CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
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Group V Oxides and Chalcogenides: Crystalline Complexes with Halogens[1]

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Received April 9, 1962

Phosphine sulfides and selenides form stable, crystalline 1–1 complexes with iodine, or the interhalogens, but no stoichiometrically pure phosphine oxide complexes have been isolated. In addition, a very stable crystalline solid in which three moles of iodine is complexed with two moles of triphenylphosphine sulfide has been isolated. Arsine sulfides react irreversibly with iodine with rupture of the As–S bond and the formation of trialkyliodoarsonium triiodides. Triphenylarsine oxide and iodine form a stable 1:1 complex in solution. We have been *unable to prepare* other trialkylarsine oxides.

Introduction

The literature dealing with molecular complexes involving the halogens has been reviewed recently through 1959.[2] The results of initial investigations concerned with complexing between the group V oxides or chalcogenides and the halogens have been described recently,[3] and this paper is concerned primarily with the preparation and identification of pure crystalline solids which are formed between these molecules.

Reported herein are the first examples of crystalline addition compounds which have been found to form between various phosphine sulfides, or selenides, and the halogens. The irreversible decomposition which occurs upon the interaction of iodine with arsine sufides also is described as well as the solution equilibrium observed to take place between triphenylarsine oxide and iodine.

Experimental

Arsine Oxides and Sulfides.—The arsines were prepared by the reaction of arsenic trichloride with the corresponding Grignard reagent. Triphenylarsine oxide, m.p. 194°, was prepared by oxidation of triphenylarsine.[4] Triphenylarsine sulfide, m.p. 162°, was prepared according to the method of Zukerkandl,[5] which involves the addition of sulfuryl chloride to triphenylarsine and the reaction of the resulting addition compound with hydrogen sulfide. Trimethylarsine sulfide, prepared by the reaction of sulfur with trimethylarsine, m.p. 183–184°, was obtained in the form of colorless needles from ethanol; m.p. reported 177.5°,[6] 174°.[7] Triethylarsine sulfide was prepared similarly from triethylarsine and sulfur and its m.p. was 119–120° after recrystallization from ethanol; m.p. reported 119.5°.[8] Tricyclohexylarsine sulfide, m.p. 179–180°, is a new compound and details on its preparation will be given elsewhere.[9]

Phosphine Sulfides and Selenides.—Triphenylphosphine sulfide, m.p. 161°, was prepared by fusion of sulfur with triphenylphosphine (Metal and Thermit Corporation); m.p. reported 157.5°.[10] Triphenylphosphine selenide, prepared by fusion of triphenylphosphine with selenium at 180–200° followed by recrystallization from benzene and alcohol, gave colorless crystals, m.p. 187–188°; m.p. reported 185°.[10]

Tricyclohexylphosphine Selenide.—This compound was prepared by fusion of tricyclohexylphosphine with selenium at 150–160° under nitrogen, m.p. 192°. Details of this preparation are given elsewhere.[11]

Attempts to prepare trialkylarsine oxides, either by oxidation of the arsines or hydrolysis of the dichloride, gave either the dialkylarsinic acids or the dialkylacid anhydride. The synthesis of arsine oxides is under investigation.

Halogen Addition Compounds.—These compounds were formed by the direct combination of the halogen, or interhalogen, with saturated solutions of the respective phosphine sulfide, or selenide. When an interhalogen is involved it is preferable to use carbon tetrachloride as the solvent. The rate of formation of the crystalline addition compounds, and the size of the crystals obtained, depends largely upon the concentrations used. When saturated solutions are employed, cooling of the solution mixture in ice and the addition of dry ether brings about rapid precipitation. Large single crystals are best grown by allowing dilute carbon tetrachloride solutions to stand on a vibration-free surface for a period of from several hours to

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[1] Some of this work was described at the Halogen Symposium, 140th National Meeting, American Chemical Society, Chicago, Illinois, September 6, 1961.

[2] L. J. Andrews and R. M. Keefer, *Advan. Inorg. Chem. Radiochem.*, **3**, 91 (1961).

