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# Dynamic NMR Study of Dimethylarsenic Condensation Reactions

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*Dimethylarsine, $(CH_3)_2AsH$, and dimethylhalo(or pseudohalo)arsines, $(CH_3)_2AsX$, X = Cl, Br, I or CN, reversibly form tetramethyldiarsine and HX in benzene. As followed by pmr spectroscopy, several pmr-rapid processes are observed which involve the exchange of parts among equilibrium components. Where available, equilibrium and thermodynamic parameters have been obtained. The activational parameters for the exchange processes suggest that exchange occurs through an associative intermediate. When X = Br or I, significant quantities of $H_2$ are also found.*

## Introduction

Primary organoarsenic hydrides and halides combine to form a large variety of condensed, As–As bonded products. Accompanying these reactions is a complex series of interrelated equilibria involving the exchange of many different groups among monomers, oligomers and polymers. The reaction of methylarsine, $CH_3AsH_2$, with methyldihaloarsine, $CH_3AsX_2$, in benzene, for instance, can generate simultaneously in solution compounds capable of exchanging hydrogen, $CH_3As<$ units, and/or halogen: $CH_3AsH_2$, $CH_3AsHX$, $CH_3AsX_2$, HX, variously-substituted dimethyldiarsines, and higher polymethylpolyarsines in both ring and chain modifications [1, 2]. To increase our understanding of these equilibria, we have studied the related reactions of secondary methylarsenic compounds where functionality necessarily constrains condensation to dimer (diarsine) species, thereby reducing considerably the number of simultaneous equilibria requiring individual characterization.

Dehn first observed that the reaction of dimethylarsine and dimethylchloroarsine at 100 °C produced tetramethyldiarsine and hydrogen chloride in unknown yield [3]:

$$(CH_3)_2AsH + (CH_3)_2AsCl \longrightarrow (CH_3)_2AsAs(CH_3)_2 + HCl$$

Cullen has obtained a 26% yield of tetramethyldiarsine by the same reaction, but also observed the formation of hydrogen which could not be explained by either a thermal decomposition of dimethylarsine, or by the reaction of hydrogen chloride and dimethylarsine, both reactions having been independently studied and found not to produce hydrogen [4]. Diphenylarsine and diphenylhaloarsine form tetraphenyldiarsine in good yield but the reaction was not studied under conditions where hydrogen production could have been detected [5]. A 51% yield of tetrakis(trifluoromethyl)diarsine was obtained from the bis(trifluoromethyl)arsenic chloride and hydride [4]; no hydrogen was observed.

## Results and Discussion

In the present study the reactions of $(CH_3)_2AsH$ and $(CH_3)_2AsX$, X = Cl, Br, I, CN, were followed in benzene (approx. 10% solutions) in sealed nmr tubes at several molar ratios by periodic monitoring of pmr spectra. The samples were maintained at 30 °C until no further evidence of chemical change was seen (one to six months). The tubes were then opened and products fractionated. Fractionation proved unsatisfactory for quantitative product analysis due to extensive volatility-controlled redistribution of equilibrium components. The pmr spectra of the systems containing initially equimolar quantities of $(CH_3)_2AsH$ and $(CH_3)_2AsX$ display features found in all of the investigated systems and is shown in Fig. 1. For all systems, from evidence cited below, equilibrium (1) is established upon combination.

$$(CH_3)_2AsH + (CH_3)_2AsX \rightleftharpoons (CH_3)_2AsAs(CH_3)_2 + HX \qquad (1)$$

X = Cl, Br, I or CN

Identical spectra for a given As:X ratio are obtained by approaching the equilibrium from the right through the combination of tetramethyldiarsine and HX.

Several features of these spectra require further explanation. For the halogen systems, but not for cyanide, the anticipated doublet multiplicity for

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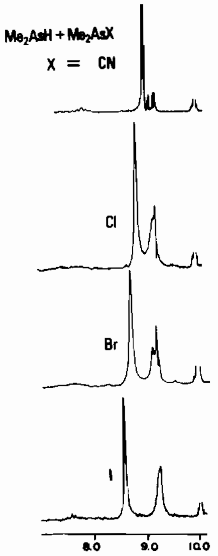

Figure 1. Equilibrium pmr spectra of initially equimolar mixtures of $(CH_3)_2AsH$ and $(CH_3)_2AsX$ as 10% benzene solutions. The peak between τ8.0 and τ9.0 represents the averaged chemical shift of $(CH_3)_2AsX$ and $(CH_3)_2AsAs(CH_3)_2$. At about τ9.2 is the methyl-group resonance for $(CH_3)_2AsH$ showing in some cases the anticipated doublet multiplicity. The sharp peak at τ9.24 is $(CH_3)_3As$ (see text).

