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. Stock[6] 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 determinations[7]; 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 $P_{12}H_6$.

Hackspill[8] 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

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

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

The Chlorination of Arsenic(III) Fluoride[1]

BY HOWARD M. DESS, ROBERT W. PARRY AND GUIDO L. VIDALE

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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 data[2] 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 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 Kolditz[3] 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.

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[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).

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

The Oxidation of Arsenic(III) Fluoride with Chlorine

(1) **Rigorously Anhydrous Conditions.**—When carefully dried Cl_2 was passed into strictly anhydrous liquid AsF_3, no reaction was ever observed. Varying the temperature of the AsF_3 from its freezing point (−9°) to its boiling point (57°) had no effect. Visible, infrared and ultraviolet light were without catalytic influence, as were hydrogen fluoride (HF), antimony(V) chloride ($SbCl_5$) and arsenic(III) oxide (As_2O_3).

(2) **Water Present in Small Quantities.**—If water was added to the strictly anhydrous system until the mole ratio of AsF_3 to H_2O fell in the range of 40/1 to 8/1, oxidation took place as described by the equation

$$2AsF_3 + 2Cl_2 \xrightarrow[\text{trace amounts}]{H_2O} [AsCl_4][AsF_6] + \text{oxyhalides} \qquad (1)$$

The $[AsCl_4][AsF_6]$ produced was inevitably contaminated with oxyhalides, the amount of contamination increasing with the water content of the system.[4] HCl was always detectable in the exit gases.

The velocity of the oxidation was determined in large measure by the amount of water present; times required for the appearance of solid product ranged from 8 to 10 hours near the AsF_3/H_2O ratio of 40/1 down to 20–40 minutes near the ratio of 8/1. Further increase in the water content changed the nature of the products.

By prolonged passage of the Cl_2 stream, almost quantitative yields of impure $[AsCl_4][AsF_6]$ resulted from the exothermic oxidation.

The purification of $[AsCl_4][AsF_6]$ was achieved by chlorinating AsF_3 in arsenic(III) chloride ($AsCl_3$) or by rechlorinating the impure solid using liquid $AsCl_3$ as a solvent. The process can be formally represented as shown

$$AsCl_3 + Cl_2 \rightleftarrows AsCl_4^+ + Cl^- \qquad (2)$$

$$AsCl_4^+ + [AsCl_3OH][AsF_6] \longrightarrow [AsCl_3OH^+] + [AsCl_4][AsF_6] \qquad (3)$$

The oxyhalide impurity is assumed to be $[AsCl_3OH][AsF_6]$. Although a mechanism for chlorination was never established, it is significant that the reverse process for equation 2, involving interaction between $[AsCl_4^+]$ and Cl^-, was observed. Best results were obtained if the original oxidation of AsF_3 was carried out in the $AsCl_3$–Cl_2 solution.

(3) **Properties of Tetrachloroarsenic(V) Hexafluoroarsenate.**—The structure $[AsCl_4][AsF_6]$, assigned to the solid by Kolditz, was verified independently in this Laboratory. The colorless, crystalline, very hygroscopic material is somewhat soluble in $AsCl_3$ and very soluble in AsF_3. It is insoluble in and does not react with CCl_4 nor with specially purified $CHCl_3$. If the small amount of alcohol (0.75%) added to chloroform as a preservative is not removed, reaction ensues. Reactions of an undetermined nature occurred between $[AsCl_4][AsF_6]$ and diethyl ether, pyridine, benzene and nitrobenzene. A sample of at least 95% purity has a density of 2.8 g./ml. at 25°.

A Debye–Scherrer powder pattern of crystalline $[AsCl_4][AsF_6]$ gave the interplanar spacings shown in Table I.

TABLE I

DEBYE–SCHERRER X-RAY POWDER DATA FOR $[AsCl_4][AsF_6]$, RELATIVE INTENSITY OF REFLECTIONS AND INTERPLANAR SPACINGS IN Å.

