted. After 23 h, all of the Me_2AsNMe_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 $Me_2AsAsMe_2$ and $MeAsH_2$ with a concomitant increase in the intensities of the $(MeAs)_5$ 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 $\delta_C = -3.69, 0.38, 7.08, 7.19, 7.57$ and 8.78 ppm and $\delta_H = 0.91, 0.93, 0.95, 1.02, 1.05$ 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% $Me_2AsAsMe_2$, 5% $(MeAs)_5$ 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 $MeAsH_2/MeAsI_2$ system [3] suggest that the overall reaction of $MeAsH_2$ with Me_2AsNMe_2 to give $(MeAs)_5$ 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, $Me_2AsAs(H)Me$, form. The latter then undergoes a facile exchange to yield the symmetrical diarsines, $Me_2AsAsMe_2$ and $Me(H)AsAs(H)Me$.

$$MeAsH_2 + Me_2AsNMe_2 \longrightarrow Me_2NH + Me_2AsAs(H)Me$$

$$2Me_2AsAs(H)Me \longrightarrow Me_2AsAsMe_2 + Me(H)AsAs(H)Me$$

Subsequent condensation and exchange reactions give Me_2AsH and the $Me(H)As(AsMe)_xAs(H)Me$ species, which cyclize via $MeAsH_2$ elimination to $(MeAs)_5$.

This formation of $Me(H)AsAs(H)Me$ and $Me(H)As(AsMe)_xAs(H)Me$ is analogous to that of $Me(H)AsAs(I)Me$ and $Me(H)As(AsMe)_xAs(I)Me$ as proposed [3] in the $MeAsH_2/MeAsI_2$ system. Several competing exchange equilibria that involve reactants, different intermediate species, and products (discussed below) influence the relative rates of consumption of Me_2AsNMe_2, $Me_2AsAsMe_2$, $MeAsH_2$, and Me_2AsH at different stages of $(MeAs)_5$ formation; the stoichiometric ratios of the products; and the Me_2N-moiety spectral line width.

Reaction of $MeAsH_2$ with $\overline{Me_2AsNMe_2}\cdot BH_3$

The ^1H, ^{11}B, and ^{13}C NMR spectra of an equimolar mixture of $MeAsH_2$ and $\overline{Me_2AsNMe_2\cdot B}H_3$ in toluene-d_8 solution also showed no reaction over the −80 to −20 ℃ temperature range. After 30 min at −10 ℃, very low intensity NMR peaks assignable to $Me_2NH\cdot BH_3$, $Me_2AsAsMe_2$, 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 $Me_2AsAsMe_2$. The $Me_2AsAsMe_2$ peak then reappeared after $17\frac{1}{2}$ h and the presence of new resonances assignable to $(MeAs)_5$ was observed.

No significant spectral changes were noted after 40 h when all the $\overline{Me_2AsNMe_2\cdot B}H_3$ was consumed. The ^1H NMR intensity data indicate the presence of 86% characterized [9% $MeAsH_2$, 23% Me_2AsH, 3% $Me_2AsAsMe_2$, 3% $(MeAs)_5$ and 48% $Me_2NH\cdot BH_3$] 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 $MeAsH_2/Me_2AsNMe_2$ reaction and assigned to As–As bonded oligomers.

These results suggest that the reaction of $MeAsH_2$ with $\overline{Me_2AsNMe_2\cdot B}H_3$ yields $Me_2\overline{NH\cdot B}H_3$ and all the arsenic-containing products observed in the $MeAsH_2/Me_2AsNMe_2$ 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 $\overline{Me_2AsNMe_2\cdot B}H_3$ relative to that of Me_2AsNMe_2 in the $MeAsH_2/Me_2AsNMe_2$ 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 $\overline{Me_2AsNMe_2\cdot B}H_3$ or Me_2AsNMe_2 indicates a significantly lower Me_2AsH:$Me_2AsAsMe_2$ ratio for the $MeAsH_2/\overline{Me_2AsNMe_2\cdot B}H_3$ system than for the $MeAsH_2/Me_2AsNMe_2$ system.

This suggests that the bonding of the $\mathrm{BH_3}$ to the nitrogen atom in $\mathrm{Me_2AsNMe_2 \cdot BH_3}$ also diminishes the relative significance of exchange processes (see discussion below) that involved $\mathrm{Me_2AsNMe_2}$ 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 $\mathrm{MeAsH_2/Me_2AsNMe_2}$ system, since $\mathrm{Me_2AsAsMe_2}$ and $\mathrm{Me_2AsH}$ are present as reaction products. All except >AsN</>NH and >AsN</>AsAs< processes are also present in the $\mathrm{MeAsH_2/Me_2AsNMe_2 \cdot BH_3}$ system. Several additional exchange processes involving $\mathrm{(MeAs)_5}$ and $\mathrm{MeAsH_2}$ with $\mathrm{Me_2AsNMe_2}$, $\mathrm{Me_2AsNMe_2 \cdot BH_3}$, $\mathrm{Me_2NH}$ and $\mathrm{Me_2AsH}$ 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 $\mathrm{MeAsH_2/Me_2AsNMe_2}$ and $\mathrm{MeAsH_2/Me_2AsNMe_2 \cdot BH_3}$ systems. The results are summarized below.

