At a purely empirical level, it is found that *all* octahedral metal–carbonyl clusters have an 86-outer-electron configuration, and that no electron-rich or electron-deficient redox products have yet been encountered. Thus, the $H_2Ru_6(CO)_{18}$ molecule is very stable and can be recovered quantitatively after boiling a CH_2Cl_2 solution in air for a prolonged period.

Finally, it should be noted that iron forms a hexanuclear octahedral anion of identity $[Fe_6(CO)_{16}C^{2-}]$, rather than $[Fe_6(CO)_{18}{}^{2-}]$.[48]

Acknowledgments. We thank Dr. M. J. Mays (Cambridge University, England) for providing the sample of $H_2Ru_6(CO)_{18}$. Financial support was provided (in part) by the National Science Foundation (Grants No. GP-8077 and GP-26293) and the Advanced Research Projects Agency. J. W. acknowledges, with gratitude, the award of a Graduate National Fellowship from Harvard University for 1967–1970.

[48] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, **93**, 3073 (1971).

A Rearrangement of Tetramethyldiarsine Disulfide

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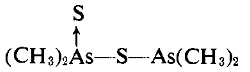
Received May 25, 1970

Abstract: The proton nmr spectra of solutions of tetramethyldiarsine disulfide in various solvents are inconsistent with both the solid-state structure, $R_2As(S)SAsR_2$, and the formulation $R_2As–S–S–AsR_2$. The intensities of the observed resonance peaks are dependent upon the solvent, concentration, time, and temperature. The spectral behavior in tetrachloroethane has been interpreted in terms of the equilibrium $R_2As–S–S–AsR_2 \leftrightarrows R_2As(S)SAsR_2$. The interpretation is supported by infrared data. Equilibrium constants, enthalpy changes, entropy changes, and free energy changes for the reaction have been calculated at several temperatures.

In our attempts to prepare dimethyldithioarsinic acid by the reaction of dimethylarsinic acid with H_2S, the disulfide II was isolated. This compound was first reported by Bunsen[1] in 1843. It was assumed to possess a disulfide link and two trivalent arsenic atoms, as is shown in I. However, current evidence is consistent with structure II. Synthesis of the compound from bis(dimethylarsine) sulfide and an excess of sulfur[1] suggests the presence of pentavalent arsenic, since trivalent arsines usually react with sulfur to produce pentavalent derivatives.[2] Furthermore, it has been found that the compound undergoes reaction with metal ions to produce salts of dimethyldithioarsinic acid, $(CH_3)_2As(S)SH$.[1] Also, the action of trifluoromethyl iodide on $(CH_3)_4As_2S_2$ has been reported to yield dimethyl(trifluoromethyl)arsine sulfide, $(CH_3)_2As(S)CF_3$, and dimethyl(trifluoromethyl)arsine, $(CH_3)_2AsCF_3$.[3] Finally, in 1964, Camerman and Trotter[4] determined the structure of $(CH_3)_4As_2S_2$ by single-crystal X-ray analysis and found that the compound contains trivalent and pentavalent arsenic atoms, as shown in II.

$(CH_3)_2As—S—S—As(CH_3)_2$

I



$(CH_3)_2\overset{\overset{S}{\uparrow}}{As}—S—As(CH_3)_2$

II

Consideration of structure II suggests that the proton nmr spectrum should display two peaks of equal intensity. However, in the present study, three methyl resonances were observed whose intensity ratios (determined on equilibrated solutions) were dependent on the solvent employed. In order to explain the apparent discrepancy between the predicted and observed proton nmr spectra of II, the work herein reported was undertaken.

Results and Discussion

Proton Nmr Spectra. The peak intensities observed in the nmr spectra of $(CH_3)_4As_2S_2$ were found to be dependent upon the solvent, concentration, temperature, and the time elapsed between the preparation of the solution and the nmr measurement.

