

yellow solid resulting from biphosphine which had decomposed in our purification train, analyzed as $P_9H_{4.02}$. We are not prepared to state unambiguously that our products represent true chemical entities, although our results suggest this to be the case.

It is a fact that materials containing more or less hydrogen are readily obtainable by adjusting the temperature and time of decomposition and other conditions. Stock⁶ reported that P_2H was formed at room temperature, and this was formulated $P_{12}H_6$, as a result of Schenck's molecular weight determinations⁷; but as may be seen in Table II, our decompositions proceeded smoothly through this combination. When decompositions were carried out in sealed tubes it was apparent that residues analyzing as $P_{12}H_6$ contained substantial quantities of undecomposed biphosphine. But when we decomposed biphosphine in the presence of water vapor, as did Stock, we obtained air-stable samples whose compositions in two cases were $P_{12}H_{5.93}$ and $P_{12}H_{5.77}$, respectively. These results are entirely comparable with data reported by Stock. There is no question but that moisture in some way stabilizes substances whose composition averages somewhere near $P_{12}H_6$.

Hackspill⁸ reported that the substance P_5H_2 may be obtained on heating Stock's $P_{12}H_6$ ^{6,7} to 80° , and considered Stock's hydride to be P_5H_2 containing absorbed H_4P_2 . Although we are inclined to doubt this interpretation, we fully believe that such a composition might be realized under proper conditions. In terms of our representation, Hackspill's compound may be written $P_9H_{3.6}$. This is not far removed from our substance, P_9H_4 ; but the difference is well outside our experimental error, so that

we may state without hesitation that our decompositions at room temperature did not proceed to the level demanded by Hackspill's formulation.

When we heated yellow hydride samples in high vacuum for two hours at 160° we obtained substances corresponding to $P_9H_{3.02}$ and $P_9H_{2.92}$, respectively, in two experiments. Again we are inclined to believe it was fortuitous that substances were formed which corresponded closely to P_3H . By altering conditions slightly we could probably alter the P/H ratio.

Finally, it was reported by Stock that the red hydride, P_9H_2 , could be obtained by heating $P_{12}H_6$ up to 220° . Again this seems perfectly reasonable. In the case of substances of about this composition there exists a considerable body of chemical evidence pointing to their existence as compounds of definite proportions.^{6,10} We shall have more to say regarding the chemistry of these substances in our next paper.

In conclusion we feel that yellow hydrides prepared by decomposing biphosphine at room temperature contain absorbed, undecomposed biphosphine if the H/P ratio exceeds 4/9. When the ratio is close to 4/9 the elimination of phosphine becomes undetectable, and the substances are stable in air. A continuous elimination of hydrogen as phosphine appears possible on heating, yielding substances of variable composition depending on conditions. The decomposition of biphosphine in the presence of water vapor apparently follows a somewhat different course. Moisture seems to stabilize compositions in the neighborhood of $P_{12}H_6$.

PHILADELPHIA, PENNSYLVANIA

(10) R. Schenck, *Ber.*, **36**, 979, 4204 (1903).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Chlorination of Arsenic(III) Fluoride¹

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The oxidation of arsenic(III) fluoride by chlorine is dependent upon the water content of the system. In an anhydrous system no reaction occurs. In the presence of a small amount of water impure tetrachloroarsenic(V) hexafluoroarsenate is obtained. The properties of this compound and methods for its purification are described. In the presence of an excess of water arsenic(III) fluoride is converted quantitatively by chlorine to arsenic acid. In systems of intermediate water content both reactions occur simultaneously. Nitrogen(III) chloride reacts with arsenic(III) fluoride to give tetrachloroarsenic(V) hexafluoroarsenate. The experimental results are discussed.

