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Arsine Oxides

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A total of nine trialkylarsine oxides have been synthesized by the oxidation of the parent arsines with hydrogen peroxide and/or mercuric oxide. The direct conversion of arsines to arsinic acids on their exposure to the moist atmosphere has been observed. Some preliminary results on the formation of compounds between arsine oxides, selenides, and sulfides with metal salts, halogens, and interhalogens are also described. The fundamental As–O stretching vibration has been located in a number of arsine oxides in the range 855–910 cm.$^{-1}$.

Introduction

As part of a systematic study of the chemistry of the donor properties of the trialkyl group V chalcogenides,[1] we attempted to prepare a series of trialkylarsine oxides. Although the history of these compounds dates back to 1854, it became apparent that there exists a serious lack of adequate data concerning both the preparation and physical properties of these compounds as reported by previous workers.[2–12] Although repeated and painstaking efforts were made to reproduce the earlier work, all attempts either failed or gave results which differed greatly from those described. It was, therefore, decided to undertake a complete re-examination of the preparation and properties of these compounds. The results of this study are described in this paper.

It was found that the exposure of solutions of triethyl- or tri-*n*-butylarsine in ether to the normal laboratory atmosphere, the bubbling of air through them, or their treatment with excess 30% aqueous solution of hydrogen peroxide resulted in the separation of crystals of diethyl- or di-*n*-butylarsinic acid and not of the oxide, as previously reported.[2,3] Burrows[9] also observed that the exposure of phenyldimethylarsine to the moist atmosphere resulted in its conversion to phenylmethylarsinic acid, $C_6H_5CH_3As(O)OH$.

The successful preparation of the lower trialkylarsine oxides was accomplished by the mercuric oxide oxidation of acetone solutions of the arsines. Once the arsine oxide was identified and its physical properties had been established, it was prepared again by oxidation of the arsines with aqueous 30% hydrogen peroxide. In both methods the reactions were carried out under nitrogen, as suggested by Kamai and Chernokal'skii,[12] in order to eliminate oxidation by molecular oxygen.

The availability of this homologous series of pure arsine oxides made it possible to establish the location of the fundamental stretching vibration, ν_{As-O}, with a high level of confidence.

Experimental Section

Materials.—Arsenic trichloride and the usual solvents were of reagent grade and were used without further purification. Alkylarsonic acids and dialkylarsinic acids, which were used as starting materials for the preparation of alkylarsine dichlorides and dialkylarsine chlorides, were furnished free of charge by the Vineland Chemical Co., Vineland, N. J.

The trialkylarsines were purified by fractional distillation through a Nester–Faust 30-in., gold-plated, spinning-band column under dry nitrogen at atmospheric or reduced pressure.

Infrared spectra were recorded on a Beckman IR-8 spectrometer. The instrument was calibrated by means of a polystyrene standard.

Melting points of these extremely hygroscopic compounds were determined in a Hershberg melting point apparatus with a thermometer calibrated against total immersion standards from the National Bureau of Standards. Four finely ground samples of each compound were placed in dry capillaries inside a carefully dried, nitrogen-filled drybox in which the sample tubes were sealed with heavy Celvacene grease. They were then flame sealed, and melting points were determined immediately. The molten samples were allowed to cool, and the melting points were redetermined to establish the reproducibility of the observed values and to be sure that no structural changes resulted from fusion. These values were then redetermined after a period of 3 months with freshly prepared samples. This care was necessary because of the rapid and extreme lowering of the melting points of these extremely hygroscopic compounds upon their exposure to air.

Boiling points reported here are uncorrected.

pK_a values of dialkylarsinic acids are based upon half-equivalence points obtained from titration curves recorded on a Sargent recording titrator.

Molecular weights were determined by means of a Mechrolab vapor pressure osmometer.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The services of Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Alfred Bernhardt, Ruhr, Germany, were also utilized to confirm the data.

Warning! We urge extreme caution and diligent care in handling the volatile, lower alkylarsines which are highly flammable and the exercise of even greater care in the handling of alkylarsine halides. The use of protective gloves and respirators and working in an efficient hood are *absolutely essential*. The haloarsines cause painful burns that become evident several hours after contact. After this time medical treatment is less effective, and painful blisters will persist for weeks and cause scarring. It is obvious that severe lung damage can result from inhalation of the vapors of these materials.

