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NMR Studies of the Reaction of $MeAsH_2$ with $Me_2AsAsMe_2$

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The studies of the reactions of primary and secondary organo-arsines with As–N and As–As bonded compounds have been of continued interest to us with most of the attention being directed toward reactivity with As–N bonded systems [1–4]. These results establish the fact that the As–H bond undergoes facile reactions with As–N bonded compounds. Recently, we reported a novel route [2] for the preparation of $Me_2AsAsMe_2$ from the reaction of Me_2AsH with Me_2AsNMe_2.

There are no reports in the literature on the reactivities of primary arsines with As–As bonded compounds, except in our recent report [3] on the reaction mechanism of the $MeAsH_2/Me_2AsNMe_2$ system. Thus, we have undertaken a systematic study of the reactions of primary arsines with As–As bonded compounds to elucidate the mechanism of these reactions and to understand the effects that various substituents may have on the course of the reactions. Herein, we report a ^1H and ^{13}C NMR study of the reaction of $MeAsH_2$ with $Me_2AsAsMe_2$ in toluene-d_8 solution.

Standard high vacuum line techniques and a Vacuum Atmospheres Model HE-43 Dri-lab equipped with a Model HE-493 Dri-train were used for storing and handling of all compounds. Toluene-d_8 and Me_4Si were purchased from Aldrich Chemical Company and were stored over molecular sieves. $Me_2AsAsMe_2$, (60 °C/25 torr) [2, 5], $(MeAs)_5$ (178 °C/15 torr) [6, 7], Me_2AsH (36 °C) [8], and $MeAsH_2$ [9] were synthesized by reported methods. The purity of all compounds was checked by NMR spectroscopy prior to use. All the reactions were protected from exposure to light to minimize photochemical side reactions involving $(MeAs)_5$ [6]. Care was also taken to ensure that the exchange processes were not acid catalyzed by carrying out reactions in NMR tubes that were not acid washed.

^1H and ^{13}C NMR spectra were recorded on a Nicolet 300 MHz multinuclear FT NMR spectrometer operating at 300.1 and 75.4 MHz, respectively. ^1H and ^{13}C NMR chemical shifts were measured with respect to tetramethylsilane as an internal reference. The following ^1H and ^{13}C NMR spectral data (δ, ppm (TMS)) in toluene-d_8 solution were determined in this laboratory on independently synthesized compounds identified in the reaction mixture at −10 °C. ^1H NMR data: $MeAsH_2$: 0.69 (MeAs, t, $^3J(HH) = 7.2$ Hz) and 1.96 (AsH_2, q). Me_2AsH: 0.77 (Me_2As, d, $^3J(HH) = 7.0$ Hz) and 2.39 (AsH, septet). $Me_2AsAsMe_2$: 0.96. $(MeAs)_5$: 1.54, 1.50 and 1.48. ^{13}C NMR Data: $MeAsH_2$: −8.74 ($^1J(CH) = 134.4$ Hz). Me_2AsH: 1.43 ($^1J(CH) = 132.5$ Hz). $Me_2AsAsMe_2$: 5.94 ($^1J(CH) = 132.6$ Hz). $(MeAs)_5$: 3.78, 5.23 and 6.81 ($^1J(CH) = 134.9$ Hz).

The reactions of $MeAsH_2$ (1.0 mmol) with equimolar amounts of $Me_2AsAsMe_2$ or $(MeAs)_5$ and $(MeAs)_5$ (1.0 mmol) with equimolar amounts of Me_2AsH or $Me_2AsAsMe_2$ were carried out in toluene-d_8 solution using the following procedure. The appropriate amount of the less volatile compound dissolved in toluene-d_8 and a drop of TMS were added to the NMR tube (10 mm × 22.5 cm; pyrex) equipped with a greaseless vacuum stopcock. The tube was degassed using standard vacuum line techniques. At liquid nitrogen temperature, an equimolar amount of the more volatile compound was condensed into the NMR tube. The total volume of the solution was maintained at 4.0 ml. The tube was sealed, agitated gently at −95 °C (toluene slush), and inserted into the precooled (−90 °C) probe of the NMR spectrometer. The reaction was then followed at the selected temperatures by recording the ^1H and ^{13}C NMR spectra as a function of time.

The $MeAsH_2/Me_2AsAsMe_2$ system was monitored over the temperature range of −80 to −10 °C as a function of time. The NMR study was restricted to −10 °C due to the low boiling point of $MeAsH_2$ [9]. The ^1H and ^{13}C NMR spectra at −80 °C consisted of very low intensity peaks assignable to Me_2AsH and uncharacterized As–As bonded compounds and high intensity resonances due to the reactants. Homonuclear ^1H NMR decoupling experiments indicated the presence of a terminal Me(H)As– moiety in the oligomeric species with $\delta H = 0.94$ ppm (MeAs<, d, $^3J(HH) = 7.2$ Hz) and $\delta H = 2.05$ ppm (>AsH, q).

By −40 °C, the peaks attributed to the Me(H)As– moiety in the −80 °C ^1H NMR spectrum disappeared and three low intensity peaks assigned to $(MeAs)_5$ [10] appeared in both the ^1H and ^{13}C NMR spectra.