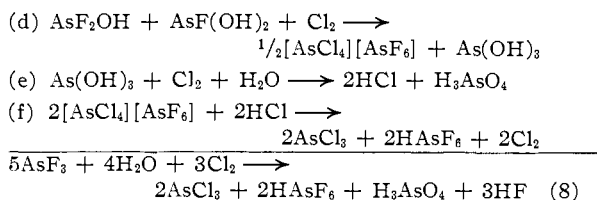
The early data² on the oxidation of arsenic(III) fluoride (AsF_3) by the halogens were either inconclusive or contrary to expected periodic relationships. For example, a reaction was reported with bromine but not with chlorine. If anything, the reverse might have been anticipated. Early studies in this Laboratory revealed that on certain

(1) Abstracted from a thesis submitted on February 9, 1955, to the Horace H. Rackham School of Graduate Studies of the University of Michigan by Howard M. Dess, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) O. Ruff and H. Graf, *Ber.*, **39**, 67 (1906); O. Ruff, K. Stauber and H. Graf, *Z. anorg. Chem.*, **58**, 325 (1908); H. Moissan, *Compt. rend.*, **99**, 874 (1884).

occasions liquid AsF_3 was oxidized by chlorine to give impure tetrachloroarsenic(V) hexafluoroarsenate ($[AsCl_4][AsF_6]$), a compound which was described independently by Kolditz³ concurrent with the completion of this work. On other occasions no solid product could be obtained. The foregoing anomalies have been correlated with the water content of the AsF_3 . Not only the speed but the course of the reaction is dependent upon the amount of water present. Results on the chlorination process are summarized in this paper.

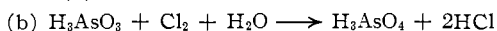
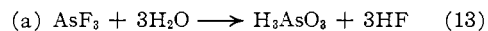
(3) L. Kolditz, *Z. anorg. Chem.*, **280**, 313 (1955).



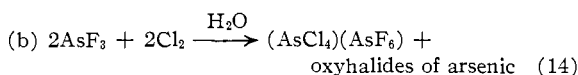
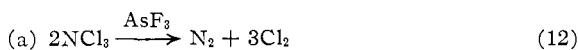
The exchange steps presented above (12c,d) are only a few out of a large number of possibilities and are thought to be representative of a class of reactions rather than as the only routes by which fluoride-hydroxyl exchange could occur.

One other point is important. The H-F produced from the hydrolysis of AsF_3 has been assumed to play no further role as a fluorinating agent. In another paper⁶ it is shown that KAsF_6 does *not* result from the action of 48% aqueous HF on KH_2AsO_4 , although KAsF_6 is formed by the action of *anhydrous HF* on KH_2AsO_4 . Since the maximum HF concentration in the equimolar AsF_3 - H_2O mixture is 13% the formation of AsF_6^- by HF seems improbable.

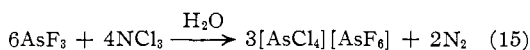
The suggestions contained in reaction sequence (12) are of further value in considering the oxidation of AsF_3 by chlorine in the presence of a large excess of water. The latter reaction can be considered as an initial hydrolysis of AsF_3 followed by oxidation of the resulting H_3AsO_3 . The appearance of no more than 2% of the arsenic in the form of HAsF_6 can be justified since it is known that HF will not produce AsF_6^- from KH_2AsO_4 in water solution.⁶ The equations are



2. The Oxidation of Arsenic(III) Fluoride by Nitrogen(III) Chloride.—The action of AsF_3 on NCl_3 contrasts quite sharply with its action on the *formally* analogous PCl_3 . With PCl_3 halogen exchange occurs; with NCl_3 oxidation is observed.



or directly



The $[\text{AsCl}_4][\text{AsF}_6]$ was always impure due to its hydrolysis by traces of water in the NCl_3 system.¹²

The differences between NCl_3 and PCl_3 suggest apparent differences in the N-Cl and P-Cl bond moments; chemical evidence indicates that the chlorine in NCl_3 is more positive in character than that in PCl_3 , hence, NCl_3 does not take part in the usual metathetical reactions involving replacement

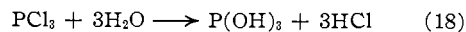
(11) The fact that a small amount of AsF_6^- was produced in one trial on this system would seem to indicate that the AsF_3 was not completely hydrolyzed at the time that the chlorination was started; relatively slow hydrolysis of AsF_3 has been postulated by others.