The spectrum of a freshly prepared CCl_4 solution of $(CH_3)_4As_2S_2$ at 37° showed three sharp singlets at 2.14, 1.55, and 1.40 ppm having an intensity ratio of 1.0:1.0:0.50. After 20 min the peaks became equal in intensity and did not change thereafter. Fresh solutions in methanol displayed two resonances of equal intensity at 2.14 and 1.50 ppm. On standing, however, a new peak at 1.37 ppm was observed. At equilibrium, an intensity ratio of 1.0:0.95:0.17 was reached. The time required to reach equilibrium varied with the solvents. The location and relative intensities of the proton nmr signals at equilibrium in various solvents at 37° are given in Table I.

In most cases the spectra display three sharp peaks. The peaks at about 2.10 and 1.50 ppm were of approximately equal intensity in most solvents. However, the relative intensity of a peak at about 1.36 ppm was found to vary widely, depending on the solvent used.

Comparison of the spectra of $(CH_3)_4As_2S_2$ with those of similar compounds aided in the assignment of the peaks. The methyl proton resonances of $(CH_3)_2As—As(CH_3)_2$ [1.02 ppm;[5] 1.02 ppm (this work)], $(CH_3)_3As$

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[1] R. Bunsen, *Justus Liebigs Ann. Chem.*, **46**, 1 (1843).

[2] R. A. Zingaro, R. E. McGlothlin, and R. M. Hedges, *Trans. Faraday Soc.*, 59, 484 (1963).

[3] W. R. Cullen, *Can. J. Chem.*, **41**, 2424 (1963).

[4] N. Camerman and J. Trotter, *J. Chem. Soc.*, 219 (1964).

[5] R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

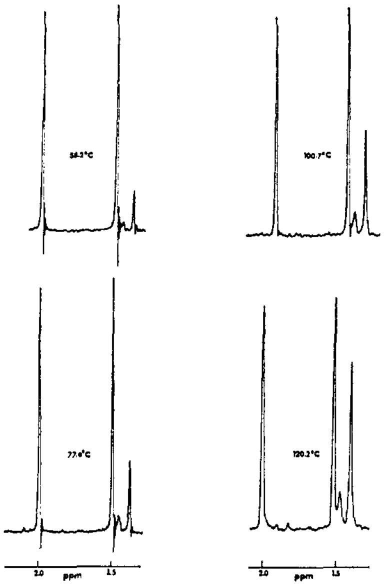


Figure 1. The temperature dependence of the nmr spectrum of equilibrated solutions of $(CH_3)_2As(S)$–S–$As(CH_3)_2$ in 1,1,2,2-tetrachloroethane (0.25 *M*).

(0.90 ppm),[6] $(CH_3)_3As{=}CH_2$ (0.82 ppm),[7] and $(CH_3)_2AsH$ (0.93 ppm)[8] have been observed. For $(CH_3)_2As$–S–$As(CH_3)_2$, a sharp singlet at 1.33 ppm was observed (this work). In $(CH_3)_2As$–SCH_3 and $(CH_3)_2AsS(CH_2)_2SAs(CH_3)_2$,[9] the protons in the $(CH_3)_2As$ units resonate at 1.25 and 1.30 ppm, respectively. Bonding to the electronegative sulfur atom causes the methyl hydrogens to resonate at lower fields. In the light of these observations it seems reasonable to associate the high-field peaks (1.50–1.28 ppm) with methyl hydrogens attached to the As(III) atom of I and II. The hydrogen atoms of the methyl groups bonded to the pentavalent arsenic atom, $(CH_3)_2As(S)S$–, would be expected to resonate at still lower fields due primarily to the bonding to two electronegative sulfur atoms. The methyl hydrogen resonances in $(CH_3)_2As(S)SNa$, for example, were observed as a singlet at 1.95 ppm (this work). Thus, it seems reasonable to assign the low-field peak at 1.83–2.14 ppm to the methyl hydrogens of the pentavalent unit, $(CH_3)_2As(S)S$–, of II. The nmr evidence shows that in solution $(CH_3)_4As_2S_2$ exists in two tautomeric forms.