1.53 VW	1.96 VW	2.78 VW
1.57 VW	2.08 W	2.96 VW
1.66 VW	2.19 W	3.31 S
1.73 W	2.55 VW	3.66 MS
1.89 VW	2.63 VW	4.39 S

The $[AsCl_4^+]$ cation of tetrachloroarsenic(V) hexafluoroarsenate reacts vigorously and rapidly with water in accordance with the equation

$$[AsCl_4^+] + 4H_2O \longrightarrow H_3AsO_4 + 4HCl + H^+ \qquad (4)$$

Contrary to earlier reports[5] the AsF_6^- anion is very resistant to hydrolysis.[6]

Dry HCl and pure *dry* $[AsCl_4][AsF_6^-]$ do not react, but if a trace of moisture is present, equation 2 is reversed to give $AsCl_3$ and Cl_2. This reaction justifies an earlier observation of Gutmann[7] who reported that during hydrolysis of $[AsCl_4^+][PCl_6^-]$ partial reduction of the arsenic occurred unless special precautions were taken. The HCl for reaction with $AsCl_4^+$ would arise from hydrolysis of the PCl_6^- ion as well as from hydrolysis of $AsCl_4^+$.

Bromine did not react with $[AsCl_4][AsF_6]$ under conditions comparable to those used for the HCl reaction.

Pure $[AsCl_4][AsF_6]$ decomposes without melting. The solid can be sublimed above 70° *in vacuo;* however, the sublimed product invariably contained more oxyhalides than the starting material. This may have been the result, in part, of a high temperature reaction between the halide and the glass. Due to rather serious experimental difficulties the molecular weight of the compound in the vapor phase was not determined.

Thermal decomposition of the solid in glass yielded AsF_3 and $AsCl_3$ as major products; smaller amounts of silicon(IV) fluoride (SiF_4) and boron(III) fluoride (BF_3) apparently arose from the action of the fluoride on the Pyrex glass. Some HCl found in the products is assumed to have arisen from the attack of gaseous products on the "Halocarbon" stopcock grease, which was visibly damaged. Only traces of free chlorine were found in the decomposition products. Since free chlorine does not attack "Halocarbon" greases or glass, its absence in the products may be taken as evidence against such processes as those illustrated by

$$[AsCl_4][AsF_6] \longrightarrow 2AsF_3Cl_2 \longrightarrow 2AsF_3 + 2Cl_2 \qquad (5)$$

$$\begin{aligned} 5[AsCl_4][AsF_6] &\longrightarrow 4AsCl_5 + 6AsF_5 \\ &\qquad\quad \lfloor\!\longrightarrow 4AsCl_3 + 4Cl_2 \qquad (6) \end{aligned}$$

The latter mode of decomposition was originally considered by analogy with PF_3Cl_2 and assumes

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[4] Because of difficulties inherent in handling $[AsCl_4][AsF_6]$ and because of errors which can easily appear in its analysis, unusual care is needed to demonstrate the extent of contamination of the product with oxyhalides.

[5] W. Lange and E. Muller, *Ber.*, **63**, 1058 (1930).

[6] H. M. Dess and R. W. Parry, THIS JOURNAL, **78**, 5735 (1956).

[7] V. Gutmann, *Monatsh.*, **82**, 473 (1951).

that $AsCl_5$ would undergo immediate decomposition, especially at higher temperatures.

Analysis of the solid residues left in the glass vessel indicated a non-stoichiometric mixture consisting of: As(V), 32.1%; As(III), trace; AsF_6^-, 7.4%; Cl^-, 30.0%; F^-, 25.6% + other residues, probably resulting from the action of fluorides on glass.

The foregoing facts suggest a process represented by equation (7) as a reasonable *primary* decomposition process

$$[AsCl_4][AsF_6] \longrightarrow AsCl_3 + ClF + AsF_5 \quad (7)$$

Both ClF and AsF_5 would be expected to react further with the glass and "Halocarbon" grease in the system.[8] Positive proof of the decomposition process must await thermal destruction of the compound in non-glass apparatus.