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(1) See, for example, R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, **1**, 771 (1962).

(2) H. Landolt, *Ann.*, **89**, 325 (1854).

(3) A. Cahours, *ibid.*, **112**, 230 (1859).

(4) A. Michaelis and V. Paetow, *Ber.*, **18**, 44 (1885).

(5) F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 1754 (1922).

(6) W. J. C. Dyke, G. Davies, and W. J. Jones, *ibid.*, 185 (1931).

(7) W. J. Jones, G. Davies, W. J. C. Dyke, D. C. Griffiths, and J. H. E. Webb, *ibid.*, 2284 (1932).

(8) F. G. Mann, *ibid.*, 958 (1932).

(9) G. J. Burrows, *J. Proc. Roy. Soc. N. S. Wales*, **68**, 72 (1935).

(10) G. A. Razuvaev, V. X. Malinovskii, and D. A. Godina, *J. Gen. Chem. USSR*, **5**, 721 (1935); *Chem. Abstr.*, **30**, 1057^8 (1936).

(11) M. G. Petit, *Compt. rend.*, **209**, 111 (1939).

(12) G. Kamai and B. D. Chernokal'skii, *Tr. Kazansk. Khim. Tekhnol. Inst.*, **26**, 117 (1959).

Table I

Trialkylarsine Oxides

Deriv.	M.p., °C.		% C		% H		% As		Mol. wt.	
	Found	Lit.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(1) Trimethyl-	191.2–195.2		26.49	26.30	6.62	6.74	55.14	55.14	136	150
				26.32		6.84		55.27		
(2) Triethyl-	105–106.5	Oil,[2] 116[12]	40.46	40.11	8.49	8.63	42.06	42.13	178	176
				40.57		8.69		42.04		186
(3) Tri-*n*-propyl-	96.1–96.8	61–63[12]	49.10	48.77	9.61	9.70	34.02	33.79	220	228
(4) Tri-*n*-butyl-	109.1–110	Paste[6]	54.96	55.02	10.37	10.20	28.56	28.60	262	261
(5) Tri-*n*-octyl-	69.6–71.2		66.95	66.81	11.94	11.76	17.40	17.70	431	439
				66.71		11.69		17.57		423
(6) Tricyclohexyl-	210–212		63.52	63.14	9.77	9.97	22.01	21.69	340	353
				63.27		9.65		21.72		344
(7) Dimethyl-*n*-butyl-	93.2–93.7	93–98[12]	40.46	35.90	8.49	8.86	42.06	37.08	178	234
				35.68		8.98		36.92		236
				38.40		8.99		37.66		250
				38.39		8.87		43.21		244
(8) Methyldiethyl-	97.6–98.6		36.60	36.37	7.99	7.99	45.66	45.76	164	172
				36.03		8.11		45.07		180
(9) Diethyl-*n*-butyl-	36–37	103[7]	39.57	42.85	10.52	9.48	41.13	33.19	182	281
				42.53		9.41		33.44		290
(10) Di-*n*-propyl-*n*-butyl-	86.2–87.2	106[7]	51.30	48.92	9.98	9.90	32.00	32.68	234	263
				48.79		9.93		32.55		
(11) Methyldi-*n*-butyl-	65.6–66.7	61–63[12]	49.10	48.93	9.61	9.59	34.02	34.09		
				48.53		9.82		33.60		
(12) Diphenylmethyl-	152.7–153.8	142[9]	60.02	59.87	5.04	5.02	28.79	28.62	260	263
				60.06		5.16		28.87		268

Arsines.—The preparation of the arsines has been described previously.[13] The following arsines were prepared, and their boiling or melting points are noted: trimethyl-, 49–51° (747 mm.),[14] 53% yield; triethyl-, 138° (755 mm.),[15] 78% yield; tri-*n*-propyl-, 36° (0.15 mm.),[16] 71% yield; tri-*n*-butyl-, 74–78° (1.10 mm.),[17] 83% yield; tri-*n*-octyl-, 166–167° (0.04 mm.),[18] 78% yield; dimethyl-*n*-butyl-, 51° (35 mm.),[8] 59% yield; diethylmethyl-, 107° (755 mm.),[19] 48% yield; diethyl-*n*-butyl-, 83–84° (29 mm.),[7] 90% yield; di-*n*-propyl-*n*-butyl-, 112° (23 mm.),[7] 78% yield; diphenylmethyl-,[20] prepared only as the crude product; tri-4-bromophenyl-, 136–138°[21]; di-*n*-butylmethyl-, 82–83° (2.5 mm.),[7] 79% yield.