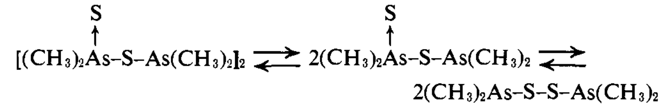
Table I. Chemical Shifts and Intensities for Methyl Resonances of $(CH_3)_4As_2S_2$ Following Equilibration in Various Solvents

Solvent	Concentration, *M*	Chemical shift, ppm[a]	Peak intensities
CCl_4	0.0936	2.14, 1.55, 1.40	1.00:1.00:1.00
$CHCl_3$	0.115	2.11, 1.55, 1.36	1.00:1.00:0.18
CH_2Cl_2	0.095	2.07, 1.49, 1.33	1.00:1.12:0.13
$C_2H_2Cl_4$	0.098	2.04, 1.43, 1.28	1.00:1.06:0.05
C_6H_6	0.121	1.83, 1.42, 1.35	1.00:1.00:0.50
CH_3OH	0.098	2.14, 1.50, 1.37	1.00:0.95:0.17
Pyridine	~0.100	1.83, 1.10	1.00:1.05
Aniline	0.121	1.73, 1.21	1.00:1.11
Dimethylamine (25% in water)		1.93, 1.77, 1.56	1.00:0.70:0.16

[a] Relative to internal TMS.

Dilution of a concentrated equilibrated solution of the disulfide II in CCl_4 brought about a change in the relative intensities of the peaks. A 1.73 *M* solution exhibited an intensity ratio of 1.00:1.00:0.76. Upon didilution, the intensities of the low-field peaks decreased relative to that of the high-field peak. At a concentration of 0.41 *M* and lower the resonances displayed an intensity ratio of 1:1:1.

It has been reported[4] that in the crystalline state $(CH_3)_2As(S)$–S–$As(CH_3)_2$ molecules are associated in pairs with the shortest intermolecular contact of 3.24 Å between two As(III) atoms. This value is smaller than the sum of the van der Waals radii (4.0 Å) and suggests charge-transfer bonding which may very likely involve the donation of nonbonded electrons in sp^3 hybrid orbitals of each As(III) to vacant 4d orbitals in the other As(III) atom. A similar type of dimer formation may take place in concentrated solutions of $(CH_3)_2As(S)SAs(CH_3)_2$ with the occurrence of the following equilibria



$$[(CH_3)_2\overset{S\uparrow}{As}\text{–S–}As(CH_3)_2]_2 \rightleftharpoons 2(CH_3)_2\overset{S\uparrow}{As}\text{–S–}As(CH_3)_2 \rightleftharpoons 2(CH_3)_2As\text{–S–S–}As(CH_3)_2$$

Molecular mass determinations in CCl_4 gave a value of 276 for a 0.015 *M* solution (vpo) and 358 for a 0.268 *M* solution (freezing point depression), indicating association in solution at higher concentrations. This would explain the concentration effects observed in the nmr spectra, since monomer formation is favored in dilute solutions. However, the association in solution does not result in any observable change in chemical shifts.

The nmr spectra obtained with $(CH_3)_4As_2S_2$ in 1,1,2,2-tetrachloroethane were independent of concentration in the range 0.05–1.00 *M*. Molecular mass determinations in this solvent, which is more polar than carbon tetrachloride, gave no indications of dimerization. However, the concentration independence of the equilibrium constant obtained from nmr measurements (Table III) is a more reliable indicator of the absence of associated species.

The effect of temperature on the spectrum was investigated using methylene chloride and 1,1,2,2-tetrachloroethane as solvents for temperatures ranging from −70 to 120°. The results are shown in Figure 1 for the higher temperatures. At −70° the peaks showed a 1.0:1.0:0.1 intensity ratio. Up to room temperature, very little change was observed. At higher temperatures, a steady increase in the intensity of the peak at 1.33 ppm and a concurrent decrease in the intensities of the downfield peaks was noted. When the heated sample was allowed to cool, the relative intensities of the peaks returned to the initial values. These observations are indicative of an equilibrium between two or more tautomers.[10]

The signals at about 2.10 and 1.50 ppm arise from the compound of structure II. The peak at 1.33 ppm which becomes predominant at higher temperatures can be attributed to a species in which all protons are equivalent. This rearrangement was found to be reversible in all of the nonbasic solvents listed in Table I. The starting

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(6) H. H. Sisler and S. R. Jain, *Inorg. Chem.*, 7, 104 (1968).

