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Homoatomic Organoarsine Ladder Polymers. Synthesis and Physical Properties

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High molecular weight ladder polymers of the $CH_3As<$ moiety have been prepared in a macrocrystalline form by the reaction of methylarsine with a variety of halogen sources and by the catalyzed rearrangement of the cyclic oligomer $(CH_3As)_5$. Rates of polymer formation decrease with increasing halogen atomic weight and are associated with the increasing ability of the heavier hydrogen halides to cleave forming As–As bonds. Optical and thermal measurements indicate that the polymers are semiconductors with an energy gap of about 1.2 eV. At 300°K the polymer's rather low conductivity of 4.8×10^{-10} mho cm^{-1} is attributed to a low charge-carrier mobility rather than a low charge-carrier concentration. The low mobility is thought to arise from the presence of significant mobility anisotropies in the polymer samples. The polymers show pronounced photoconductive properties.

Introduction

Few well-documented examples of homocatenated group V polymers exist despite the impressive thermal stability of the oligomeric cyclopolyphosphines and -arsines.[2] Pentamethylcyclopentaarsine, $(CH_3As)_5$, undergoes ring opening on treatment with I_2 in benzene to produce high-molecular-weight iodine-terminated polymers.[3] Structurally ill-defined red-brown solids of approximate empirical composition $(CH_3As)_x$ commonly accompany synthesis of $(CH_3As)_5$. These solid by-products are generally thought to be linear polymers of CH_3As units.[4]

In a detailed study of the products of the equilibrium-condition reaction of excess primary methylarsine and methyldiiodoarsine (or iodine which with methylarsine forms methyldiiodoarsine) we observed that a benzene-soluble family of hydrogen- and/or iodine-terminated polymethylpolyarsines is one of the condensation end products. Upon longer standing (0.5-3 years depending upon the initial CH_3AsH_2:CH_3AsI_2 ratio), those samples initially containing the largest excess of methylarsine (5:1 CH_3AsH_2:CH_3AsI_2) began first to precipitate well-formed purple-black crystals of empirical formula CH_3As.[5]

A two-dimensional crystallographic structural analysis[6] of the purple-black solid performed on samples from our laboratory determined that this modification of polymethylpolyarsine possesses a novel ladder structure (Figure 1).[7] The horizontal or ladder rung distance of 2.4 Å is the normal As-As single bond distance while the vertical separation between rungs is 2.9 Å suggesting a partial bond order in this direction. The solid may be viewed as the stacking of $CH_3\overset{|}{\underset{|}{As}}-\overset{|}{\underset{|}{As}}CH_3$ units. The As–C bond distance of 1.97 Å is typical for As-C linkages.

The presence of a homoatomic metalloid framework suggested that these novel materials might possess interesting electrical properties. We now know that the methylarsine ladder polymer is an intrinsic semiconductor. We have also developed several more convenient synthesis procedures.

Experimental Section

Standard synthesis procedures were used for methylarsine,[8] the methyldihaloarsines,[9] and pentamethylcyclopentaarsine.[10] Reagents of high purity were found essential to the formation of macrocrystalline ladder polymers. Accordingly, methylarsine was fractionally condensed trap to trap until a constant molecular weight of 91.76 (calculated 91.96) was obtained. The methyldihaloarsines were fractionally vacuum distilled. Pentamethylcyclopentaarsine was washed repeatedly with 5% aqueous NaOH and then distilled H_2O; it was dried over molecular sieve, distilled under high vacuum, and finally subjected to repeated freeze-pump-thaw cycles at 10^{-4} mm. Samples of pentamethylcyclopentaarsine so prepared remained as a clear, moderately viscous yellow oil indefinitely when stored in darkness. All prepared reagents were found to be spectroscopically (mass, ir, and nmr) pure. The benzene employed in all studies was Spectrograde and thiophene free. Prior to each experiment, the benzene was distilled from sodium on the vacuum line and repeatedly degassed by freeze-pump-thaw cycles. Experimental procedures for the electrical measurements are published elsewhere.[11]

The following instrumentation was used: mass spectra, Du Pont 491 and Varian M-66; nmr spectra, Varian A-60d and Perkin-Elmer R20B; ir spectra, Perkin-Elmer 221G, uv-vis spectra, Cary 14. All nmr chemical shifts are referred to benzene (TMS = 10.0) which was the solvent or reference in all nmr studies. When sufficient sample quantities permitted, nmr tubes were filled as nearly to capacity as the sealing procedure allowed to minimize the quantities of volatile materials in the gas phase. Coupling constants were measured from minimum sweep width spectra and reported values represent an average of not less than five scans. Absolute concentrations were measured by reference to a known quantity of TMS added to each sample. These concentrations were used in the equilibrium constant determination (eq 2) and for the qualitative kinetic observations.

Methyldiiodoarsine and Methylarsine (Benzene). In a typical experiment, 46.0 mg of CH_3AsH_2 (0.50 mmol) and 0.070 mmol of TMS (as both a chemical shift and integration standard) were distilled into a degassed solution of 34.4 mg (0.10 mmol) of CH_3AsI_2 in 1.00 ml of benzene contained in a standard-wall, 5-mm nmr tube and sealed on the vacuum line at −196°. On warming to room temperature, pmr spectra showed that the resulting pale yellow solution contained CH_3AsHI in addition to the starting materials. After about 1.5 yr at 60°, large (2 mm^3) purple-black crystals formed. Similarly prepared tubes opened earlier than 1.5 yr contained quantities of

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[2] E. Wiberg, M. Van Ghemen, and G. Muller-Schiedmayer, *Angew. Chem., Int. Ed. Engl.*, 2, 646 (1963).