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

$\mathrm{(MeAs)_5}$ undergoes exchange with $\mathrm{Me_2AsAsMe_2}$ at −80 °C to yield $\mathrm{Me_2As(AsMe)_xAsMe_2}$ compounds. At −10 °C, the reaction reached equilibrium in 7 days. The NMR intensity data indicate the presence of 74% characterized [38% $\mathrm{(MeAs)_5}$, and 36% $\mathrm{Me_2AsAsMe_2}$] 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 $\mathrm{Me_2AsAsMe_2}$ and $\mathrm{(MeAs)_5}$ predominate because of the relatively large value of the pertinent ring–chain equilibrium constants.

$\mathrm{(MeAs)_5}$ reacted slowly with $\mathrm{Me_2AsH}$ at −10 °C to yield $\mathrm{Me_2AsAsMe_2}$, $\mathrm{MeAsH_2}$ and uncharacterized As–As bonded oligomeric species. The intensity data at equilibrium (44 h) indicate the presence of 84% characterized [29% $\mathrm{Me_2AsH}$, 41% $\mathrm{(MeAs)_5}$, 5% $\mathrm{Me_2AsAsMe_2}$, and 9% $\mathrm{MeAsH_2}$] and 16% uncharacterized compounds in solution.

The reaction involving $\mathrm{(MeAs)_5}$ and $\mathrm{Me_2AsNMe_2}$ occurred slowly at −10 °C to produce $\mathrm{Me_2AsAsMe_2}$, As–As bonded oligomers and unidentified products containing the $\mathrm{Me_2N}$– moiety. At equilibrium (4 days), the intensity data indicate the presence of 81% characterized compounds [10% $\mathrm{Me_2AsAsMe_2}$, 32% $\mathrm{Me_2AsNMe_2}$, and 39% $\mathrm{(MeAs)_5}$] and 19% uncharacterized species in the reaction mixture.

$\mathrm{MeAsH_2}$ reacted with $\mathrm{Me_2AsAsMe_2}$ at −80 °C to produce $\mathrm{Me_2AsH}$ and As–As bonded oligomers. Decoupling of the quartet at $\delta_H = 2.05$ ppm (>AsH) collapsed the $\delta_H = 0.94$ ppm doublet (MeAs<). This suggests the presence of a terminal Me(H)As– moiety in an oligomeric compound. At −40 °C, this quartet disappeared with the concomitant appearance of the peaks associated with $\mathrm{(MeAs)_5}$. The intensity data at equilibrium (24 h, −10 °C) indicate the presence of 88% characterized [10% $\mathrm{MeAsH_2}$, 61% $\mathrm{Me_2AsH}$, 10% $\mathrm{Me_2AsAsMe_2}$ and 7% $\mathrm{(MeAs)_5}$] and 12% uncharacterized species in the reaction mixture.

In order to examine the possibility of self exchange of the $\mathrm{Me_2As}$– moiety in $\mathrm{Me_2AsNMe_2}$, we investigated the reaction of $\mathrm{Me_2AsNMe_2}$ with $\mathrm{Et_2AsNEt_2}$. A slow reaction occurred at −80 °C to yield $\mathrm{Me_2AsNEt_2}$ and $\mathrm{Et_2AsNMe_2}$. The intensity data (−10 °C) indicate the presence of 23% each of $\mathrm{Et_2AsNMe_2}$ and $\mathrm{Me_2AsNEt_2}$ and 27% each of $\mathrm{Me_2AsNMe_2}$ and $\mathrm{Et_2AsNEt_2}$ in solution at equilibrium.

Our studies on the reaction of $\mathrm{MeAsH_2}$ with $\mathrm{Me_2AsNMe_2}$, (a),

$$\mathrm{MeAsH_2 + Me_2AsNMe_2 \longrightarrow Me_2AsAs(H)Me + Me_2NH} \rightleftarrows \ldots \qquad \text{(a)}$$

suggest that the exchange process (b)

$$\mathrm{Me_2As\mathbf{NMe_2} + Me_2NH} \rightleftarrows \mathrm{Me_2AsNMe_2 + \mathbf{Me_2NH}} \qquad \text{(b)}$$

is of prime importance in slowing down the rate of reaction when significant concentrations of $\mathrm{Me_2AsNMe_2}$ and $\mathrm{Me_2NH}$ are present [4]. Processes (c), (d), (e) and (f)