(7) H. Schmidbaur and W. Tronich, *ibid.*, 7, 168 (1968).

(8) T. Birchall and W. L. Jolly, *ibid.*, 5, 2177 (1966).

(9) L. S. Sagan, Dissertation, Texas A&M University, 1970.

(10) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, p 481.

material (II) was recovered unchanged from these solvents. The behavior of II in basic solvents is quite complicated and presently not understood.

The small peak at 1.40 ppm (Figure 1) amounts to approximately 5% of the total intensity of the other three signals. The intensity of this peak is independent of concentration and does not seem to vary with temperature. It cannot be assigned with any confidence at the present time.

The nmr spectrum of II was measured in the molten state. Two broad peaks were observed at 3.08 and 2.38 ppm, with an intensity ratio of 1.00:1.48. The high-field peak appeared to be composed of two broad peaks separated by about 5 cps. This separation was not observed at higher temperatures. Although the resonance frequencies are shifted downfield, they compare favorably with those of the disulfide in solution. As the temperature was raised there was observed an increase in the intensity of the upfield peak and a concurrent decrease in the intensity of the peak at 3.08 ppm. These results are recorded in Table II.

Table II. Chemical Shifts and Intensities of Molten $(CH_3)_4As_2S_2$

Temp, °C	Chemical shift,[a] ppm		Intensity ratio
70	3.08	2.38	1.00:1.48
90	3.06	2.38	1.00:1.57
100	3.07	2.40	1.00:2.60
110	2.45[b]		

[a] External TMS. [b] Single broad signal.

The broadening of the lines is to be expected in view of the viscosity of the melt. This viscosity broadening made it impossible to resolve the two upfield peaks. However, the observed changes in the relative intensities are easily explained in terms of the proposed equilibrium. The use of TMS as an external reference together with intermolecular association in the molten state could be important contributing factors in the observed downfield shift.

Infrared Spectra. The infrared spectrum of $(CH_3)_2As(S)$-S-$As(CH_3)_2$ was recorded as the solid in potassium bromide and in solution in CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_2Cl_4$, C_6H_6, CS_2, and acetone. Bis(dimethylarsine) sulfide was measured at 30° as the neat liquid in a cesium bromide cell of 0.1-mm path length.

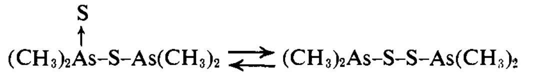
At 30° little difference was observed among the solid or solution spectra of $(CH_3)_4As_2S_2$; neither did the spectra of solutions which had equilibrated for periods in excess of a day show any significant differences from those of the freshly prepared solutions.

All the spectra were characterized by three bands in the As–C stretching region at 630, 601, and 584 cm^{-1}. The latter two bands appeared as doublets. The 584-cm^{-1} band may be assigned to the As^{III}–C stretching frequency, while the band at 601 cm^{-1} could arise from either an As^{V}–C or As^{III}–C stretching mode. Sharp bands at 580 cm^{-1} have been observed in $(CH_3)_2As$-S-$As(CH_3)_2$ in this study and in $(CH_3)_2AsCl$.[11] In the case of $(CH_3)_2As$-S-CH_3[8] and $(CH_3)_2As$-SCH_2CH_2S-$As(CH_3)_2$,[8] ν(As–C) was observed at 578 cm^{-1}. The additional peak at 630 cm^{-1} may be assigned to the As^{V}–C stretching frequency since it usually occurs at frequencies 10–50 cm^{-1} higher than As^{III}–C stretching frequencies.[12] This is in agreement with the observations made in the present study for pentavalent arsenic compounds, including $(CH_3)_2As(S)SNa$, $(CH_3)_2As(O)ONa$, and $(CH_3)_2As(O)OH$, all of which have strong As^{V}–C bands in the 650–600-cm^{-1} region.