$(C\underline{H}_3)_2AsH$ is collapsed to a singlet or is a very broadened doublet, a result identical to that seen in primary arsine reactions and explicable by an nmr-fast hydrogen exchange between dimethylarsine and hydrogen halide [1].

$$(CH_3)_2AsH + H'X \rightleftharpoons (CH_3)_2AsH' + HX \tag{2}$$

If, to a system containing an excess of dimethylarsine, is added a quantity of pyridine sufficient to precipitate all HX formed in eq 1, then eq 1 is shifted entirely to the right and the doublet multiplicity returns to the dimethylarsine spectrum.

Also as a result of eq 2, the nmr signals for the exchanging hydrogen atoms are absent from the spectrum due to extensive line broadening, *i.e.*, both the HX and $(CH_3)_2As\underline{H}$ resonances have merged with the baseline (under favorable circumstances the AsH proton signal can, nonetheless, be integrated). For the cyanide system, both HCN and $(CH_3)_2As\underline{H}$ resonances are clearly seen (the AsH heptet still shows some line broadening due to incomplete quadrupolar relaxation of the $^{75}As$ nucleus, $I = 3/2$).

The cyanide system is, therefore, distinguished from the halogen systems by a very large equilibrium constant (greater than 100 at 30 °C) for eq 1; whichever of the two starting materials, $(CH_3)_2AsH$ or $(CH_3)_2AsCN$, was the limiting reagent, it was not spectroscopically detectable. For the halogen systems the equilibrium constant is always less than 1.0 at 30 °C, *i.e.*, eq 1 favors starting materials for X = Cl, Br or I. Furthermore, eq 2 for X = CN appears to be too slow to cause a collapse in doublet multiplicity in systems containing excess $(CH_3)_2AsH$. Both of these features of eq 1 and 2 which differ markedly for X = CN are explicable by the differences in the HX bond energies [6] (HI, 295 kJ $mol^{-1}$; HBr, 362; HCl, 428; and HCN, 531).

The formation of hydrogen through the interaction of HX and $(CH_3)_2AsH$ was measured by opening the nmr tubes at various times in a calibrated volume at −196 °C. At a time when no further chemical change was observed in the pmr spectra, no non-condensable pressure was observed for X = CN, an immeasurably small amount for X = Cl, and 5.1 and 15.3% of the theoretical yield of hydrogen (eq 3) for X = Br and I, respectively. The rate of $H_2$ production is very much slower than the rate of proton-proton exchange. The yield of hydrogen depends upon both the availability of excess dimethylarsine and hydrogen halide produced in eq 1 according to the equation:

$$\begin{aligned} &(CH_3)_2AsH + HX \overset{a}{\rightleftharpoons} [(CH_3)_2AsH\cdot HX \\ &\text{or} \\ &(CH_3)_2AsH_2{}^+X^-] \overset{b}{\rightleftharpoons} (CH_3)_2AsX + H_2 \end{aligned} \tag{3}$$

Since it is evident that both HX and $(CH_3)_2AsH$ can still be present in significant quantities after chemical change has ceased, the inability of the system to produce the maximum yield of hydrogen could indicate that, contrary to previous results [1], eq 3b may be reversible. The ordering of the ability of the various systems to produce hydrogen is $I > Br \gg Cl > CN$, the differences again corresponding to the HX bond energies.