The values observed for the boiling points, with two exceptions, were in agreement with those previously reported when one value was extrapolated to the pressure of the other. In the case of the tri-*n*-octyl compound, the previously reported value[19] was 238–240° (9–10 mm.). Our preparation analyzed as follows: C, 69.70; H, 12.55; As, 18.09. The calculated values are: C, 69.56; H, 12.39; As, 18.09. Vaughn and Tarbell[22] reported a melting point of 93–95° for tri-4-bromophenylarsine. This was in serious disagreement with our observed value of 136–138°. The crude product isolated from the Grignard reaction was vacuum distilled, and the distillate, which solidified on cooling, was recrystallized from petroleum ether to a constant melting point of 136–138°. The recrystallized product analyzed as follows: As, 13.81; Br, 44.10. The calculated values are As, 13.61; Br, 44.34.

Preparation of Arsine Oxides.—These were prepared by either oxidation of a given arsine by red mercuric oxide in acetone or oxidation by aqueous 30% hydrogen peroxide in diethyl ether solution.

When mercuric oxide was the oxidizing agent, the procedure was to reflux, under nitrogen, an acetone solution of the arsine with finely powdered red mercuric oxide in a mole ratio of 1:1 for a period of time sufficient to reduce the mercuric oxide to elemental mercury.[22] It was no longer necessary to work under an atmosphere of nitrogen once the oxidation was completed. Isolation and purification of the oxide was accomplished by removal of the solvent by distillation followed by repeated extraction of the arsine oxide with water to remove mercury and unreacted mercuric oxide. The aqueous solution, if colored, was treated with activated charcoal. Any unreacted arsine was removed by extraction of the water solution with diethyl ether. Crystalline arsine oxides were obtained by evaporating the aqueous extract almost to dryness. The concentrated aqueous solution was then taken to dryness with heating under vacuum (*ca.* 0.05 mm.) until dry, crystalline solids remained. These were transferred to a sublimation apparatus in a drybox and purified by sublimation *in vacuo*. The following description of the preparation of tri-*n*-propylarsine oxide will serve to furnish details.

Into a three-necked flask, equipped with a nitrogen inlet, stirrer, and condenser, was placed a mixture containing 41.1 g. (0.20 mole) of redistilled tri-*n*-propylarsine, 43.7 g. of red mercuric oxide, and 60 ml. of acetone. The mixture was refluxed for 18 hr., after which the mixture was removed and centrifuged to remove the precipitate consisting of elemental mercury, unreacted mercuric oxide, and organic mercurials that were formed. The acetone was removed by distillation, and a dark brown, heavy liquid remained. Water and ether were both added to the liquid in order to separate any unreacted arsine (ether soluble) from the arsine oxide (water soluble). The liquid layers were separated, and the water layer was evaporated under reduced pressure with heating. Additional solids separated during the evaporation. These were removed periodically. The concentrated aqueous layer was decolorized by boiling with charcoal, filtered, and evaporated under high vacuum with heating. The solid which remained weighed 11.9 g. (27% yield). The crude product thus obtained was transferred to a sublimator in a drybox and sublimed to the pure crystalline product.

Oxidation by aqueous 30% hydrogen peroxide was carried out by the dropwise addition of the peroxide to an ether solution of the arsine with very vigorous stirring. The reactions were quite exothermic. Following addition of the peroxide, stirring and

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(13) R. A. Zingaro and A. Merijanian, *Inorg. Chem.*, **3**, 580 (1964).

(14) E. J. Rosenbaum and C. R. Sandberg, *J. Am. Chem. Soc.*, **62**, 1623 (1940).

(15) A. G. Kali-Chemie, British Patent 768,765 (Feb. 10, 1957).