Intense bands at 488, 399, and 365 cm^{-1} which are observed in the spectra of the disulfide may be associated with the As–S stretching frequency. It has been estimated that the fundamental As–S stretching frequency[2] should lie in the region 555–372 cm^{-1}. The band at 488 cm^{-1} is very probably associated with ν(As=S). This is in agreement with observations made in the case of compounds of the type $R_3As{=}S$,[2] which are characterized by ν(As=S) in the 470–490-cm^{-1} region. A strong As–S single-bond absorption was observed at 399 cm^{-1} for $(CH_3)_2As$-S-$As(CH_3)_2$, at 382 cm^{-1} for $(CH_3)_2As$-S-CH_3,[8] and at 390 cm^{-1} for $(C_2H_5)_2As$-S-C_2H_5.[8] It seems reasonable, therefore, to assign the low-frequency bands at 399 and 365 cm^{-1} in the spectrum of the disulfide to the As–S single-bond stretching frequency. Symmetric and antisymmetric modes may account for the appearance of two bands. There exists also the possibility that the splitting may result from the differences in the As^{III}–S and As^{V}–S single bonds.

At temperatures above 30°, changes in the relative intensities of the bands in the ir spectra were observed. The temperature was raised to 70° using CCl_4 as the solvent and to 130° using $C_2H_2Cl_4$ as the solvent. Some of the results are shown in Figure 2. At the higher temperatures, the relative intensity ratios of ν(As=S) at 488 cm^{-1} to ν(As—S) at 398 cm^{-1} changed in favor of ν(As—S). This corroborates the idea that $(CH_3)_2As(S)$-S-$As(CH_3)_2$ rearranges at elevated temperatures to a species in which the arsenic–sulfur double bond is replaced by an arsenic–sulfur single bond.

Although the disulfide has been found to have structure II in the solid state, the nmr and ir spectra show that, in solution, an equilibrium is established with a different species. The following equilibrium is postulated.



$$\underset{\text{II}}{(CH_3)_2\overset{\overset{\displaystyle S}{\uparrow}}{As}\text{-S-}As(CH_3)_2} \rightleftharpoons \underset{\text{I}}{(CH_3)_2As\text{-S-S-}As(CH_3)_2}$$

II I

It is unlikely that $(CH_3)_2As(S)$-$As(S)(CH_3)_2$ participates in the equilibrium since the ir spectra, at elevated temperatures, show a decrease in the intensity of the vibration which arises from the presence of an arsenic–sulfur double bond. The ir spectral data do not differentiate unequivocally between species I and $(CH_3)_2As$-S-$As(CH_3)_2$, a possible decomposition product of II. Attempts to synthesize II by the reaction of tetramethyldiarsine sulfide with sulfur at 25° were unsuccessful. However, under more drastic conditions the reaction does occur.[1] Any sulfur formed in the decomposition of II to $(CH_3)_2As$-S-$As(CH_3)_2$ would have certainly precipitated. We failed, however, to observe any precipitate in our nmr and ir experiments. Thus, $(CH_3)_2As$-S-$As(CH_3)_2$ is not likely to be in equilibrium with species II under the conditions employed in this study. An equilibrium between species II and I most logically satisfies the experimental data obtained during this study.

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(11) E. G. Claeys and G. P. Van der Kelen, *Spectrochim. Acta*, **22**, 2103 (1966).

(12) W. R. Cullen, G. B. Deacon, and J. H. S. Green, *Can. J. Chem.*, **43**, 3193 (1965).

Table III. Equilibrium Quotients for the Tetramethyldiarsine Disulfide Rearrangement[a]

Temp, °K	$1/T$, $(°K)^{-1} \times 10^3$	K[b]	$-\log K$	ΔG, kcal/mol	ΔS, cal/(mol °K)
302.4	3.31	0.027 ± 0.001[c]	1.57	2.18	15.2
331.4	3.01	0.081 ± 0.011	1.09	1.65	15.4
350.8	2.85	0.147 ± 0.009	0.83	1.33	15.5
361.9	2.76	0.190 ± 0.008	0.72	1.19	15.4
373.9	2.67	0.242 ± 0.011	0.62	1.05	15.3
383.9	2.61	0.302 ± 0.011	0.52	0.91	15.3
393.4	2.54	0.412[d]	0.38	0.69	15.4
ΔH = +6.77 kcal/mol					

[a] Data were obtained in $C_2H_2Cl_4$ at 0.05, 0.10, 0.25, 0.465, 0.7, and 1.0 M solute on a Varian HA-100 spectrometer. [b] Average deviation reported. [c] Data from 0.1 and 0.46 M solutions only. [d] 0.25 M solution.