(12) The decomposition of NCl_3 was catalyzed by silver halides as well as by AsF_3 . The order of increasing catalytic efficiency was $\text{AgF} < \text{AgCl} < \text{AgBr} < \text{AgI}$. The alkali and alkaline earth halides were without effect. Details are available elsewhere (H. M. Dess, Ph.D. Dissertation, University of Michigan, February, 1955, p. 106).

of Cl^- by X^- , but instead the slightly positive chlorine combines with the negative part of many reagents. The following equations are representative



PCl_3 , on the other hand, hydrolyzes according to the equation



and no reduction of PCl_3 by HCl has been reported. For PCl_3 halogen exchange is the expected and observed reaction.

Experimental

1. Reagents. (a) **Arsenic(III) Fluoride.**— AsF_3 was prepared by the method of Moissan as modified by Hoffman and Lutton.¹³ It was purified by refluxing over anhydrous NaF for several hours.¹⁴ All operations were carried out in Pyrex apparatus; no etching of glass was observed unless appreciable quantities of water were present.

(b) **Chlorine.**—Reagent grade commercial Cl_2 gas was passed through a column packed with anhydrous $\text{Mg}(\text{ClO}_4)_2$. It was then bubbled directly into the reaction vessel.

(c) **Nitrogen(III) Chloride.**— NCl_3 was prepared by the method of Noyes.¹⁵ Cl_2 was bubbled through an aqueous solution of $(\text{NH}_4)_2\text{SO}_4$; NCl_3 was extracted with carbon tetrachloride. The product was dried for several days over anhydrous calcium chloride or calcium sulfate and stored in a dark bottle until used. Because the solution is rather unstable, it was used as soon after preparation as possible.

2. The Reaction of Arsenic(III) Fluoride with Chlorine.—The reaction vessel was a tube about 25 mm. in diameter and 130 mm. long. An $\text{F} \frac{24}{40}$ (inner) joint was sealed on top, and a gas inlet tube with a sintered glass bubbler was sealed into the bottom. Exit gases passed out the top through a column packed with $\text{Mg}(\text{ClO}_4)_2$ or into a trap cooled in liquid nitrogen. The temperature, maintained by a bath around the reaction tube, varied from -8 to 60° . Most runs were conducted at 0° . If purified AsF_3 was *distilled* directly into the reactor and dry Cl_2 was introduced through the bubbler, no reaction occurred. On the other hand if AsF_3 was poured through the air into the reactor, enough water was absorbed to give a slow (several hours) chlorination. Additional water could be added as desired. All gaseous products from the chlorination were trapped in liquid nitrogen and fractionated using standard vacuum line procedures. Stopcocks in the reaction system and vacuum line were all greased with "Halocarbon" grease.¹⁶ Mercury in manometers, etc., was protected from corrosive gases by mineral oil buffer U-tube manometers.

3. The Preparation and Purification of Tetrachloroarsenic(V) Hexafluoroarsenate.—The reaction vessel just described was modified by sealing a $19/35 \text{ F} \frac{24}{40}$ joint just below the top $24/40$ joint at right angles to the reaction tube. To this joint a glass-stoppered U trap could be fastened.

Dried AsCl_3 (40 ml.) was distilled directly into the main reactor tube. A 10-ml. sample of AsF_3 was distilled into the attached U-trap. About 0.1 ml. of water was then added to the AsF_3 . The AsCl_3 was saturated with Cl_2 at room temperature. When the trap containing the moist AsF_3 was rotated about the connecting joint, the AsF_3 flowed into the AsCl_3 - Cl_2 solution. The solid crystalline product formed within several minutes. The chlorine stream was allowed to flow for an additional 20 minutes.