[3] (a) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961); (b) R. A. Zingaro, R. E. McGlothlin, and E. A. Meyers, *ibid.*, in press.

[4] R. L. Shriner and C. N. Wolf, *Org. Syn.*, **30**, 97 (1950).

[5] F. Zukerkandl and M. Sinai, *Ber.*, **54B**, 2485 (1921).

[6] W. M. Dehn and B. Wilcox, *Am. Chem. J.*, **35**, 37 (1906).

[7] A. Hantzsch and H. Hibbert, *Ber.*, **40**, 1515 (1907).

[8] G. W. Raiziss and J. L. Gavron, "Organic Arsenical Compounds," Chemical Catalog Co., Inc., New York, N. Y., 1923, p. 88.

[9] R. A. Zingaro, R. E. McGlothlin, and R. M. Hedges, manuscript in preparation.

[10] E. Krause and I. A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Edwards Bros., Inc., Ann Arbor, Michigan, 1943, p. 447.

[11] C. G. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

several weeks. Large single crystals of $2[(C_6H_5)_3PS]\cdot 3I_2$ up to 2 cm. on edge were grown from 200 ml. of a solution containing 25.13 g./l. of $(C_6H_5)_3PS$ in carbon tetrachloride and 50 ml. of a saturated solution of iodine in the same solvent which stood at room temperature for 15 days.

Triethyliodoarsonium Triiodide.—Addition of 50 ml. of a saturated solution of iodine in chloroform to 1 g. of triethylarsine sulfide dissolved in the minimum volume of chloroform leads to separation of a heavy dark colored oil from which the solvent is removed by decantation. Addition of anhydrous ether causes the oil to crystallize. Purification is accomplished by repeated redissolution in chloroform and reprecipitation with ether in an ice bath until crystals having a constant melting point are obtained. This salt was found to decompose into an oily liquid upon standing several days, even in a dry, inert atmosphere. This apparent instability was not noted for any of the other compounds.

Tricyclohexyliodoarsonium Triiodide.—To a solution containing 1.8 g. of tris-(cyclohexyl)-arsine sulfide dissolved in the minimum volume of chloroform, is added 25 ml. of a saturated iodine solution in the same solvent. The solution is cooled in ice and anhydrous ether is added continually until clouding just begins. Crystallization occurs on continued cooling, more ether being added to induce crystallization, if necessary. Purification again is accomplished by redissolution in chloroform and crystallization with ether.

The trimethyl- and triphenyl- compounds are prepared in essentially the same manner.

Equilibrium Studies.—No stable crystalline addition compound could be isolated from a solution containing triphenylarsine oxide and iodine. The formation of a complex in solution, however, was clearly demonstrated by the change in the color of iodine solutions from violet to brown upon addition of the oxide. The solution equilibrium was studied spectrophotometrically in chloroform using a Beckman DK-I spectrophotometer. The "blue-shift," *i.e.*, the shift in the iodine absorption band at 525 mμ to a higher frequency upon complex formation, is shown in Fig. 1. Using the data of Fig. 1, the graphical method of Rose and Drago[12] was used to calculate the extinction coefficient and the equilibrium constant of the 1:1 complex. The method involves the use of the linear equation

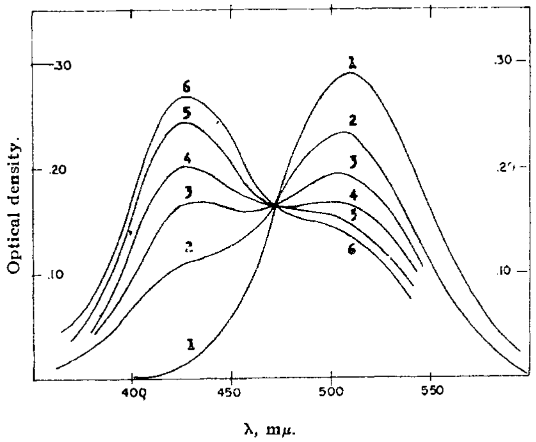

Fig. 1.—Spectrum of the iodine–triphenylarsine oxide (TPAsO) system in chloroform. In each case the total iodine concentration is 3.41×10^{-4} *M* and the TPAsO concentration is: 1, 0; 2, 8.80×10^{-3} *M;* 3, 1.76×10^{-2} *M;* 4, 2.64×10^{-2} *M;* 5, 3.52×10^{-2} *M;* 6, 4.40×10^{-2} *M.* At the concentrations used TPAsO cuts off at 270 mμ and no charge transfer band was observed up to this frequency.