[3] M. Ya. Kraft and V. V. Katyshkina, *Dokl. Akad. Nauk SSSR*, 66, 207 (1949); M. Ya. Kraft, *ibid.*, 131, 1074, 1342 (1960).

[4] (a) J. Waser and V. Schomaker, *J. Amer. Chem. Soc.*, 67, 2014 (1945); (b) J. H. Burns and J. Waser, *ibid.*, 79, 859 (1957); (c) F. Knoll, H. C. Marsmann, and J. R. Van Wazer, *ibid.*, 91, 4986 (1969); (d) P. S. Elmes, S. Middleton, and B. O. West, *Aust. J. Chem.*, 23, 1559 (1970); (e) L. K. Krannich and H. H. Sisler, *Inorg. Chem.*, 8, 1032 (1969).

[5] A. L. Rheingold and J. M. Bellama, *Chem. Commun.*, 1058 (1969); an additional report[4e] appeared shortly after our disclosure on the preparation of similar or identical solid materials from a potentially related reaction; see also J. C. Summers and H. H. Sisler, *Inorg. Chem.*, 9, 862 (1970).

[6] J. J. Daly and F. Sanz, *Helv. Chim. Acta*, 53, 1879 (1970).

[7] No other examples of homoatomic ladder polymers in the literature could be found.

[8] W. H. Dehn and B. B. Wilcox, *Amer. Chem. J.*, 35, 1 (1906), with modifications by R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 67 (1949).

[9] G. P. Van der Kelen, *Bull. Soc. Chim. Belg.*, 65, 343 (1956).

[10] C. S. Palmer and A. B. Scott, *J. Amer. Chem. Soc.*, 50, 536 (1928).

[11] J. E. Lewis, *Phys. Status Solidi A*, 16, 161 (1973).

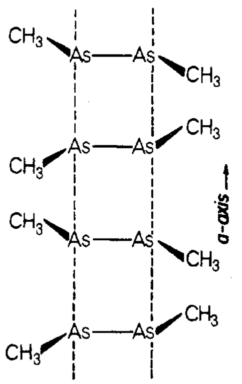


Figure 1. The ladder structure of purple-black, macrocrystalline $(CH_3As)_x$.

noncondensable gas identified as hydrogen by its pump sound in an amount approximating the stoichiometry of eq 3.

On cautious opening of the nmr tubes (about 20% ruptured explosively due to the hydrogen pressure) the polymer was removed by filtration, and washed with ether. A 11.4-mg amount of a purple-black lustrous solid possessing a faint but distinctly arsine-like odor was obtained. No other solid products were found. The solid was insoluble in all solvents tested. *Anal.* Calcd for $(CH_3As)_x$: C, 13.34; H, 3.36; As, 83.30. Found: C, 13.30; H, 3.40; As, 83.9.

In earlier attempts to study the reactions of CH_3AsH_2 and CH_3AsI_2 employing less well-purified starting materials and solvent the precipitate isolated was largely the reddish brown microcrystalline polyarsine mixed with various amounts of the purple-black polyarsine modification.

In none of the experiments dealing with the exchange of hydrogen and halogen on the $CH_3As<$ moiety, was there evidence for the exchange of halogen and alkyl groups. This is in contrast to similar antimony systems in which facile halogen-alkyl exchange occurs at 60°.[12]

Methyldichloroarsine and Methylarsine. In an nmr tube 0.0675 g (0.75 mmol) of CH_3AsH_2 and 0.121 g (0.75 mmol) of CH_3AsCl_2 were combined as described above. On warming to the benzene melting point, a vigorous reaction occurred with immediate precipitation of the ladder polymer, but in much smaller particle size than found in the iodine systems. Upon opening the tube on the vacuum line, 0.0512 g (1.40 mmol) of HCl (identified by its ir spectrum) was recovered.

Methyldihaloarsines and Methylarsine (Pyridine). When pyridine was substituted for benzene in the above experiments, CH_3AsX_2 (X = Cl, Br, or I) and CH_3AsH_2 in a 1:1 molar ratio immediately precipitated the purple-black polymer along with pyridinium halide. The solid products were removed by filtration and washed with hexane to remove pyridine. Pyridinium halide was extracted with H_2O, and halide ion precipitated from the combined washings as AgX. In all cases the AgX obtained quantitatively accounted for the halogen introduced in CH_3AsX_2. Ladder polymer yields were nearly quantitative for all halogens, but the product formed as a very fine powder.

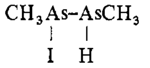
Pentamethylcyclopentaarsine and Methyldichloroarsine. A 2.25-g sample of $(CH_3As)_5$ (5.0 mmol) and 0.040 g (0.25 mmol) of CH_3AsCl_2 were combined in 50 ml of benzene and stirred under N_2 at 27° until ladder polymer precipitation commenced (~10-20 min). Stirring was then stopped to provide larger crystal size. Ladder polymer samples digested in 1 *M* HNO_3 followed by addition of $AgNO_3$ did not show the presence of halogen.