$$\mathrm{Me_2AsNMe_2 + Me_2AsH \longrightarrow Me_2AsAsMe_2 + Me_2NH} \qquad \text{(c)}$$

$$\mathrm{Me_2AsAsMe_2 + MeAsH_2} \rightleftarrows \mathrm{Me_2AsAs(H)Me + Me_2AsH} \rightleftarrows \ldots \qquad \text{(d)}$$

$$\mathrm{Me_2AsAsMe_2 + (MeAs)_5} \rightleftarrows \mathrm{Me_2As(MeAs)_5AsMe_2} \rightleftarrows \ldots \qquad \text{(e)}$$

$$\mathrm{(MeAs)_5 + Me_2AsH \longrightarrow Me_2As(MeAs)_4As(H)Me} \rightleftarrows \ldots \qquad \text{(f)}$$

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 $\mathrm{Me_2AsNMe_2}$ as compared to that of $\mathrm{MeAsH_2}$ in the reaction mixture can be attributed to the occurrence of competitive reactions of $\mathrm{MeAsH_2}$ and $\mathrm{Me_2AsH}$ (produced in the reaction mixture) with $\mathrm{Me_2AsNMe_2}$, processes (a) and (c), respectively. Reaction (c) should be favored over (a), since the

As–H bond strength is lower in Me_2AsH than in $MeAsH_2$ [19]. Thus, Me_2AsNMe_2 is consumed in reactions (a) and (c); while some of the $MeAsH_2$ remains unreacted. The reactions represented by equations (g), (h), (i), and (j), undoubtedly occur

$$Me_2AsAsMe_2 + \mathbf{Me_2}\mathrm{AsH} \rightleftarrows Me_2As\mathbf{AsMe_2} + Me_2AsH \qquad (g)$$

$$\mathbf{Me_2AsAsMe_2} + Me_2AsAsMe_2 \rightleftarrows \mathbf{Me_2As}AsMe_2 + \mathbf{Me_2As}AsMe_2 \qquad (h)$$

$$\mathbf{Me_2AsAsMe_2} + Me_2AsNMe_2 \rightleftarrows Me_2As\mathbf{AsMe_2} + \mathbf{Me_2As}NMe_2 \qquad (i)$$

$$\mathbf{Me_2AsNMe_2} + Me_2AsNMe_2 \rightleftarrows \mathbf{Me_2}AsNMe_2 + Me_2As\mathbf{NMe_2} \qquad (j)$$

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.

$$(MeAs)_5 + Me_2AsNMe_2 \longrightarrow Me_2As(MeAs)_5NMe_2 \rightleftarrows \ldots \qquad (k)$$

In the reaction of $MeAsH_2$ with $Me_2As\overline{NMe_2\cdot B}H_3$, (l),

$$MeAsH_2 + Me_2As\overline{NMe_2\cdot B}H_3 \longrightarrow Me_2AsAs(H)Me + Me_2NH\cdot BH_3 \rightleftarrows \ldots \qquad (l)$$

bonding of BH_3 to Me_2NH and Me_2AsNMe_2 eliminates the occurrence of processes (b), (i), (j) and (k). Those reactions represented by (d), (e), (f), (g), (h), and (m) occur in

$$Me_2As\overline{NMe_2\cdot B}H_3 + Me_2AsH \longrightarrow Me_2AsAsMe_2 + Me_2NH\cdot BH_3 \qquad (m)$$

the $MeAsH_2/Me_2As\overline{NMe_2\cdot B}H_3$ system and influence the rate of reaction and the relative product yields. Since the reaction of $MeAsH_2$ with $Me_2AsAsMe_2$, (d), is more facile than that with $Me_2As\overline{NMe_2\cdot B}H_3$, (l), the $Me_2AsAsMe_2$ initially produced in the $MeAsH_2/Me_2As\overline{NMe_2\cdot B}H_3$ system is consumed within 4 h at −10 °C. Once the concentration of the $MeAsH_2$ is sufficiently low and that of the Me_2AsH produced from reactions (d) and (l) sufficiently high, a net formation of $Me_2AsAsMe_2$ from competing reactions (m) and (d) is observed. At the point of consumption of the As–N bonded starting material, the Me_2AsH:$Me_2AsAsMe_2$ stoichiometric ratio was noted to be significantly lower in the $MeAsH_2/Me_2As\overline{NMe_2\cdot B}H_3$ system than in the $MeAsH_2/Me_2AsNMe_2$ system. This difference in stoichiometric ratios appears to be a consequence of the slower rate of consumption of Me_2AsH in process (m) than in process (c).

In addition to the above delineated exchange processes, several other $MeAs\langle/Me_2As–/Me(H)As–$ moiety exchange reactions involving different oligomeric intermediate compounds are possible in the $MeAsH_2/Me_2AsNMe_2$ and $MeAsH_2/Me_2As\overline{NMe_2\cdot B}H_3$ 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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