$$K^{-1} = \frac{A}{\epsilon_c} - C_I - C_D + \frac{C_D C_I}{A}(\epsilon_c)$$

in which K is the equilibrium constant; A, the absorbancy of the complex; ϵ_c, the extinction coefficient of the complex; and C_I and C_D are the initial concentrations of acceptor and donor, respectively. Values of ϵ_c then are assumed and corresponding values of K^{-1} are calculated. Plots of K^{-1} *vs.* ϵ_c then give a series of straight lines which have a common intercept which corresponds to the correct values of ϵ_c and K^{-1}.

Results and Discussion

Phosphine Sulfide or Selenide–Halogen Addition Compounds.—Five phosphine sulfide, or selenide halogen addition compounds have been isolated in pure crystalline form. The pertinent analytical data and physical properties are listed in Table I.

Single crystals of $(C_6H_5)_3PS\cdot IBr$ and $2(C_6H_5)_3PS\cdot 3I_2$ were examined by means of X-rays using a precession camera and Mo and Cu radiation. For $(C_6H_5)_3PS\cdot IBr$ the unit cell dimensions are a = 9.40 Å., b = 9.52 Å., c = 10.31 Å., and α = 90°, β = 78.0°, and γ = 90°; the corresponding values for $2(C_6H_5)_3PS\cdot 3I_2$ are a = 8.95 Å., b = 9.66 Å., c = 12.47 Å., and α = 87.6°, β = 74.3°, and γ = 83.4°. TPPS·IBr is monoclinic, and shows systematic extinctions only of the type ($0k0$) with k odd. Selecting the space group $C_2^2 - P2_1$, with two molecules of the complex in a unit cell, gives a calculated density of 1.84 g./cc. as compared to the measured density of 1.824 g./cc. From an examination of molecular models, it seems unlikely that TPPS possesses a plane of symmetry.

$2(C_6H_5)_3PS\cdot 3I_2$ is triclinic and for one molecule of the complex in the unit cell the calculated density is 2.19 g./cc., compared to the measured density of 2.13 g./cc. The space groups possible are C_1^1–P1 or C_i^1–P$\bar{1}$. In the second case the complex $2(C_6H_5)_3PS\cdot 3I_2$ must possess a center of symmetry which coincides with a center of symmetry in the unit cell.

The stoichiometry of the $2(C_6H_5)_3PS\cdot 3I_2$ complex is quite novel. In solution,[3b] the system $(C_6H_5)_3PS$–I_2 is characterized by typical 1:1 complex formation so that the unusual stoichiometry of

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[12] R. S. Drago and N. J. Rose, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

TABLE I

CRYSTALLINE PHOSPHINE SULFIDE AND SELENIDE–HALOGEN COMPLEXES

Anal., %	$(C_6H_5)_3PS\cdot IBr$	$(C_6H_5)_3PS\cdot ICl$	$2(C_6H_5)_3PS\cdot 3I_2$	$(C_6H_{11})_3PSe\cdot IBr$	$(C_6H_5)_3PSe\cdot I_2$
C, calcd.	43.1	47.2	32.02	38.18	
found	43.0	47.2	32.04	38.04	
H, calcd.	3.02	3.31	2.24	5.87	
found	2.92	3.16	2.26	5.92	
P, calcd.	6.18	6.77			
found	6.13	6.77			
S, calcd.	6.40	7.00			
found	6.75	7.20			
I, calcd.	25.3	27.7	56.39	22.41	42.3
found	25.3	27.9	56.33	22.20	42.1
Br, calcd.	15.9			13.94	
found	16.0			14.12	
Cl, calcd.		7.75			
found		7.86			
Color	Red-orange	Orange	Blue-black	Gold-brown	Dark maroon
M.p.	151.5°	124°	140°	176°	149°

the solid apparently is related to the crystal structure. It is surprising that *no* 1:1 crystalline solid could be isolated.