Methylarsine and Carbon Tetrachloride. A 92.0-mg sample of CH_3AsH_2 (1.00 mmol) was distilled into 1.05 ml of degassed Spectrograde CCl_4 contained in a 5-mm nmr tube and sealed. Fifteen minutes after warming the solution to room temperature, several new pmr peaks between τ 8 and 9 appeared in addition to those expected from CH_3AsH_2 (see text for details). Polymethylpolyarsine precipitation commenced after 24 hr when the mixture was maintained at 60°. The crystals dotted the tube wall, continued to grow for several days until completely covered, and thereafter precluded further pmr monitoring.

Regardless of the synthesis procedure used to obtain the purple-black polymethylpolyarsine, all samples produced essentially identical X-ray powder diffraction patterns.

Results and Discussion

Synthesis Procedure. The reaction of excess methylarsine and methyldihaloarsine was monitored by pmr spectroscopy. Figure 2 shows a typical sequence of spectra for a single sample (2:1 CH_3AsH_2:CH_3AsI_2 at a combined concentration of 1.140 *M*) in a sealed 5-mm tube (stored in darkness at 60° between spectra) as a function of time. Within minutes of the time of mixing (zero days) the spectrum shows the doublet (τ 8.48)-quartet (τ 6.77) pattern ($J_{HH'}$ = 7.3 Hz) for CH_3AsHI, a singlet (τ 7.51) for CH_3AsI_2, and only a broad singlet (τ 8.80) for the CH_3 group in CH_3AsH_2. The collapse of methyl group multiplicity and absence of the arsinyl group signal for CH_3AsH_2 are attributed to rapid (nmr time scale) proton-proton exchange between the arsinyl protons and HI (eliminated in the condensation equilibrium, eq 1). The normal (no exchange) CH_3AsH_2 spectrum is indicated by the dashed line. Since the chemical shift of HI in benzene is considerably upfield from the $-AsH_2$ signal, exchange averaging has the effect of broadening the $-AsH_2$ signal beyond detectability. An alternative explanation for these effects involving direct H-I exchange (eq 2) can be ruled out by the absence of related effects in the CH_3AsHI spectrum. The broad peak (τ 8.04) is attributed to



$$CH_3\underset{I}{As}-\underset{H}{As}CH_3$$

and other condensed As-As bonded species.

At 7 days, essentially all of the HI produced has been consumed by reaction with excess CH_3AsH_2 (eq 3), full multiplicity in the methyl resonance of CH_3AsH_2 reappears, and the $-AsH_2$ quartet emerges at τ 7.70, broadened by residual coupling to the $I = {}^3/_2$ ^{75}As nucleus (100% isotopic abundance) and partially obscured by the polyarsine signal. Both CH_3AsI_2 and CH_3AsHI show a marked reduction in concentration. At 62 and 134 days the decrease in CH_3AsHI and CH_3AsI_2 concentrations continues while the benzene-soluble family of hydrogen and iodine-terminated polyarsines increases in concentration.

The single, broad pmr line seen for the family of soluble polyarsines supports Van Wazer's observation of an nmr rapid exchange of parts in related systems containing dimethylbromoarsine and arsenomethane where coalescence to a single, broad peak is also seen. Van Wazer observed an exchange lifetime of about 10^{-3} sec at 35°.[4c] The trend we observe of the heavier halogen-containing compounds causing more facile cleavage of As-As bonds would suggest a faster exchange rate for iodine systems than for their bromine analogs, and if systems containing dimethylhaloarsines are compared to ones containing methyldihaloarsines, the exchange rate should be faster for the dimethyl systems due to their greater basicity. In confirmation of these expectations, while we observe a single polyarsine peak for the CH_3AsH_2-CH_3AsI_2 system, the CH_3AsH_2-CH_3AsBr_2 system, after 30 days' reaction time at 60°, shows at least four resolved polyarsine peaks between τ 7.42 and 8.59, spanning the chemical shift of the single polyarsine peak in the iodine system. No assignment of the individual peaks was attempted but it would be expected that the lowest field peak represents the terminal methyl group (nearest the end bromine atom) and that the successively more interior methyl groups would show increasingly higher field shifts. The areas of the four most prominent peaks were unexpectedly all very nearly equal.

After about 400 days, precipitation of the purple-black solid becomes visually evident. Simultaneous to the initiation of precipitation is a slow decrease in the polyarsine peak

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(12) H. Weingarten and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **88**, 2700 (1966).