The reaction was then followed at −10 °C. As the reaction progressed, the intensities of the peaks corresponding to $(MeAs)_5$, Me_2AsH, and uncharacterized As–As bonded compound increased and the intensities of the resonances assigned to $Me_2AsAsMe_2$ and $MeAsH_2$ decreased. After 24 h the ^1H and ^{13}C NMR spectra indicated that the overall reaction mixture achieved equilibrium. Very low intensity peaks observed in the spectra ($\delta H = 0.86$, 0.91, 0.93, 0.94,

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1.01, 1.03 and 1.09 and $\delta C = -3.72$, 0.36, 7.05, 7.26, 7.56, and 8.75 ppm) are attributed to $MeAs<$ moieties of uncharacterized As–As bonded oligomers. At equilibrium, the ^1H NMR intensity data indicated the presence of 88% characterized [10% $MeAsH_2$, 61% Me_2AsH, 10% $Me_2AsAsMe_2$ and 7% $(MeAs)_5$] and 12% uncharacterized species.

We propose that the reaction of $MeAsH_2$ with $Me_2AsAsMe_2$ involves the formation of a concerted, four-centered activated intermediate [11, 12] which undergoes As–As and As–H bond dissociation and formation to yield Me_2AsH and the unstable intermediate $Me_2AsAs(H)Me$ (eqn. (1)).

$$MeAsH_2 + Me_2AsAsMe_2 \longrightarrow Me_2AsH + Me_2AsAs(H)Me \qquad (1)$$

The latter can then undergo self-exchange [4] to give the symmetrical diarsines, $Me_2AsAsMe_2$ and $Me(H)AsAs(H)Me$ (eqn. (2)).

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

Subsequent condensation reactions involving different reactants and products can then yield the $Me(H)As(AsMe)_xAs(H)Me$ species which may cyclize via $MeAsH_2$ elimination to form $(MeAs)_5$. The formation of $Me(H)AsAs(H)Me$, $Me(H)As(AsMe)_xAsH(Me)$, and analogous intermediates has been proposed for the $MeAsH_2/Me_2AsNMe_2$ [3] and $MeAsH_2/MeAsI_2$ [11, 13] systems.

Several reactions involving different reactants/intermediates/products could possibly be important in influencing the rate of reaction as well as the relative product yields. Therefore, we investigated independently the following possible reaction systems under conditions analogous to those in the $MeAsH_2/Me_2AsAsMe_2$ system.

The ^1H NMR data of an equimolar mixture of $(MeAs)_5$ with $MeAsH_2$ indicated no reaction over the temperature range of −80 to −10 °C.

The NMR spectral data for the $(MeAs)_5/Me_2AsH$ system indicated a slow reaction at −10 °C to yield $Me_2AsAsMe_2$, $MeAsH_2$, and uncharacterized As–As bonded oligomers. The ^1H NMR intensity data at equilibrium (44 h) indicated the presence of 84% characterized (29% Me_2AsH, 41% $(MeAs)_5$, 5% $Me_2AsAsMe_2$ and 9% $MeAsH_2$) and 16% uncharacterized compounds.

The NMR spectral data of the $(MeAs)_5/Me_2AsAsMe_2$ reaction system indicated reactivity at −80 °C to give $Me_2As(AsMe)_xAsMe_2$ species [14]. As the temperature was raised slowly to −10 °C, more oligomeric species formed. Equilibrium was attained in 7 days. The ^1H NMR intensity data indicate the presence of 74% characterized (38% $(MeAs)_5$, 36% $Me_2AsAsMe_2$) and 26% uncharacterized As–As bonded compounds.

Our investigations suggest that $MeAsH_2$ undergoes a facile exchange reaction with $Me_2AsAsMe_2$ to yield an equilibrium mixture of $(MeAs)_5$, $Me_2AsAsMe_2$, Me_2AsH, $MeAsH_2$, and uncharacterized As–As bonded compounds. The overall reaction to produce $(MeAs)_5$ appears to be complex and involves multiple condensation reactions and competing exchange equilibria. For example, reactions involving the $(MeAs)_5/Me_2AsH$ and $(MeAs)_5/Me_2AsAsMe_2$ systems should occur in the reaction mixture. These competing reactions influence the rate of formation of $(MeAs)_5$ as well as yield.

Possibly other reactions may occur and influence the overall rate of reaction because of the demonstrated lability of the As–As and As–H bonds [2–4, 15, 16]. For example, exchange equilibria involving the $MeAs</Me_2As-/Me(H)As-$ moieties on the different intermediate oligomeric compounds would not be unexpected. Such reactions could not be studied independently, since there is insufficient spectroscopic information to characterize the various individual intermediate oligomers in solution. Furthermore, the intermediates could not be isolated by conventional separation methods, because of the multiple temperature-dependent equilibria involved [16].

The fact that $MeAsH_2$ readily reacts with $Me_2AsAsMe_2$ at −80 °C, while no reaction occurs up to −20 °C with Me_2AsNMe_2 [3], suggests that the As–As bond is more labile toward reaction with the As–H bond than with the As–N bond. The $>AsH_2/$ $>AsAs<$ system is being studied further to determine the electronic and steric effects that various substituents have on the stability of the different intermediates and the course of the reaction.

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