4. The Chlorination of Arsenic(III) Fluoride in the Presence of an Equimolar Quantity of Water.—The chlorination of an equimolar mixture of AsF_3 and H_2O did *not* produce $[AsCl_4][AsF_6]$ as an end product. The major recovered products of the reaction were $AsCl_3$, $HAsF_6$ and H_3AsO_4. A few minutes after the start of the exothermic chlorination process, the $AsCl_3$ began to separate as a second (upper) liquid layer. The equation which best reproduces the experimental ratios of products for the equimolar mixture is

$$5AsF_3 + 4H_2O + 3Cl_2 \longrightarrow 2AsCl_3 + 2HAsF_6 + H_3AsO_4 + 3HF \quad (8)$$

The actual experimental ratios at the start were 1.9 AsF_3 and 1.9 H_2O, for every mole of Cl_2 used. Molar ratios of compounds in the products were: $AsCl_3$, 2.0; $HAsF_6$, 2.3; H_3AsO_4, 1.0; AsF_3, negligible, HF not measured. It should be noted that only for the limiting cases $AsF_3 << H_2O$ and $AsF_3 >> H_2O$ can unique stoichiometric equations be written for the chlorination process. Since the AsF_3–water ratio determines the yields of various products for all intermediate cases, a veritable spectrum of reactions is possible.

5. The Chlorination of Arsenic(III) Fluoride in the Presence of Excess Water.—When chlorine was bubbled through a solution of AsF_3 in a large excess of water (mole ratio $AsF_3/H_2O = 1/30$) an exothermic reaction took place which is best represented by the equation

$$AsF_3 + 4H_2O + Cl_2 \longrightarrow 2HCl + H_3AsO_4 + 3HF \quad (9)$$

HCl, HF and excess H_2O could be swept from the vessel by Cl_2 and air streams to leave a viscous, blue tinted sirup of H_3AsO_4.

The Reaction of Arsenic(III) Fluoride with Nitrogen Trichloride

Phosphorus(III) fluoride is easily synthesized by means of the reaction

$$PCl_3 + AsF_3 \longrightarrow PF_3 + AsCl_3 \quad (10)$$

The formally analogous reaction between AsF_3 and a 10 to 15% solution of nitrogen(III) chloride (NCl_3) in carbon tetrachloride gave N_2, Cl_2 and impure $[AsCl_4][AsF_6]$, *not* NF_3.

Discussion

1. The Oxidation of Arsenic(III) Fluoride by Chlorine.—All significant observations on the oxidation of nearly anhydrous AsF_3 by Cl_2 are faithfully reproduced by the following equations which are suggested to describe the process

$$\begin{aligned}
&(a)\ AsF_3 + H_2O \longrightarrow AsF_2OH + HF\\
&(b)\ AsF_2OH + Cl_2 \longrightarrow AsF_2Cl_2OH \qquad (11)\\
&(c)\ AsF_2Cl_2OH + AsF_3 \longrightarrow AsF_3Cl_2 + AsF_2OH\\
&\qquad\qquad\qquad\qquad\qquad\quad \llcorner\!\!\longrightarrow {}^1/_2[AsCl_4][AsF_6]
\end{aligned}$$

The identification of AsF_2OH as the oxidizable species is suggested by the fact that water is necessary for the reaction but neither As_2O_3 nor HF, the ultimate hydrolysis products of AsF_3, seem to exert any type of positive catalytic influence. The low water content of the system suggests AsF_2OH rather than $AsF(OH)_2$ as the intermediate.

Difficulties in oxidizing pure AsF_3 can be attributed to the strong polarizing action exerted by the fluorides of AsF_3 upon the unshared electron pair attached to the As(III). Since these electrons will be held tightly to the arsenic as a result of the strong polarization, the strongest oxidizing agents such as F_2 will be required if oxidation is to be achieved without catalytic help.[9] If one of the fluorides were replaced by hydroxyl, the lone electron pair of AsF_2OH would be loosened enough to permit electron removal by weaker oxidizing agents such as Cl_2. The hydroxyl–fluoride exchanges postulated are reasonable in view of the known similarity between the two ions.