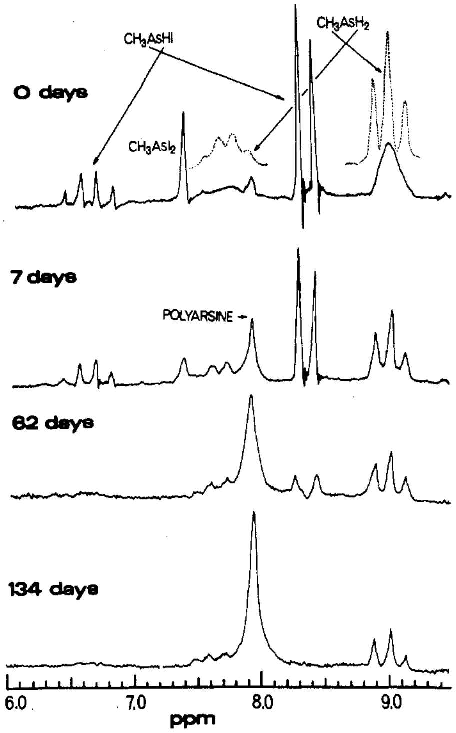

Figure 2. Pmr spectra at various times for a reacting mixture of CH_3AsH_2 and CH_3AsI_2 (2:1 molar ratio) in benzene (TMS = τ 10.00). Dotted line spectrum is CH_3AsH_2 alone at the same concentration as the initial mixture.

suggesting the extrusion of high molecular weight polymers (eq 5). After 900 days, no further precipitation is observed, and the polyarsine resonance has reached a minimum value while at the same time the line width has narrowed considerably, a trend already evident in the 134-day spectrum. Because of its insolubility in benzene no resonance is seen for the iodine-free polymer. A more detailed description of the subject of halogen-hydrogen exchange on the $CH_3As<$ moiety will be the subject of a future publication.

The purple-black solid, now identified as a ladder polymer of CH_3As units (Figure 1), is believed formed through a complex sequence of condensation steps. The pmr results are essentially similar in benzene, cyclohexane, tetrahydrofuran, and dimethoxyethane; the addition of neither azobis(isobutyronitrile) or quinone to the pmr samples altered appreciably the products, product ratios, or rates of product formation. No available evidence points to the involvement of either free-radical or ionic mechanisms. Rather the evidence strongly suggests that the various steps that lead to arsine polymerization involve concerted, four-centered activated complexes, a mechanism well established for reactions of this type.[13]

We can speculatively summarize our results with the sequence of steps

$$CH_3AsH_2 + CH_3AsI_2 \overset{a}{\rightleftharpoons} CH_3(H)AsAs(I)CH_3 + HI \overset{b}{\rightleftharpoons} 2CH_2AsHI \quad (1)$$

$$CH_3AsH_2 + CH_3AsI_2 \rightleftharpoons 2CH_3AsHI \quad (2)$$

$$CH_3AsH_2 + HI \rightarrow CH_3AsHI + H_2 \quad (3)$$

$$CH_3(H)AsAs(I)CH_3 \xrightarrow{\substack{CH_3AsH_2 \\ CH_3AsHI \\ CH_3AsI_2}} CH_3(H)As\text{-}(CH_3As)_x\text{-}As(I)CH_3 \quad (4)$$

$$CH_3(H)As\text{-}(CH_3As)_x\text{-}As(I)CH_3 \rightarrow \underset{\substack{\text{ladder} \\ \text{polymer}}}{(CH_3As)_y} + CH_3(H)As\text{-}(CH_3As)_z\text{-}As(I)CH_3 \quad (5)$$

where $x = y + z$.

We have found no persuasive evidence for or against *direct exchange* (through a condensation complex without HX elimination) of hydrogen and halogen on combining CH_3AsH_2 and CH_3AsX_2 (X = Cl, Br, or I) (eq 2) although there is definite evidence for the presence of the exchange product, CH_3AsHX, in such mixtures.[5] Rather there is strong mass spectral evidence in support of the production of CH_3AsHX by *indirect exchange* (eq 1b) (condensation with HX elimination) in which the cleaving HX molecule is differently oriented than in eq 1a; all such mixtures contain a high abundance of X-, H-, and CH_3-substituted As_2 fragments. Precedent for the exchange of parts through associative (condensation) mechanisms appears well established for organophosphines[14] and can be logically extended to organoarsines. The presence of initially large quantities of HI are difficult to account for without stipulation of a condensation-elimination step.

The question of whether H-X redistribution occurs predominantly through condensation-elimination equilibria or by direct exchange of parts is currently unanswered. Although evidence for direct exchange was not found, the compounds in eq 2 are apparently equilibrium related; despite a wide range of initial ratios of CH_3AsH_2 to CH_3AsI_2, the K_{eq}-(33°) for eq 2 is always 3.1 ± 0.1 when all three species are present at pmr-detectable levels.

Condensation beyond dimerization is initially restricted by the ability of HI reversibly to cleave As-As bonds. Only after consumption of HI through irreversible reaction with excess CH_3AsH_2 (eq 3) does further condensation occur. The transient presence of HI in these reactions is demonstrated by the reappearance of the full multiplicity of the methyl group pmr signal after 7 days. Our observations fit well the observed increase in metallic properties on descending group V. CH_3NH_2 and CH_3PH_2 form thermally stable onium salts,[15] while CH_3SbH_2 rapidly evolves H_2 on reaction with HCl.[16]

Following reduction of the HI concentration to some critically low level, further condensation can occur (eq 4) involving any of the monomer or polymer species present. The product of eq 4 (and also eq 5) is meant to represent a generalized species that may have any combination of H or I end group functionality. From this polymer mixture eventually precipitates the purple-black ladder polymer possibly through the extrusion of interior units (eq 5).