Measurement of the Equilibrium Constant and Related Parameters. The concentration equilibrium quotients (K) were calculated from the intensities of the

$$K = \frac{[(CH_3)_2As\text{-}S\text{-}S\text{-}As(CH_3)_2]}{[(CH_3)_2As(S)\text{-}SAs(CH_3)_2]}$$

nmr peaks obtained with solutions of 0.05, 0.10, 0.25, 0.46, 0.70, and 1.00 M concentrations at various temperatures. The sum of the intensities of the two downfield peaks arising from two sets of methyl protons is proportional to the concentration of species II, while the intensity of the peak furthest upfield is a measure of the concentration of species I, in which all protons are equivalent.

The free energy changes were calculated from the values of K. The enthalpy of formation was calculated in the conventional manner from the slope of a plot of log K *vs.* $1/T$ (Figure 3). The entropy was then calculated from the measured values for ΔG and ΔH. The results are summarized in Table III. The values of K were found to be independent of the concentration.

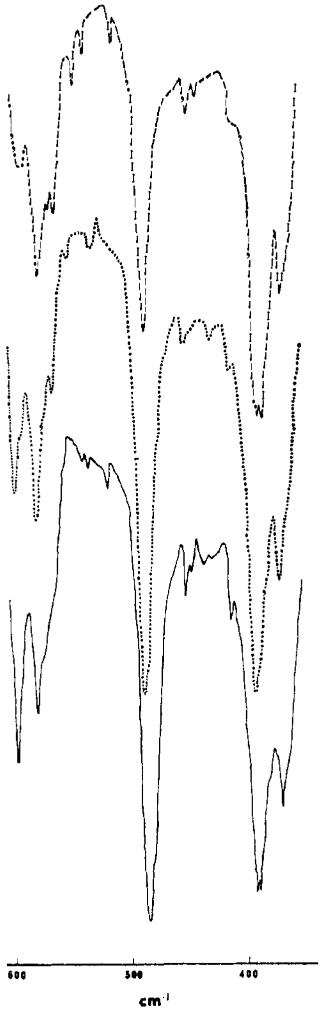

Figure 2. The temperature dependence of the ir spectrum of equilibrated solutions of $(CH_3)_2As(S)\text{-}S\text{-}As(CH_3)_2$ in carbon tetrachloride and 1,1,2,2-tetrachloroethane (1.6 M): ——, 30°; · · ·, 60°; - - -, 75°.

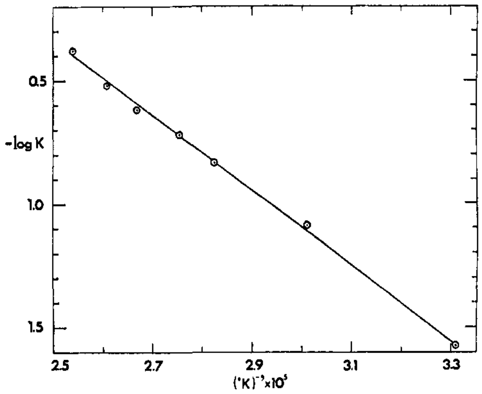

Figure 3. Plot of log K_{eq} *vs.* $1/T$ for the equilibrium II $\rightleftarrows$ I.

The structure of the corresponding phosphorus analog has been considered by Cowley and coworkers.[13,14] On the basis of a series of physical measurements, they concluded that the structure of the phosphorus compound is best represented by $(CH_3)_2P(S)\text{-}P(S)(CH_3)_2$. Thus, there are present two equivalent pentavalent phosphorus atoms, each bearing a sulfur atom and two methyl groups. The phosphorus atoms are bonded *via* a P–P link. That this structure is probably correct is corroborated by the work of Dutta and Woolfson.[15] Using single-crystal X-ray techniques, they established that the structure of $(C_2H_5)_4P_2S_2$ does, in fact, involve two pentavalent phosphorus atoms and a P–P bond. The sulfur atoms bonded to the respective phosphorus atoms occupy trans positions. Based upon infrared data,[14] the P–P bond appears to remain intact in solution.