(16) E. Krause and A. Von Grosse, "Die Chemie der metallorganischen Verbindungen," Edwards Brothers Inc., Ann Arbor, Mich., 1943, p. 458.

(17) J. Seifter, *J. Am. Chem. Soc.*, **61**, 530 (1939).

(18) E. C. Shokal, U. S. Patent 2,840,617 (June 24, 1958).

(19) A. Cahours, *Ann.*, **122**, 220 (1862).

(20) F. F. Blicke and E. L. Cataline, *J. Am. Chem. Soc.*, **60**, 420 (1938).

(21) J. R. Vaughn and D. S. Tarbell, *ibid.*, **67**, 144 (1945).

(22) A period of 24 hr. was sufficient in most cases, but 6 days was needed to oxidize tricyclohexylarsine.

TABLE II

ARSINIC ACIDS FROM AIR OXIDATION OF ARSINES

Compd.	M.p., °C.	p*K*	Monomer formula wt.	Equiv. wt. found	Mol. wt.[a] found
$(C_2H_5)_2As(O)OH^b$	137.5–138	6.51	166	165	...
$(n\text{-}C_3H_7)_2As(O)OH^c$	134–135.5	6.62	194	192	374
$(n\text{-}C_4H_9)_2As(O)OH^d$	139	7.13	221	222	...
$(n\text{-}C_5H_{11})_2As(O)OH^e$	131	...	250	...	426
$(C_6H_{11})_2As(O)OH^f$	179–181	7.25	274	271	535

[a] Molecular weights were measured at concentrations of *ca.* 0.8 *M.* [b] Yield: 4–5%. [c] Yield: 3–5%. [d] *Anal.* Calcd.: C, 43.33; H, 8.53; As, 33.74. Found: C, 43.23; H, 8.53; As, 33.74. Yield: 2.5%. [e] *Anal.* Calcd.: C, 48.00; H, 9.20; As, 30.00. Found: C, 48.18; H, 8.67; As, 30.56. Yield: 3%. [f] *Anal.* Calcd.: C, 52.56; H, 8.38; As, 27.31. Found: C, 52.61; H, 8.32; As, 27.33. Yield: 1–2%.

heating of the reaction mixture was continued for 1–2 hr. The aqueous phase was separated, and the water extracts containing the arsine oxides were extracted with additional ether to remove any unreacted arsine. The water extract was then treated in a manner identical with that described in the preceding paragraph.

The higher alkylarsine oxides, such as the octyl derivative, were best purified by freezing out the oxide from *n*-hexane under anhydrous conditions, followed by drying *in vacuo* with further heating.

The tertiary arsine oxides prepared by both methods are listed in Table I along with pertinent data.

TABLE III

COORDINATION COMPOUNDS OF SOME ARSINE OXIDES, SELENIDES, AND A SULFIDE

Complex	M.p., °C.	%			%			%			Ratio of Br or Cl to I
		Element	Calcd.[a]	Found	Element	Calcd.[a]	Found	Element	Calcd.	Found	
$(C_2H_5)_3AsSe + I_2$	68 dec.	C	14.58	12.92 13.15	H	3.27	2.59 2.66	I	51.28	55.61 55.90	...
$(C_6H_{11})_3AsSe + I_2$	160–161 dec.	C	32.80	29.20	H	5.00	4.23	I	38.7	38.61 41.28	...
$(C_6H_{11})_3AsO + I_2$	88–90 dec.	As	12.60	10.27 10.18	...	...	...	I	42.72	56.03 56.28	...
$(C_6H_{11})_3AsO + IBr$	137–139	As	13.70	16.22 16.39	Total halogen	37.84	I 17.34 Br 14.91 32.25 I 17.13 Br 14.66 31.79	...	...	...	2
$(C_6H_{11})_3AsO + ICl$	154–157	As	14.90	15.68	Total halogen	32.30	I 15.25 Cl 9.14 24.39	...	...	...	2
$[(C_6H_{11})_3AsO]_4Ni(ClO_4)_2$	...	C	53.41	53.38 53.49	H	8.23	8.33 8.44	Ni	3.62	3.34	...
$[(C_6H_{11})_3AsO]_2CoCl_2$	...	Co	7.38	7.54	As	18.45	18.32	Cl	8.73	8.57	...
$[(C_2H_5)_3AsS]_2CoCl_2$	...	As	28.91	28.66	Cl	13.68	13.44	...	...	...	...

