Existence of Methylmonohalogeno-arsines in Equilibrium Reactions of Methylarsine and Halogen Sources

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Summary Methylmonohalogeno-arsines, CH_3AsHX, are formed in reactions of CH_3AsH_2 with X_2, CH_3AsX_2, or HX (X = Br, I) under equilibrium conditions in sealed n.m.r. tubes.

ALTHOUGH speculations on the existence of organomonohalogeno-arsines RAsHX (X = Cl, Br, I), as intermediates in reactions of $RAsH_2$ with various halogen sources are frequently cncountered,[1] physical evidence for their existence or for the analogous RPHX species has not previously been demonstrated.

Efforts to prepare pure and characterizable quantities of CH_3AsHX led uniformly to the conclusion that isolated samples of CH_3AsHX rapidly and irreversibly decompose to form various solid polymethylpolyarsines according to the equation:

$$n\mathrm{CH_3AsHX} \rightarrow (\mathrm{CH_3As})_n + n\mathrm{HX} \qquad (1)$$

When, however, CH_3AsH_2 reacts with CH_3AsX_2, X_2, or HX (X = Br, I) under equilibrium conditions, the existence of CH_3AsHX (X = Br, I) is clearly demonstrated. Qualitatively similar results to those described below are obtained with each halogen source.

In a typical reaction, a tube containing CH_3AsH_2 and I_2 (4 : 1 molar ratio; 10% by wt. reactants in benzene solution) is warmed to room temperature and monitored by ^1H n.m.r. The I_2 is immediately decolorized and CH_3AsHI,CH_3AsI_2, and HI are formed. The multiplicities, the consistent 1 : 3 integrated peak ratios, and the identical $J_{HH'}$ (7·3 Hz.) for the quartet at τ 6·77 and the doublet at τ 8·48 (Figure) are consistent with their assignment to CH_3AsHI. The chemical shifts follow the trend expected from electronegativity considerations; a down-field shift of both resonances is experienced with each iodine substitution from CH_3AsH_2 to CH_3AsHI to CH_3AsI_2.

It might be noted that in the "fresh" spectrum in the figure the CH_3 resonance of CH_3AsH_2 is seen as a singlet instead of the expected triplet. This collapse of multiplicity is a phenomenon commonly associated with a confusion of spin states produced by a rapid proton-exchange equilibrium in which the duration of spin–spin coupling is less than $1/J$.[2] Thus, the observation of only a somewhat broadened singlet is consistent with an initial proton-exchange equilibrium between the AsH_2 protons of CH_3AsH_2 and HI (equation 2A) in which the lifetime of the AsH_2 group is short compared to $1/J$ ($J_{HH'}$ 7·1 Hz.). The AsH_2 signal in the "fresh" spectrum is not observed as the expected quartet since the exchange with HI protons leads to an averaging of the line positions for each signal. The wide separation of the AsH_2 and HI resonances causes the resultant to be a very broad structure extending from τ 7·7 to 9·7. This broad structure, which is typical of intermediate exchange rates, is difficult to observe directly but can be detected from integration of the spectrum. As the reaction progresses and the HI initially formed is consumed, the expected multiplicities and chemical shifts of the CH_3AsH_2 signals are observed. The amount of hydrogen evolved after a given time is determined by the consumption of HI (equation 2B) and therefore is quantitatively related to the degree of resolution of the CH_3AsH_2

$$\mathrm{CH_3AsH_2 + HI} \overset{\mathrm{A}}{\rightleftharpoons} [\mathrm{CH_3AsH_3I}] \overset{\mathrm{B}}{\rightarrow} \mathrm{CH_3AsHI + H_2} \qquad (2)$$

resonances. Although no resonance attributable to HI is directly observed, its presence is inferred from the factors attributable to the initial proton-exchange equilibrium and also from experiments conducted in pyridine, an HX acceptor. In such cases pyridinium iodide is precipitated and the reaction is driven rapidly to completion with the formation of pentamethylcyclopenta-arsine $(CH_3As)_5$, τ 8·34 (ref. 3) (equation 1).

Changes observed in the spectrum with continued monitoring indicate that reactions continue with the eventual production of polymethylpolyarsines at the expense of CH_3AsHI (equation 1). After 200 days no further spectral changes occur, and the spectrum then consists of unreacted CH_3AsH_2 and a broad, unresolvable resonance at τ 7·99 attributed to a family of soluble, iodine-terminated polymethylarsines (confirmed by mass spectra). The maximum number of catenated arsenic atoms in a given system is found to increase with the initial As : I ratio.

In systems containing Cl or Br, more rapid reactions occur. When X = Cl immediate precipitation of a purple-black, lustrous solid (empirical formula, CH_3As) precludes further n.m.r. analysis, whereas when X = Br slower precipitation of both purple-black and red-brown solids (both empirically CH_3As) occurs, permitting identification of CH_3AsHBr at τ 5·32 for AsH and τ 8·61 for CH_3 ($J_{HH'}$ 7·3 Hz.). The increase in the rate at which systems containing lighter halogens condense to polymethylpolyarsines can be explained by the decreasing poorer ability of the lighter hydrogen halides to cleave the As–As bonds formed by condensation reactions involving CH_3AsHX.[4] Thus, in reactions involving chlorine, it is observed that HCl is virtually incapable of promoting cleavage, and condensation to polyarsines immediately occurs.

Results from the extension of these studies to systems containing phosphorus indicate an essential similarity in the behaviour of phosphorus and arsenic regarding the intermediate nature of CH_3MHX (M = P, As).

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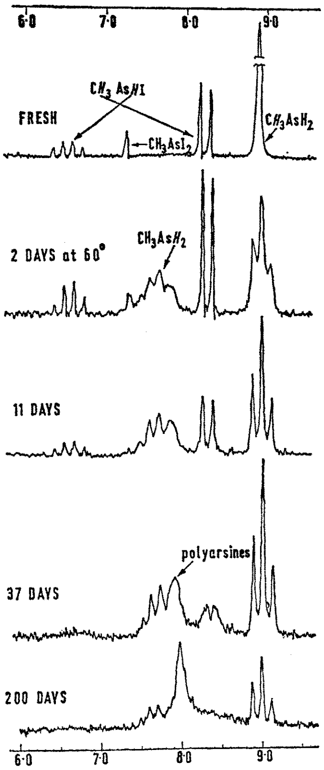

FIGURE: *60 MHz. spectra of the reacting mixture of* CH_3AsH_2 and I_2 in 4 : 1 *molar ratio in benzene solution.*

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