Since our initial report of the preparation of purple-black polymethylpolyarsine we have developed additional and more convenient syntheses requiring considerably less than the 1-3 years needed in the original investigation. The equilibrium reaction in eq 1 is highly halogen dependent. When the halogen is chlorine instead of iodine, condensation occurs much more rapidly due to the poorer ability of HCl, as compared to HI, to cleave the As-As bonds formed.[17] When the

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(13) J. C. Lockhart, "Redistribution Reactions," Academic Press, New York, N. Y., 1970, p 158; K. Moedritzer, *Organometal. React.*, **2**, 1 (1971).

(14) H. C. E. McFarlane and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1189 (1972); F. Ramirez and E. A. Tsolis, *J. Amer. Chem. Soc.*, 92, 7553 (1970).

(15) H. C. Brown, *J. Amer. Chem. Soc.*, 67, 503 (1945).

(16) A. B. Burg and L. R. Grant, *J. Amer. Chem. Soc.*, 81, 1 (1959).

(17) Similar effects are observed in the HX cleavage of Si-Si bonds in polysilanes: A. G. MacDiarmid in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968, Chapter 8.

halogen is chlorine, precipitation of the $(CH_3As)_x$ ladder polymer occurs immediately upon thawing the benzene solutions and long before noticeable hydrogen evolution occurs, an indication that eq 3 is no longer a necessary step in the formation of organoarsine polymers in the chlorine systems. Intermediate behavior is found in bromine systems where observable precipitation of $(CH_3As)_x$ occurs after several days' standing and after some hydrogen evolution is evidenced by the development of noncondensable (at −196°) pressure.[18]

The addition of pyridine as an HX acceptor to these benzene solutions (or in neat pyridine solutions) caused immediate precipitation of both the polymer and pyridinium halide for all of the halogens studied.[19] The time saved in the polymer preparation by using lighter halogens or HX acceptors is, however, at the expense of crystal size. Crystals of up to 1 mm in length precipitated from the long-term iodine system reactions, whereas a much finer powder is formed upon more rapid precipitation.

We have studied the advantage of obtaining larger crystal dimensions through the *in situ* generation of one of the reactants. Soon after warming a 10% solution of CH_3AsH_2 in CCl_4 to room temperature, pmr-detectable concentrations of CH_3AsHCl and CH_3AsCl_2 are observed. From similar chemical shift, multiplicity, and consistent coupling constant considerations used in the identification of CH_3AsHI,[5] CH_3AsHCl ($\tau(CH_3)$ 8.47, $\tau(AsH)$ 4.78, $J_{HH'} = 6.9$ Hz) is identified in the reaction of CCl_4 and CH_3AsH_2. In addition, both CH_3AsCl_2 and $CHCl_3$ are observed and their concentrations progressively increased in intensity relative to CH_3AsH_2. The presence of CH_3AsHCl is transient, appearing after 24 hr and disappearing after 72 hr when maintained at 60°. Coincidental to the appearance of the monochloride is a collapse in methyl group multiplicity associated with the presence of HCl (formed presumably by a reaction analogous to eq 1 but essentially irreversible when chlorine replaces iodine). One day after mixing, well-formed crystals of the ladder polymer appear and continue to grow for several days thereafter. This procedure has now replaced earlier techniques in our laboratory. By this procedure we have also been able to prepare the ethyl, benzyl, and allyl analogs (all purple-black), but characterizational studies are not yet available except for confirming elemental analyses.

The results in CCl_4 may be speculatively summarized as

$$CH_3AsH_2 + CCl_4 \rightarrow CH_3AsHCl + CHCl_3 \qquad (6)$$

$$CH_3AsHCl + CCl_4 \rightarrow CH_3AsCl_2 + CHCl_3 \qquad (7)$$

$$CH_3AsCl_2 + CH_3AsH_2 \rightarrow CH_3As(Cl){-}As(H)CH_3 + HCl \qquad (8)$$

$$HCl + CH_3AsH_2 \rightarrow CH_3AsHCl + H_2 \qquad (9)$$

The products of reactions 6-8 appear shortly after mixing. Reaction 9 is much slower; concentrations of CH_3AsHCl thereby produced are below pmr detectability. The large excess of CCl_4 probably precluded the formation of CH_2Cl_2.

When either I_2 or CH_3AsI_2 is combined with CH_3AsH_2 in CCl_4 the results are generally similar to those found in benzene (in addition to the solvolysis reactions), except for the appearance of a new peak at τ 7.78 tentatively assigned to CH_3AsClI. This chemical shift is intermediate to that of CH_3AsCl_2 (τ 8.35) and CH_3AsI_2 (τ 6.91).

A synthesis procedure obviating the necessity of vacuum-line manipulation of the primary arsines utilizes the ability of As–X functional molecules to cleave the $(CH_3As)_5$ ring to form the ladder polymer.[4c] When traces of CH_3AsCl_2 are combined with $(CH_3As)_5$ (mole ratios of $(CH_3As)_5$ to CH_3AsCl_2 of 100:1 and higher), polymer precipitation occurs over a period of hours in benzene.[20]

$$(CH_3As)_5 \xrightarrow[CH_3AsCl_2]{\text{trace of}} (CH_3As)_x \qquad (10)$$

At high dilutions unstirred solutions form crystals of halogen-free polymer in lengths over 2 mm. The *in situ* procurement of large crystal dimensions (needed for structural and electrical property studies) is essential as a result of the insolubility of the polymers in potential crystal growth media. The ring-opening polymer preparation is mechanistically related to Kraft's work[3] where the reaction of I_2 and $(CH_3As)_5$ likely forms initially some CH_3AsI_2 although in our CH_3AsCl_2 systems no incorporation of halogen in the product is observed.