There appears to be no solid evidence upon which to base an explanation for the stabilities of these various

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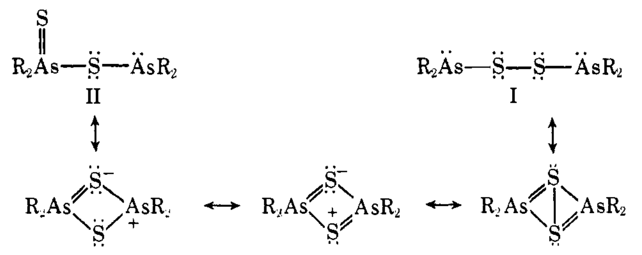
(13) A. H. Cowley and H. Steinfink, *Inorg. Chem.*, 4, 1827 (1965).

(14) A. H. Cowley and W. D. White, *Spectrochim. Acta*, 22, 1431 (1966).

(15) S. N. Dutta and W. M. Woolfson, *Acta Crystallogr.*, 14, 178 (1961).

structures. However, the following mechanism for the conversion of species II to I is quite reasonable.



Mass Spectrum. The mass spectrum of $(CH_3)_4As_2S_2$ was measured in order to determine whether a similar rearrangement as observed in solution might take place in the gas phase. The mass spectral data (Figure 4) are consistent with the reported structure. The most intense peaks occur at *m/e* values of 227 and 259, which correspond to the fragments $(CH_3)_3As_2S$ and $(CH_3)_4As_2S$, respectively. The molecular ion peak is of relatively low intensity. The predominant fission reactions involve therefore the rupture of the As=S and/or As—CH_3 bonds. A decision as to whether a rearrangement from structure II to I occurs in the gas phase cannot be made at this time due to the lack of data on the mass spectral behavior of arsenic–sulfur compounds.

Experimental Section

The proton nmr spectra were recorded using Varian Associates Models A-60 and HA-100 spectrometers equipped with variable-temperature probes. The temperature of the probe was determined by recording the spectrum of ethylene glycol at a given temperature and comparing the separation between the two peaks with published data. In the case of the molten disulfide, TMS was employed as the external standard in a sealed tube. The spectra of tetramethyldiarsine and bis(dimethylarsine) sulfide were obtained using the neat liquids with TMS as the external standard. Sodium dimethyldithioarsinate was dissolved in methanol (1.65 *M*).

The infrared spectra were recorded on a Beckman Model IR-12 spectrophotometer using potassium bromide pellets or solutions. A cesium iodide cell, equipped with a heating jacket, was used to obtain spectra of heated samples. In order to compensate for the emission of energy by the heated cell, the chopping between the sample and the detector was stopped. In this way, any heat energy emitted by the sample cell which reached the detector was of the dc type and not amplified. Because the source radiation was still being chopped, however, a usable detector response was still available. The temperature was monitored by means of a copper–constantan thermocouple.

The mass spectrum was obtained with a Bell & Howell 21-110-B mass spectrometer. The probe and the ion source temperatures were 35 and 180°, respectively. The molecules were ionized with 70-eV electrons.

The molecular mass determinations were carried out with a Hewlett-Packard vapor pressure osmometer, Model 302-B, at 38° in CCl_4 and $C_2H_2Cl_4$ solutions employing benzil as the standard.

All solvents used in this study were of spectral grade quality except for $C_2H_2Cl_4$. It was purified by shaking with concentrated sulfuric acid followed by steam distillation, drying over potassium carbonate, and fractionation. Dimethyliodoarsine and sodium disulfide were prepared according to methods described in the literature.[16,17]

$(CH_3)_2As(S)$-S-$As(CH_3)_2$. Preparation of this compound was carried out according to a procedure adapted from a method first reported by Bunsen.[1]

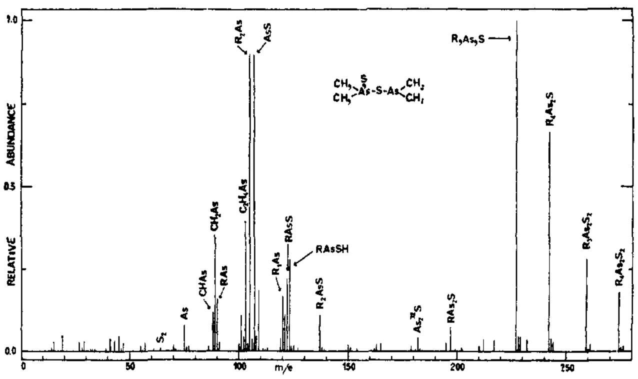


Figure 4. The mass spectrum of $(CH_3)_4As_2S_2$.