Very little can be said about the structure of the phosphine sulfide–halogen addition compounds in the absence of a complete single crystal X-ray analysis. Based upon solution ultraviolet data,[3b] and allowing for solvent and concentration effects, the spectrum of $(C_6H_5)_3PS\cdot IBr$ suggests an "inner-complex" structure of the type $[(C_6H_5)_3PSI]^+(IBr_2)^-$. It is to be emphasized, however, that considerable caution needs to be exercised in the extension of solution data to the solid.

The Triphenylarsine Oxide–Iodine Equilibrium.—The excellent isosbestic point in the spectral curves shown in Fig. 1 suggests the formation of a well defined 1:1 complex between $(C_6H_5)_3AsO$ and iodine. For the equilibrium defined by the equation

$$(C_6H_5)_3AsO + I_2 \rightleftarrows (C_6H_5)_3AsO\cdot I_2$$

in chloroform solution at 25°, $\lambda_{max} = 425$ mμ, ϵ_1 at $\lambda_{max} = 1340 \pm 25$, and $K = 41.2 \pm 2.0$. These calculations were carried out as described in the Experimental part.

One of the principal goals of this effort has been to evaluate the influence of the group V atom (M) on the basic strength of the donor in molecules of the structural type R_3MZ, where Z is an oxygen or a chalcogen atom. Among the phosphine oxides, the assumption of simple 1:1 complex formation is completely inadequate to explain the spectral observations. In the case of triphenylphosphine oxide (TPPO)–iodine, a photochemical decomposition of TPPO catalyzed by iodine has been shown to take place.[3b] This precludes a direct comparison of the basicity of these molecules.

Using, as a basis of comparison, K values at 25° for the 1:1 complex with iodine, triphenylarsine oxide appears to be a much stronger donor than benzene, $K = 1.21^{13}$; stronger than dioxane, $K = 9.3^{13}$; but not as strong as dimethyl sulfide, $K = 71.5^{14}$; pyridine, $K > 100^{15}$; or triphenylphosphine sulfide, $K = 106$.[3b]

Reaction of Arsine Sulfides with Iodine.—It was assumed that a solution equilibrium involving molecular complex formation between iodine and various arsine sulfides would be observable. The typical results of such an experiment are shown in Fig. 2. It is to be noted that the amount of iodine consumed, as calculated by the difference in the iodine absorption peaks, *exceeds* the total amount of arsine sulfide initially present if 1:1 stoichiometry is assumed. The remarkable similarity in the spectra of all the arsine sulfide–iodine systems, *viz.*, a peak at 292 mμ and a second peak of lesser intensity at *ca.* 358 mμ with an absorbancy ratio of 1.96, suggests very strongly the formation of I_3^- for which, in ethylene dichloride, the reported values[16] are $\lambda = 363$ mμ and $\lambda_2 = 293$ mμ and $\epsilon_2/\epsilon_1 = 1.96$. Continuation of these experiments led to the observation that crystalline compounds were being formed when mixtures of stock solutions of arsine sulfides and iodine were allowed to stand. When carried out at higher concentration, $\sim 0.1\ M$, the addition of iodine to arsine sulfides

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(13) J. A. A. Ketelaar, "Chemical Constitution," Elsevier Publishing Co., New York, N. Y., 1958, p. 376.

(14) N. W. Tidesewell and J. D. McCullough, *J. Am. Chem. Soc.*, **79**, 1031 (1957).

(15) C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

(16) A. I. Popov and R. F. Swenson, *ibid.*, **77**, 3724 (1955).