Physical Properties. Purple-black polymethylpolyarsine can be sublimed (10^{-6} mm at 37°) unchanged (as determined from optical spectra) onto a cooled substrate in thin films although this procedure has not proved useful in the preparation of large single crystals. The arsine ladder polymer appears to be indefinitely stable at room temperature in normal laboratory atmospheres. This contrasts sharply to $(CH_3As)_5$ which we have found to be pyrophoric in thin films under similar conditions. At 150° in air polymer crystals begin a slow, irreversible change in conductivity; in a nitrogen atmosphere, samples survive temperatures of 180° indefinitely but slow decomposition ensues at about 200°. *In vacuo,* with pumping, samples show irreversible transformation at 180°, the products indicating an almost clean transformation to $(CH_3As)_5$. The decomposition of the ladder polymer to the cyclic oligomer possibly reveals the presence of the equilibrium

$$(CH_3As)_x \rightleftharpoons (x/5)(CH_3As)_5$$

which at elevated temperatures and reduced pressures is shifted to the right by the much greater volatility of the pentamer. When this decomposition occurs in a mass spectrometer inlet at 200° (10^{-6} mm), the recorded spectrum is nearly superimposible upon the spectrum of a freshly prepared sample of $(CH_3As)_5$. It shows no fragments at *m/e* greater than 450 corresponding to the ion $(CH_3As)_5^+$.[21]

Electrical resistance measurements on seven polycrystalline aggregate samples through the temperature range 293-428°K demonstrate that in the 383-428°K range all samples are intrinsic semiconductors with a band gap of 1.2 eV. In the 293-383°K range deviation from intrinsic behavior varies considerably from sample to sample (samples 2-5 in Figure 3), although one sample (sample 1) reproducibly showed no curvature throughout the entire temperature range. Deviation arises from the increasingly predominant contribution of defect structure and/or impurity energy level sources for

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[18] In contrast to these methyl-substituted systems, condensed phenylarsenic systems appear inert to As–As bond cleavage by hydrogen halides: F. F. Blicke and L. D. Powers, *J. Amer. Chem. Soc.*, **55**, 315, 1161 (1933).

[19] Sisler, *et al.*,[4e] obtained the red-brown microcrystalline polyarsine modification from the combination of CH_3AsH_2 and Cl_2 in ether in the presence of $(CH_3CH_2)_3N$. We have found, however, that the same reaction without an HX acceptor produces the purple-black form when run in benzene.

[20] As–As bonds in $(C_6H_5As)_6$ can be cleaved by $C_6H_5AsX_2$ only when X = Br or I: F. F. Blicke and F. D. Smith, *J. Amer. Chem. Soc.*, **52**, 2937 (1930).

[21] West, *et al.*,[4d] have found higher mass fragments of *m/e* 540 and 525 corresponding to the ions $(CH_3As)_6^+$ and $(CH_3)_5As_6^+$ in the mass spectrum of the red-brown microcrystalline polymethylpolyarsine modification although the gross features of the spectrum were also similar to pentamethylcyclopentaarsine.

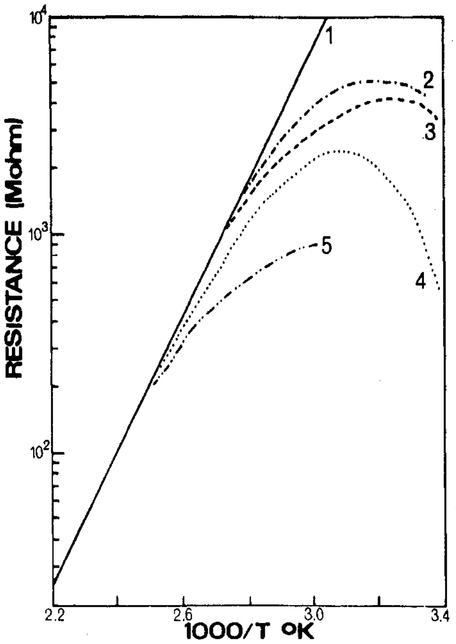

Figure 3. Resistance *vs.* $1/T$ plots for five samples of the methylarsine polymer.

liberated electrons at lower temperatures, *i.e.*, extrinsic conductivity.