[a] The calculated values, in the case of the halogen derivatives, are based upon the assumed formation of a 1:1 addition compound.

Arsinic Acids.—Exposure of the trialkylarsines or their ether solutions to the atmosphere or to excess hydrogen peroxide yielded crystalline solids which separated directly from the solutions and were identified as the arsinic acids. Those which separated in this manner and which were identified are listed in Table II along with pertinent physical data.

Coordination Compounds and Molecular Complexes.—These compounds were generally prepared by dissolving a stoichiometric quantity of each of the components in a minimum volume of warm solvent such as chloroform, carbon tetrachloride, or absolute ethanol and then mixing these solutions and allowing them to stand. If crystals did not separate on cooling, the solutions were reduced in volume by slow evaporation and then refrigerated until solid products began to form. These products were washed with appropriate solvents to remove any unreacted materials. The preparation of bis(tricyclohexylarsine oxide)-cobalt(II) chloride, for example, was carried out as follows.

In 15 ml. of absolute ethanol was dissolved 0.56 g. of $CoCl_2 \cdot 6H_2O$, to which was added a solution containing 1.5 g. of tricyclohexylarsine oxide in 15 ml. of absolute ethanol. The solution was of a deep blue color. The ethanol was evaporated under reduced pressure, and, when crystals began to form, the evaporation was terminated, and the saturated solution was placed in a desiccator over calcium chloride under aspirator pressure.

The bright blue crystals which separated were redissolved in a minimum volume of ethanol and reprecipitated by the addition of ether.

The other compounds prepared are listed in Table III with the appropriate analytical data.

Results and Discussion

Arsine Oxides and Arsinic Acids.—Nine trialkylarsine oxides have been synthesized and characterized as the anhydrous compounds.

Comparison of the melting points observed in this work (Table I) with those previously reported reveals serious disagreement in almost every case. The principal reason for these discrepancies is that the trialkylarsine oxides, as well as the mixed alkylaryl derivatives, are so extremely hygroscopic that they must be isolated in a completely moisture-free environment. Also, the exposure of trialkylarsines to moist air brings about their partial conversion to the corresponding arsinic acids, $R_2As(O)OH$, which contaminate any oxide which may be formed.

The failure of previous investigators to exercise the necessary care in completely excluding any moisture resulted in the hydration of their compounds and the resulting low values of their melting points. This difficulty also explains why, in some cases, no melting point or any other physical properties were recorded.

There is little doubt that Kamai and Chernokal'skii[12] and Burrows[9] prepared a number of arsine oxides, but the melting points which they observed were lower by as much as 35° (Table I; compounds 3 and 12), and they were unquestionably those of the partially hydrated compounds. Upon exposure to the atmosphere these compounds very rapidly absorb moisture, appear syrupy, and then form a homogenous liquid phase. Repeated, independent determinations of physical constants were necessary in order to be certain that the samples were not absorbing moisture. The characterization of triethylarsine oxide as an oil by Landolt,[2] and of tributylarsine oxide as "pasty crystals" by Dyke, *et al.*,[6] was clearly the result of attempting to isolate these compounds under ordinary laboratory conditions.

Kamai and Chernokal'skii's reported melting point of 116° for triethylarsine oxide is higher than our observed value of 105–106.5°. In order to establish the reliability of one or the other value we prepared this compound several times using both methods of oxidation and determined the melting points of numerous samples after various drying periods, some extending for several days. The observed values were consistently reproducible within 1°. It is probable that Kamai and Chernokal'skii's value is that of diethylarsinic acid (m.p. 137.5–138°) contaminated with triethylarsine oxide. This is supported by the fact that their arsine oxidation product was not purified but simply dried over P_2O_5 at 130–150°. The oxidation reaction was carried out in the presence of atmospheric oxygen, and the drying conditions employed may have caused the formation of diethylarsinic acid as was shown by the pyrolysis experiments of the same investigators.