Equation 3 is not the only process capable of $H_2$ formation. At equilibrium at 300 °K, HI is about 20% dissociated to its elements [7] (the degree of dissociation expected at equilibrium in the present heterogeneous system is unknown), but the rate for dissociation is slow and comparable to the rate of $H_2$ evolution in the early stages of the present study. Both the rates for dissociation and the degree of dissociation increase in the order $HCN < HCl < HBr < HI$, also in accord with the present observations. Further, any elemental halogen produced by the dissociation of HX would be very rapidly consumed by both $(CH_3)_2AsH$ and $(CH_3)_2AsAs(CH_3)_2$ to form $(CH_3)_2AsX$, the same byproduct of $H_2$ formation required in eq 3. In fact, when the rate of $H_2$ formation is compared for related systems containing $CH_3AsH_2$ or $C_2H_5AsH_2$ instead of $(CH_3)_2AsH$, only minor differences are seen perhaps attributable entirely to differences in dissociation catalysis of each system. It is informative to compare the reaction of HX with $(CH_3)_2AsH$ to that with other group-V analogs; dimethylphosphine combines with HX to form stable phosphonium salts without $H_2$ formation [8] while dimethylstibine evolves $H_2$ on combination with all hydrogen halides much more rapidly than is possible via dissociation of HX [9]. Note that the equation for the dissociation of HX when added to the equation for the reaction of $(CH_3)_2AsH$ with halogen is exactly eq 3.

It was possible to measure a reliable equilibrium constant in only the case where X = Cl for the process in eq 1. For the X = Br or I systems, the production of hydrogen prevented use of the assumption that $[(CH_3)_2AsAs(CH_3)_2]$ and [HX] are equal in those experiments in which these components were initially absent, an assumption made necessary by the exchange-hidden detection of the HX signal. For X = CN, the equilibrium constant is immeasurably large. In the remaining case, X = Cl, an equilibrium constant of 0.37 ± 0.05 at 30 °C is obtained; approximations of the constants for X = Br and I based upon fragmentary evidence suggest that both are of this order of magnitude.

Van Wazer, *et al.* [10] have studied independently the pmr spectrum of combined tetramethyldiarsine and dimethylbromoarsine. At 35 °C they observed a single coalesced peak at an averaged chemical shift in weighted proportion to the original mixture composition. From peak width measurements a lifetime of about $10^{-3}$ sec for As–As/As–Br exchange was calculated.

$$(CH_3)_2AsX + (CH_3)_2AsAs'(CH_3)_2 \rightleftharpoons (CH_3)_2As'X + (CH_3)_2AsAs(CH_3)_2$$

The same effect is observed in the present investigation for all three halogens, but not cyanide. In all halogen systems, the peaks for dimethylhaloarsine and tetramethyldiarsine have coalesced to a single, broad line. Since the equilibrium concentration of tetramethyldiarsine is considerably smaller than that of dimethylhaloarsine, the chemical shift of the coalesced peak is more nearly that of the dimethylhaloarsine in all cases. Fortunately, this further equilibrium relationship between solution components produces no additional uncertainties as, from mass balance considerations, it follows that:

$$[(CH_3)_2AsX]_{t=0} = [(CH_3)_2AsX]_t + [(CH_3)_2AsAs(CH_3)_2]_t$$

In the development of all quantitative results reported below, consideration is made of the two-fold statistical advantage of the diarsine in the averaging process.

Variable temperature nmr spectra in toluene-$\underline{d}_8$ between –40 and 90 °C for the halogen systems show decreased diarsine concentration at higher temperatures. A van't Hoff plot of logK *vs.* $T^{-1}$ yields $\Delta H = -7.0$ kJ $mol^{-1}$ for eq 1, X = Cl; from the value of K (30 °C), ΔG (30 °C) = 2.5 kJ $mol^{-1}$, and yields $\Delta S = 14.9$ J $deg^{-1}mol^{-1}$.

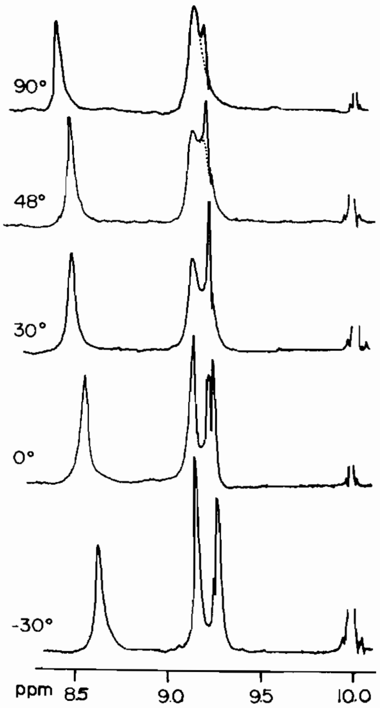

Figure 2. Variable-temperature pmr spectra of an initially 2:1 molar ratio of $(CH_3)_2AsH$ and $(CH_3)_2AsI$. The dotted line at 48 and 90 °C represents the lineshape used for analysis after the peak at $\tau$9.24 (trimethylarsine) was mechanically subtracted. The downfield shift with increase in temperature for the exchange-averaged $(CH_3)_2AsI/(CH_3)_2AsAs(CH_3)_2$ resonance (*ca.* 8.5 ppm) results from the decrease in diarsine concentration at higher temperatures.