Dimethylarsinic acid (40 g, 0.290 mol) was dissolved in 200 ml of 75% ethanol in a 500-ml Erlenmeyer flask equipped with a magnetic stirrer, gas delivery tube, and a gas exit tube. Hydrogen sulfide was bubbled through the solution for 1 hr. During the course of the reaction elemental sulfur precipitated. It was removed by filtration. The reaction mixture was concentrated in order to induce precipitation of the product. After several recrystallizations from 30% aqueous ethanol and drying over phosphorus pentoxide, the white crystalline sulfide (35.7 g, mp 70–71°, 90% yield) was obtained.

The disulfide was found to be stable under ordinary atmospheric conditions. Exposure to the atmosphere for periods of up to 1 week did not depress the melting point, and no significant changes were observed in the ir spectrum. This greatly facilitated handling procedures. The compound was stored over calcium chloride. Manipulations should be carried out in a well-ventilated hood.

Anal. Calcd for $C_4H_{12}As_2S_2$: C, 17.52; H, 4.41; As, 54.68; S, 23.39; mol wt, 274. Found: C, 17.71; H, 4.69; As, 54.90; S, 23.60; mol wt, 276 (vapor pressure osmometry, 0.015 *M* in CCl_4), 358 (freezing point depression, CCl_4, 0.268 *M*).

$(CH_3)_2As$-S-$As(CH_3)_2$. A 100-ml round-bottomed flask equipped with a magnetic stirrer and a dropping funnel was charged with nitrogen. A solution of sodium sulfide nonahydrate (15 g, 0.0624 mol) dissolved in 20 ml of water was then added. Dimethyliodoarsine (20.17 g, 0.0887 mol) was added dropwise to the vigorously stirred solution with the formation of a suspension which was initially orange in color. As the reaction proceeded, the solution became colorless and evolution of heat was noted. After stirring for 5 hr, the nonaqueous layer was separated, washed twice with water, and dried over $CaCl_2$ for 10 hr. The product was purified by vacuum distillation under nitrogen. The fraction boiling between 50.0 and 55.5° (2 Torr) was collected. The yield was 8.03 g (62.2%).

Anal. Calcd for $C_4H_{12}As_2S$: C, 19.85; H, 5.01; As, 61.90; S, 13.25. Found: C, 19.83; H, 4.92; As, 61.66; S, 13.02.

Attempted Preparation of $(CH_3)_2As$-S-S-$As(CH_3)_2$. A 100-ml round-bottom flask equipped with a magnetic stirrer, reflux condenser, and rubber septum was charged with sodium disulfide (6.00 g, 0.054 mol) dissolved in 34 ml of absolute ethanol. The apparatus was flushed with nitrogen and dimethyliodoarsine (19.99 g, 0.0864 mol) was added by means of a syringe over a period of 1 hr. After stirring for 10 hr, the yellow solution became deep red in color. The solvent was removed at reduced pressure and the resulting solid was extracted several times with warm, dry benzene. The extract was concentrated by evaporation of the solvent to induce precipitation of the product. After several recrystallizations from both benzene and aqueous ethanol and drying over phosphorus pentoxide, the white crystalline precipitate (3.7 g, 45% yield) melted at 69–70°. The melting point and its properties corresponded to those of compound II.

Acknowledgments. We express our appreciation to the Robert A. Welch Foundation of Houston, Texas, and the U. S. Atomic Energy Commission (Contract No. AT-40-1-2733) for funds in support of this work. L. J. E. also wishes to express his appreciation to the Graduate School of Texas A&M University for support in the form of a graduate fellowship.

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