Our attempts to synthesize dimethyl-*n*-butyl-, diethyl-*n*-butyl-, and di-*n*-propyl-*n*-butylarsine oxides from the parent arsines by hydrogen peroxide oxidation were not successful as indicated by the analytical data (Table I). Perhaps a redistribution of alkyl groups may have occurred *via* a free-radical mechanism with the resultant formation of a mixture of trialkylarsine oxides. Such a rearrangement may also have occurred as a result of heating during the sublimation process. This would not lead to isomerization if the three alkyl groups were identical. The oxidation of mixed arsines *via* the more moderate mercuric oxide oxidation process may be required for the successful preparation of these compounds.

The molecular weights observed for three of the arsine oxides suggests the existence of some degree of association in solutions of these compounds (Table I; compounds 7 and 9). It is possible that pyrolysis of arsine oxides yields arsinic acids,[12] which are capable of autodimerization or of association with the oxides *via* hydrogen bonding. Although the melting points of the compounds containing the mixed alkyl groups were reproducible and, in the case of dimethyl-*n*-butylarsine oxide, in relatively good agreement with that previously reported,[12] the characterization of these compounds will require further investigation.

TABLE IV

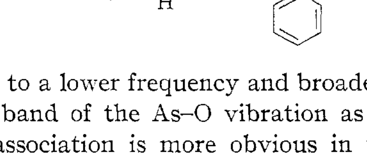
THE FUNDAMENTAL As–O STRETCHING VIBRATIONAL FREQUENCIES

Compd.	ν_{As-O}, cm.$^{-1}$	Compd.	ν_{As-O}, cm.$^{-1}$
$(CH_3)_3AsO$	903	$(CH_3)_2C_6H_5AsO$	910
$(C_2H_5)_3AsO$	885	$(C_2H_5)_2CH_3AsO$	890
$(n\text{-}C_3H_7)_3AsO$	888	CH_3AsO	825
$(n\text{-}C_4H_9)_3AsO$	892	$(4\text{-}BrC_6H_4)_3AsO$	896 889
$(n\text{-}C_8H_{17})_3AsO$	900	$(3\text{-}NH_2C_6H_4)_3AsO$	855 858
$(C_6H_{11})_3AsO$	871	$(n\text{-}C_4H_9)_2AsO_2H$	890
$2[(C_6H_{11})_3AsO]\cdot CoCl_2$	852	$(C_6H_{11})_2AsO_2H$	880
$(n\text{-}C_4H_9)_2CH_3AsO$	892		

The Fundamental As–O Vibration.—The force constants of an As–O bond as estimated by the use of Gordy's[23] rule are 8.7×10^5 and 4.6×10^5 dynes cm.$^{-1}$ for a single bond and double bond, respectively. These values, when substituted into the fundamental equation for an harmonic oscillator, give ν_{As-O} 964 and 776 cm.$^{-1}$ for a "pure" single bond and double bond, respectively. In Table IV are listed the frequencies measured for the fundamental As–O vibration in a series of compounds containing the As–O group. The parent arsines were found to be transparent in this region. The values for the As–O fundamental vibration were, in most cases, within 10–40 cm.$^{-1}$ of 920 cm.$^{-1}$, the average of the frequencies calculated for a single and double bond. The observed frequency suggests a bond order somewhat higher than one which may well result from the back donation of the $p\pi$ electrons of the oxygen atom utilizing the empty $d\pi$ orbitals of the arsenic atom.

The force constant of the As–O bond was calculated by taking ν_{As-O} 890 cm.$^{-1}$, the average value observed for trialkylarsine oxides, and substituting it into the rearranged equation of the harmonic oscillator to give a value of $k = 6.9 \times 10^5$ dynes cm.$^{-1}$.