TABLE II

TRISUBSTITUTED IODOARSONIUM TRIIODIDES, $[R_3AsI]^+I_3^-$

	R_3							
	Trimethyl-		Triethyl-		Triphenyl-		Tricyclohexyl-	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
C	5.74	6.01			26.52	26.59	25.98	26.32
H	1.44	1.66			1.84	1.89	4.00	4.18
As					9.20	9.40	9.03	9.00
I (reducible)			37.83	38.27			30.50	29.82
I (total)	80.88	81.14	75.65	75.59	62.34	62.29	60.99	61.15
M.p.	83° dec.		80° dec.		143° dec.		168° dec.	
Color	Purple-maroon		Maroon		Dark ruby-red		Maroon	

was found to be accompanied by the release of a considerable amount of heat and the almost instantaneous formation of crystalline solids. The physical properties and the analytical data obtained for a number of these solids are given in Table II.

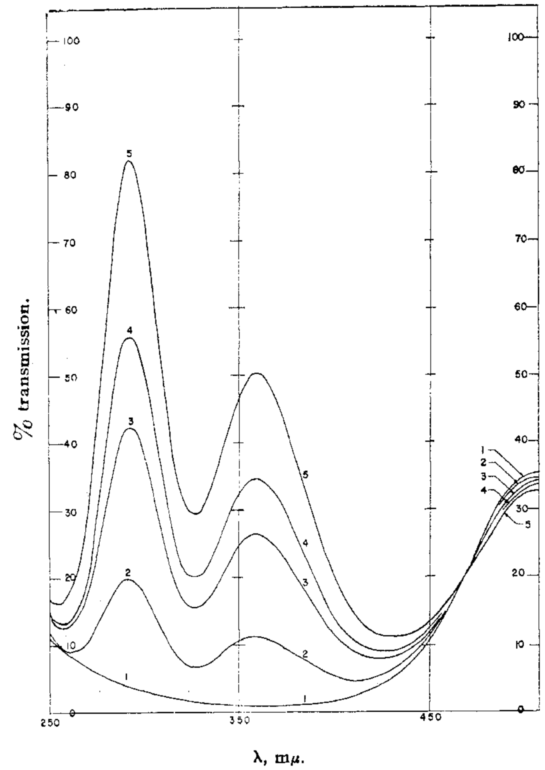

Fig. 2.—The ultraviolet spectrum of the system iodine–triethylarsine sulfide (TEAS) in chloroform. In each case the total iodine concentration is 4.05×10^{-4} *M* and the TEAS concentration is: 1, 0; 2, 3.68×10^{-6} *M*; 3, 7.36×10^{-6} *M*; 4, 1.10×10^{-5} *M*; 5, 1.47×10^{-5} *M*

The type of compound obtained by the rapid, direct interaction of iodine with trisubstituted arsine sulfides was both unexpected and interesting. The fact that these were not simple addition compounds of iodine with an arsine sulfide was established immediately by elemental analysis which showed the absence of sulfur. The determination of iodine by thiosulfate titration, when compared with the total iodine determination, revealed that the reducible iodine was equal to exactly half of the total iodine present. Because of the rapid, irreversible nature of the reaction it was assumed that under the conditions in which the ultraviolet spectra were determined, *i.e.*, a very large excess of iodine, the same irreversible reaction occurred and the same species were formed. It is to be noted in Fig. 2 that the location of the bands and the relative peak intensities very strongly suggest the presence of triiodide ion. The data are compatible with formulations of a trialkyl- (or aryl-) iodoarsonium triiodide, $[R_3AsI]^+I_3^-$. Such a compound, on thiosulfate titration, would possess two equivalents of reducible iodine, *i.e.*, $I_3^- + 2e^- \rightarrow 3I^-$. The fate of the sulfur has not been determined. The deposition of free sulfur was not observed at any time. It appears likely that the sulfur underwent chemical combination with iodine or simply was oxidized to the free element, but verification of this fact will require further experimentation.

Our lack of success in the preparation of trialkylarsine oxides by the direct oxidation of arsines indicated the necessity for a careful reinvestigation of the claims for the existence of these compounds and we are currently carrying on such a study.

Acknowledgment.—We should like to express our appreciation to the United States Atomic Energy Commission for financial support under Contract AT-(40-1)-2733. The X-ray crystal studies were performed with the assistance of Mr. Richard F. Copeland under a grant from the Robert A. Welch Foundation.