The excess supernatant liquid was decanted from the solid into the attached trap and the trap was removed. The open joint was quickly closed by a Standard Taper plug which was sealed with Pyseal. Traces of AsCl_3 , AsF_3 and

(13) C. J. Hoffman and J. M. Lutton, "Inorganic Syntheses," Vol. IV, edited by J. C. Bailar, Jr., McGraw-Hill Book Co., New York, N. Y., 1953, p. 149-150.

(14) H. Russell, Jr., R. E. Rundle and D. M. Yost, *THIS JOURNAL*, **63**, 2825 (1941).

(15) W. A. Noyes, "Inorganic Syntheses," Vol. I, edited by H. S. Booth, McGraw-Hill Book Co., New York, N. Y., 1939, p. 65.

(16) Obtained from Halocarbon Products Corp., 2012 88th St., North Bergen, New Jersey.

TABLE II
 ANALYTICAL DATA FOR THE PURIFICATION OF $[\text{AsCl}_4][\text{AsF}_6]$

Sample	Treatment	As ⁺⁺ not as fluoride complex, %	As ⁺⁺ as AsF_6^- , %	Total fluoride, %	Total chloride, %
..	Crude sample from bubbling Cl_2 through AsF_3	19.2	19.7	29.8	31.5
1	Crude sample from chlorination of AsF_3 in AsCl_3	19.6	19.6 ^a	...	33.6
2	After 1st purification	18.6	{ 19.3 ^a 18.3 ^b	...	34.1
3	After 2nd purification	18.6	34.5
4	After 3rd purification	34.65
	Best values	18.6 ± 0.2	18.3 ± 0.2	...	34.65 ± 0.04
	Theoretical	18.47	18.47	28.10	34.96

^a AsF_6^- precipitated with nitron. ^b Tetraphenylarsonium chloride used for AsF_6^- . Error estimate based on analysis using known standards.

any other gaseous products were then pumped from the system. A small portion of the crude, dry solid was then removed for analysis.

The solid was washed with 5 cc. of an AsF_3 - AsCl_3 mixture which had been distilled into the vessel. The liquid phase was saturated with Cl_2 in order to minimize the solubility of $[\text{AsCl}_4][\text{AsF}_6]$. The liquid was then sucked off through the chlorine inlet tube. After pumping off all the AsF_3 and AsCl_3 , a second sample (2) was taken for analysis.

A sample of the partially purified product was then transferred under dry nitrogen in a dry box to a smaller vessel of similar type. A second recrystallization from an AsF_3 - AsCl_3 mixture (about 5 g. of each) was conducted using chloroform as before to reduce solubility. Sample 3 was then removed for analysis. A fourth recrystallization from AsCl_3 was of limited effectiveness since little of the product dissolved before chlorine addition. Sample 4 was removed after this recrystallization.

The analytical data obtained at various stages of purification of the $[\text{AsCl}_4][\text{AsF}_6]$ are summarized in Table II. Arsenic and fluorine analyses were not performed on the final samples since the available methods were not sufficiently precise to serve as criteria of high purity. The final value of 34.65 for chloride, given in Table II corresponds to $[\text{AsCl}_4][\text{AsF}_6]$ of about 96% purity if the impurity is assumed to be $[\text{AsCl}_2\text{OH}][\text{AsF}_6]$.

4. The Reaction between Nitrogen(III) Chloride and Arsenic(III) Fluoride.—A 10 to 15% solution of NCl_3 in carbon tetrachloride was mixed with AsF_3 in a glass-stoppered vessel. A two-phase liquid system formed in which AsF_3 was the lower layer. A slow evolution of gas bubbles was observed at the interface. In one run the vessel was attached to the vacuum system and the evolved gases were identified as nitrogen, some chlorine and small amounts of HCl and SiF_4 .