An analysis of nmr lineshapes (Fig. 2) performed on the dimethylarsine methyl-group resonance in reactions with $(CH_3)_2AsI$ in toluene-$\underline{d}_8$ (same temperature range) with the assumption that all contributions to line broadening and collapse of multiplicity result from the hydrogen-hydrogen exchange in eq 2, yields the following activational parameters: $E_a = 24$ kJ $mol^{-1}$, $\Delta H^{\ddagger} = 21$ kJ $mol^{-1}$, $\Delta S^{\ddagger} = -47$ J $deg^{-1}mol^{-1}$; and $\Delta G^{\ddagger} = 34$ kJ $mol^{-1}$. Most noteworthy of these parameters is $\Delta S^{\ddagger}$; that it is negative and moderately large suggests that the exchange occurs through an associative complex, possibly one resembling quaternization, eq 3.

In the variable-temperature experiments discussed above, simultaneous with the return of multiplicity to the methyl-group resonance is a reappearance of the heptet spectrum of the arsenic-bonded proton. As the lifetime for the arsonium-like intermediate increases with decrease in temperature, the rate of proton-proton exchange decreases and equilibrium 3a (X = I) shifts to favor the associated intermediate. Under the conditions of this experiment, a solid phase separated below – 21 °C and is presumed to be the precipitation of the intermediate. Cullen [4] found that $(CH_3)_2AsH$ and HCl form a solid phase below –46 °C;

the higher dissociation temperature for X = I is consistent with the observations of other "onium" dissociations [11, 12]. A discontinuity occurs in the narrowing of the doublet linewidth below –21 °C suggesting that the formation of the solid phase imposes an additional factor in the determination of the concentration of exchangeable protons.

$$(CH_3)_2AsH + HI \rightleftharpoons (CH_3)_2AsH_2{}^+I^-_{(\phi H)} \xrightarrow{\text{below } -21\ ^\circ C} (CH_3)_2AsH_2{}^+I^-_{(s)}$$

A minor feature of all nmr spectra obtained in these experiments is a sharp singlet ($\tau 9.24$) attributed to trimethylarsine [13]. It is curious that trimethylarsine is observed as a minor by-product in at least six independent procedures involving initially secondary starting materials: the condensation of dimethylarsine and dimethylhaloarsine (the present work); hypophosphorous acid [14], sodium borohydride [16], and electrochemical [17] reduction of dimethylarsinic acid; methylation of sodium arsenide [18]; and the Cadet reaction [19]. It has not been found that trimethylarsine is a thermal decomposition product from tetramethyldiarsine at room temperature; at 400–500 °C, tetramethyldiarsine forms only elemental arsenic and hydrocarbons [20].

## Experimental

### *Reagents*

Published procedures were used for the preparation of starting materials: $(CH_3)_2AsX$; X = CN [21], Cl [21], Br [21], I [22]; $As(CH_3)_2$ [15]; and H [23]. All were found to be spectroscopically pure (pmr and ir). Pmr chemical shifts for 10% solutions in benzene were: X = CN, $\tau 9.40$; Cl, 8.89; Br, 8.77; I, 8.54; $As(CH_3)_2$, 8.96; and H, 9.21 (doublet) and 7.59 (heptet). Spectrograde benzene, toluene-$\underline{d}_8$, and t-butylbenzene were distilled from sodium and degassed by repeated freeze–pump–thaw cycles. Standard vacuum-line techniques were used for the manipulation of volatile, air-sensitive materials.

### *Physical Measurements*

Pmr spectra were obtained in sealed 5mm medium-wall tubes using a Perkin–Elmer R20B spectrometer equipped with the manufacturer's variable temperature controller; $\tau 10.00$ = TMS. Concentrations for the equilibrium constant calculation were obtained from averaged spectral integrations referenced to a known concentration of TMS added as in internal integration standard.

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