Intrinsic conductivity, achieved from the thermal excitation of valence electrons in homogeneous materials, is demonstrated by a linear plot of log conductivity *vs.* reciprocal temperature according to the equation $\log R(T) = \log R(0) + E_g/2kT$ where $R(T)$ is the measured resistance, $R(0)$ the specific resistivity, and E_g the band gap. The equation best fitting the data is $\log R = 6.2 + 7000/T$ ohms which yields a band gap of 1.2 eV. The plots shown in Figure 3 were translated to cause each curve to pass through the point (100 Megohms, $2.4 \times 10^3/T$) to show that in the intrinsic region all slopes are parallel and would, therefore, all yield the same value for E_g. The charge-carrier drift mobility and charge-carrier concentration as a function of T can be calculated using the assumption that electrons are the majority carrier; at room temperature, the mobility is 1.67 $cm^2\ V^{-1}\ sec^{-1}$ and the carrier concentration is 1.78×10^9 electrons cm^{-3}.[22] The carrier mobility calculation uses the $T^{-3/2}$ dependency of the band theory model which may be inapplicable considering the low mobility. Use of a "hopping" model, however, does not alter the results within the magnitude of experimental error. The calculated charge-carrier concentration would suggest a somewhat greater conductivity ($\sigma = 1/R$) if not limited by the rather low value for the mobility, a set of properties not unexpected for essentially one-dimensional polymer strands associated only by relatively weak van der Waals bonds. Significant mobility anisotropies are thus undoubtedly created and are accentuated in the polycrystalline aggregate samples we have studied. Representative values for the charge-carrier concentration and mobility and for the conductivity are shown at various temperatures in Table I.

If the measured band gap represents approximately the energetic separation of HOMO-LUMO electronic levels, certain conclusions can be made. MO calculations of monomeric trivalent phosphorus and arsenic compounds indicate that the HOMO level is essentially nonbonding and largely localized on the central atom,[23] while the LUMO level by analogy to cyclopolysilanes is likely to be largely d orbital in character with a potentiality for delocalization.[24] Evidence for the orbital character of the LUMO level in cyclosilanes was most clearly found by West, who studied by esr spectroscopy electrochemically generated radical anions of dodecamethylcyclohexasilane.[25] From the magnitude of the ^{13}C and ^{29}Si hyperfine coupling constants, he concluded that the orbital occupied by the odd electron is essentially d in character. Gohlke has reached similar conclusions from electron-impact studies by negative-ion mass spectroscopy.[26]

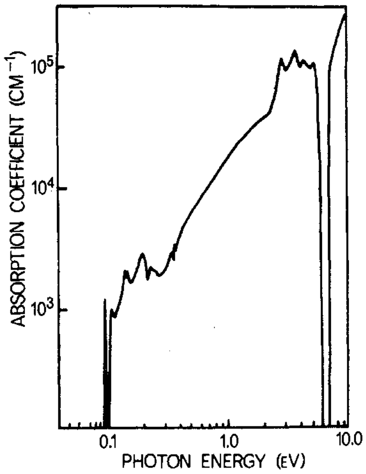

Figure 4. The optical spectrum of the methylarsine polymer derived from reflectance spectra through a Kramers-Kronig analysis.

Table I. Typical Electrical Properties of $(CH_3As)_x$

Temp, °K	σ, mho cm^{-1}	μ, $cm^2\ V^{-1}\ sec^{-1}$	n, electrons cm^{-3}
273	5.0×10^{-11}	1.9	1.7×10^{8}
300	4.8×10^{-10}	1.7	1.8×10^{9}
350	1.4×10^{-8}	1.3	6.5×10^{10}
400	1.7×10^{-7}	1.1	9.7×10^{11}
423	4.1×10^{-7}	1.0	2.6×10^{12}

Analogies to be drawn from cyclopolysilanes are perhaps tenuous, but similar results have also been noted in cyclopolyphosphines in this laboratory; this will be the subject of a future publication.

These electrical results may be compared to previously obtained optical data.[27] Reflectance spectra in the 0.095-7.3-eV (13-0.17 μm) range show a band edge at about 0.1 eV (Figure 4) which was earlier assigned to phonon absorption by carries excited from a valence to a conduction band. In light of the more recently obtained thermal conductivity data, it is more reasonable to assign the edge to a lattice vibrational mode perhaps overemphasized by the Kramers-Kronig extrapolation[28] used to extract absorption coefficient data from the reflectance spectra.

The steep rise in absorption coefficient at energies near 1 eV followed by a series of maxima in the uv-vis region are now more likely associated with the thermal gap at 1.2 eV. The conduction process in the ladder polymers is likely due

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[22] C. Kittel, "Introduction to Solid State Physics," 4th ed, Wiley-Interscience, New York, N. Y., 1971, p 361.

[23] K. Issleib and W. Grundler, *Theor. Chim. Acta*, **11**, 107 (1968); H. Oehling, W. Schafer, and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **10**, 656 (1971), and references therein.

[24] C. G. Pitt, L. L. Jones, and B. G. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5471 (1967).

[25] G. R. Husk and R. West, *J. Amer. Chem. Soc.*, **87**, 3993 (1965); E. Carberry, R. West, and G. E. Glass, *ibid.*, **91**, 5446 (1969).

[26] R. S. Gohlke, *J. Amer. Chem. Soc.*, **90**, 2713 (1968).

[27] J. E. Lewis, *Phys. Status Solidi A*, **8**, 483 (1971).

[28] J. S. Blakemore, "Solid State Physics," W. B. Saunders, Philadelphia, Pa., 1969, p 338.

to nearly free electrons moving in a periodic potential derived from the HOMO-LUMO excitations discussed above. The populating, therefore, of orbitals antibonding in nature would correspond to the "breaking" of an interatomic bond. If a bond energy of roughly 2 eV (46 kcal mol^{-1}) can be assigned to a normal As-As single bond,[29] then the value of the thermal energy gap at 1.2 eV corresponds well with the bond energy for the fractional-order As-As bonds whose bond order can be estimated from overlap calculations.[30,31] Since there are no other reported compounds possessing fractional As-As bonds, it is difficult to appraise the reliability of this assignment.