After times ranging from 4 hours to several days (depending on the water content of the system) impure $[\text{AsCl}_4][\text{AsF}_6]$ began to precipitate from the liquid phases. The $[\text{AsCl}_4][\text{AsF}_6]$ was always rather badly contaminated with oxyhalides, H_3AsO_4 and other materials as is shown by the following typical analysis of the product.

Obsd. As(V), 18.1; As(V) as AsF_6^- , 16.8, Cl^- , 31.5. Theory for $[\text{AsCl}_4][\text{AsF}_6]$: As(V), 18.45; As as AsF_6^- , 18.45; Cl^- , 35.00.

5. Analytical Methods.—(a) **Preparation of Solution for Analysis.**—The solid was transferred rapidly under a nitrogen atmosphere into a special tared weighing bottle constructed from an inner-outer 24/40 Standard Taper joint combination. After the weighing of the special bottle and its contents the inner section containing the sample was fastened rapidly to a special glass-stoppered flask by means of an outer 24/40 joint attached to a side arm of the flask. The flask contained cold (0°) 10% NaOH solution. This was poured rapidly into the solid by tipping the entire assembly. The sealed vessel was agitated until all fumes were absorbed. Finally the solution was transferred quantitatively to a volumetric flask and made up to a known volume.

(b) **Chloride.**—Chloride was determined gravimetrically as silver chloride.

(c) **Fluoride.**—In order to obtain a separate and distinct analysis for fluorine the destruction of the unusually stable AsF_6^- ion was necessary. HF was steam distilled from a solution consisting of 25 cc. of sample and 25 cc. of concentrated perchloric acid. Fluoride in the distillate was determined gravimetrically as lead chlorofluoride.¹⁷

(d) **Arsenic(V) except Hexafluoroarsenate.**—A solution containing about 2 g. of KI in 1.5 ml. of water was added to a 6 *M* solution of HCl which contained the unknown. The reduction of As(V) to As(III) was complete within a few seconds; the iodine was titrated immediately with a standard sodium thiosulfate solution. The final disappearance of the yellow iodine color was taken as the end-point.

(e) **Arsenic(III).**—Arsenic(III) was oxidized to As(V) with H_2O_2 in basic solution. The excess peroxide was destroyed by evaporating the solution to dryness on a steam-bath. The residue was dissolved in water and the total arsenic was then determined as above. Arsenic(III) was also determined directly by titration with standard iodine solution.¹⁸

(f) **Hexafluoroarsenate Ion.**—The complex anion AsF_6^- could be precipitated by nitron¹⁹ or by tetraphenylarsonium chloride. The latter reagent gave a precipitate of better physical properties than the former. The complex $[\text{AsF}_6^-]$ could also be determined in a completely independent fashion by a somewhat less accurate procedure. Fluoride was steam distilled as HF from a solution containing concentrated perchloric acid. The arsenic remaining in the stillpot was then precipitated as silver arsenate and the silver in the precipitate was determined by the Volhard method. This gave the total arsenic. Separate determinations of As(V) other than (AsF_6^-) and of As(III) on a fresh sample of unknown permitted evaluation of AsF_6^- by difference.

6. X-Ray Powder Patterns.—Samples were rapidly ground to a fine powder using an agate mortar in a dry box containing a nitrogen atmosphere. The powder was loaded into fine glass capillaries, the ends of which were then fused shut. The camera employed had a circumference of 180 mm. The X-ray unit was a G.E. model XRD type 1. Copper $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) was used. Exposure time was one hour.

Acknowledgment.—One of the authors (H.M.D.) wishes to express his sincere appreciation to the National Science Foundation for a National Science Foundation Fellowship held during the course of this research.

(17) W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1939, pp. 74-77.

(18) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1940, p. 276.

(19) W. Lange and E. Muller, *Ber.*, **63**, 1058 (1930); H. H. Willard and H. Diehl, "Advanced Quantitative Analysis," D. Van Nostrand Co., New York, N. Y., 1943, p. 341.

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