The As–O vibration in the trialkylarsine oxides behaves very much as an isolated group frequency and appears to be relatively insensitive to mass and inductive effects. In the case of the two triarylarsine oxides, $(4\text{-}BrC_6H_4)_3AsO$ and $(3\text{-}NH_2C_6H_4)_3AsO$, the frequencies were observed as doublets separated by 7 and 3 cm.$^{-1}$, respectively. The cause of the splitting cannot be unequivocally established, but intermolecular association of the arsenyl groups with adjacent phenyl ring substituents is offered as an explanation at this time. For example, a hydrogen bond involving the amino group and the arsenyl group of another molecule is not unreasonable, *i.e.*



The shift to a lower frequency and broadening of the absorption band of the As–O vibration as a result of molecular association is more obvious in the case of

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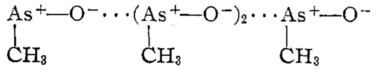
[23] W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

monomethylarsine oxide, CH_3AsO, which appears to form a tetramer in benzene (molecular weight calculated 106; found 419).[24] This may involve either an eight-membered ring or association *via* the As–O dipole, *i.e.*



$$\underset{CH_3}{As^+}-O^-\cdots(\underset{CH_3}{As^+}-O^-)_2\cdots\underset{CH_3}{As^+}-O^-$$

It is interesting to note that in the case of di-*n*-butylarsinic acid the observed As–O frequency is lower than in the tri-*n*-butylarsine oxide. The substitution of a more electronegative group would be expected to bring about a shift to a higher frequency.[25] In other words, the double-bond character of the As–O bond increases as the electronegativity of the central arsenic atom increases. This trend is observed also in the case of dicyclohexylarsinic acid and tricyclohexylarsine oxide. What is involved in these cases could well be the net result of the competing effects of electronegativity, inducing a shift to higher frequencies, and molecular association, reversing this trend.

The spectra of tricyclohexylarsine oxide, its coordination complex with $CoCl_2$, and the parent arsine, all in benzene solutions, were also measured in the region of $\nu_{\mathrm{As-O}}$. The arsenyl absorption band in the complex $2(C_6H_{11})_3AsO \cdot CoCl_2$ was lowered by 21 cm.$^{-1}$ relative to the free arsine oxide. This suggests that the coordination brings about a lowering of the frequency.[26]

Coordination Compounds.—The formation of complexes and molecular addition compounds between arsine chalcogenides and various acceptors such as transition metal salts, halogens, and interhalogens was also investigated.[12]

When either an arsine oxide or selenide was caused to react with iodine or an interhalogen, crystalline products were formed. Analysis of these solids did not reveal any simple molecular ratio between the reacting molecules. Although halogen-containing precipitates always formed, their compositions varied with each preparation. The reaction of the arsine oxides with iodine monochloride or iodine monobromide resulted in the formation of crystalline solids in which the atomic ratios of chlorine or bromine to iodine were 2:1. Based upon previous studies of iodination of pyridine with interhalogen molecules,[27] the following is offered as a purely tentative explanation

$$R_3AsOIX \longrightarrow HX + \text{iodinated } R_3AsO \qquad (1)$$

$$R_3AsOIX + HX \longrightarrow (R_3AsOH)^+IX_2^- \qquad (2)$$

Compounds of the type $(R_3AsOH)^+NO_3^-$ have been prepared by Mel'nikov and Rokitskaya,[28] and it appears that a reaction of this type might account for the observed 2:1 atomic ratio of chlorine or bromine to iodine. By no means is the formation of the pure, quaternary arsonium trihalide implied.

In addition to the iodine and interhalogen compounds discussed above, the following transition metal complexes were prepared as pure substances: $CoCl_2 \cdot 2[(C_6H_{11})_3AsO]$, $Ni(ClO_4)_2 \cdot 4[(C_6H_{11})_3AsO]$, and $CoCl_2 \cdot 2[(C_2H_5)_3AsS]$.

The stoichiometric ratios of the arsine oxide and arsine sulfide to cobalt chloride of 2:1 and to nickel perchlorate of 4:1 were in agreement with those observed by Phillips and Tyree[26] in complexes formed between these salts and triphenylarsine oxide.

It is probable in the case of the cobalt(II) complexes that a tetrahedral complex is formed in which both chlorides and two molecules of the arsine chalcogenide are coordinated to the cobalt(II) ion. The solubility of these compounds in relatively nonpolar solvents such as chloroform supports this view since they have been found to be nonelectrolytes.[26]

In the case of the nickel(II) complex a square-coplanar coordinated nickel ion is suggested. Presumably, coordination to the metal ion occurs by way of the arsenyl oxygen, as suggested by the infrared data.

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