The first of this series of maxima at about 2.9 eV (~0.43 μm) corresponds well with the observed burgundy color of the crystals in thin sections and is considerably lower in energy than previously reported electronic transitions in polyarsines,[32] an effect of the spatially much more extensive opportunity for electron delocalization in polymer strands than in cyclic oligomers.[33] The second maxima at about 3.8 eV (0.32 μm) falls at the low-energy end of the band usually associated with As-As bonding and is therefore most likely localized in the 2.4-Å As-As bonds.

The polymers also exhibit a pronounced photoconductive effect as further indication of semiconductor behavior. When strongly illuminated by an ir source, a 10-100-fold dimunition in resistance is found, a factor typical of low-mobility semiconductors. A more detailed photoconductivity study is planned. Knowledge of the threshold excitation energy for photoconductivity will be important in further interpretation of the optical spectra.

If conductivity is achieved in these methylarsine polymers through excitation of valence electrons from HOMO levels to LUMO levels in the region of predominant intrinsic behavior, then this is primarily an n → d transition. It is this excitation that is suggested to explain the uv-vis band between 0.28 and 0.32 μm of polyphosphines and arsines;[32] nonbonding electrons are delocalized through excitation to d orbital networks. Total delocalization along the polymer ladder through d-orbital centers in a strictly aromatic sense is most probably not within reality.[34] This is corroborated by the low conductivity of the polymers—but nonetheless a conductivity several orders of magnitude greater than found in most molecular organic semiconductors whose only intermolecular association is through weak van der Waals bonds.[35] Comparisons of electronic spectra of solid polymers and essentially noninteracting monomers have obvious limitations for quantitative purposes, but the close similarity in optical properties of these ladder polymers and related monomeric compounds offers encouragement for more qualitative speculations.[36]

Registry No. $(CH_3As)_x$, 29402-29-7; CH_3AsH_2, 593-52-2; CH_3AsI_2, 7207-97-8; CH_3AsCl_2, 593-89-5; $(CH_3As)_5$, 20550-47-4.

[29] C. T. Mortimer and H. A. Skinner, *J. Chem. Soc.*, 4331 (1952): 38.3 kcal mol^{-1}, $As_2(CH_3)_4$. S. R. Gunn, *Inorg. Chem.*, 11, 796 (1972): 39.9 kcal mol^{-1}, As_2H_4.

[30] Approximative overlap integral calculations based upon Clementi orbitals[31] indicate that a reduction of about 50% in overlap occurs on lengthening the As-As bond from 2.4 to 2.9 Å. If orbital overlap and bond strength are roughly proportional, then a bond energy of about 20 kcal mol^{-1} can be estimated for the partial bond.

[31] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, 38, 996 (1963).

[32] B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, p 136, and references therein.

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[34] D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, 6, 2134 (1967).

[35] Reference 33, p 448.

[36] Close similarity also exists between gas- and solid-phase electronic spectra of condensed-ring aromatics: ref 33, p 296. Also see R. C. Nelson in "Physical Methods of Chemistry," Part IIB, A. Weinberger and B. W. Rossiter, Ed., Interscience, New York, N. Y., 1971, p 214.

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Synthesis of Heteropolymetallic Silanes

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Convenient laboratory syntheses are described for the compounds $SiH_2ClCo(CO)_4$, $SiH_2[Co(CO)_4]_2$, $SiHCl_2Co(CO)_4$, $(CH_3)_2SiHCo(CO)_4$, $SiCl_2Co_2(CO)_7$, $SiH_2ClMn(CO)_5$, $SiH_2[Mn(CO)_5]_2$, and $SiCl_2[Mn(CO)_5]_2$. Of these compounds, only $SiH_2[Co(CO)_4]_2$ is previously reported. (Pentacarbonylmanganio)chlorosilane, $SiH_2ClMn(CO)_5$, reacts with dicobalt octacarbonyl, $Co_2(CO)_8$, to produce novel heteropolymetallic silanes, $SiHClMn(CO)_5Co(CO)_4$ and $SiClMn(CO)_5Co_2(CO)_7$. The general utility of this synthetic method is demonstrated by the reaction between $Fe_3(CO)_{12}$ and $SiHClMn(CO)_5Co(CO)_4$ to form $Fe(CO)_4[SiClMn(CO)_5]_2[Co_2(CO)_7]$.

Introduction

There has been, in recent years, a gratifying proliferation of knowledge in the area of transition metal chemistry. However, there remains a surprising paucity of molecular transition metal compounds combining different transition metals. Among the earliest reported examples of such "heteropolymetallic" compounds are those possessing metal to metal bonds formed, as shown in eq 1, by the reaction of

$$(CO)_nMX + NaM'(CO)_m \rightarrow NaX + (CO)_nM\text{-}M'(CO)_m \qquad (1)$$

a transition metal carbonyl halide with the sodium carbonyl metallate of a different transition metal.[2-4] Similar com-

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[1] The work herein reported in part satisfied requirements for the degree of Doctor of Philosophy for K. M. Abraham of Tufts University.

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