No trivalent mixed halides of arsenic are postulated as reaction intermediates in the formation of $[AsCl_4][AsF_6]$, since earlier Raman spectral studies[10] gave no evidence for the existence of such compounds.

As the water content of the system increases, the number of reaction routes increases rapidly and the delineation of a unique mechanism becomes impossible on the basis of available data. It is instructive, however, to extend the reaction scheme suggested for the case where $AsF_3 >> H_2O$ to include the stoichiometry for the oxidation of an equimolar AsF_3–H_2O mixture. The appearance of $AsCl_3$ and $HAsF_6$ in a 1:1 molar ratio suggests that $[AsCl_4][AsF_6]$ was the precursor of both and the cation of the complex suffered reduction by HCl in the system. The fact that $AsCl_3$ and $HAsF_6$ are produced in excess over H_3AsO_4 suggests further that part of the AsF_3 serves as a fluorinating agent. These ideas are embodied in the reaction sequence

$$\begin{aligned}
&(a)\ 3AsF_3 + 3H_2O \longrightarrow 3AsF_2OH + 3HF\\
&(b)\ 3AsF_2OH + 3Cl_2 \longrightarrow 3AsF_2Cl_2OH\\
&(c)\ 3AsF_2Cl_2OH + 2AsF_3 \longrightarrow\\
&\qquad {}^3/_2[AsCl_4][AsF_6] + AsF_2OH + AsF(OH)_2 \quad (12)
\end{aligned}$$

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[8] Fragmentary evidence was obtained for the presence of ClF among the gaseous products. A small quantity (about 20 mg.) of a gas having an appreciable vapor pressure at −126° and a molecular weight of 55 was isolated. The vapor pressure of ClF at −125.3° = 60 mm. and the molecular weight is 54.5. The unknown gas reacted with the glass and the stopcock grease during storage to give appreciable amounts of HCl. Such behavior is not unexpected for Cl–F.

[9] Oxidation with fluorine was not studied in this series, but available literature reports indicate that oxidation with fluorine will proceed under anhydrous conditions. No definitive experimental data on this point are yet available.

[10] F. Francois and M. L. Delwaulle, *J. chim. phys.*, **46**, 80 (1949).

$$\text{(d) } AsF_2OH + AsF(OH)_2 + Cl_2 \longrightarrow {}^1/_2[AsCl_4][AsF_6] + As(OH)_3$$

$$\text{(e) } As(OH)_3 + Cl_2 + H_2O \longrightarrow 2HCl + H_3AsO_4$$

$$\text{(f) } 2[AsCl_4][AsF_6] + 2HCl \longrightarrow 2AsCl_3 + 2HAsF_6 + 2Cl_2$$

$$5AsF_3 + 4H_2O + 3Cl_2 \longrightarrow 2AsCl_3 + 2HAsF_6 + H_3AsO_4 + 3HF \quad (8)$$

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 paper[6] 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

$$\text{(a) } AsF_3 + 3H_2O \longrightarrow H_3AsO_3 + 3HF \quad (13)$$

$$\text{(b) } H_3AsO_3 + Cl_2 + H_2O \longrightarrow H_3AsO_4 + 2HCl$$

$$AsF_3 + 4H_2O + Cl_2 \longrightarrow 2HCl + H_3AsO_4 + 3HF^{11} \quad (9)$$

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.

$$\text{(a) } 2NCl_3 \xrightarrow{AsF_3} N_2 + 3Cl_2 \quad (12)$$

$$\text{(b) } 2AsF_3 + 2Cl_2 \xrightarrow{H_2O} (AsCl_4)(AsF_6) + \text{oxyhalides of arsenic} \quad (14)$$

or directly

$$6AsF_3 + 4NCl_3 \xrightarrow{H_2O} 3[AsCl_4][AsF_6] + 2N_2 \quad (15)$$

The $[AsCl_4][AsF_6]$ 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 of Cl^- by X^-, but instead the slightly positive chlorine combines with the negative part of many reagents. The following equations are representative

$$NCl_3 + 3H_2O \longrightarrow NH_3 + 3HOCl \quad (16)$$

$$NCl_3 + 4HCl \longrightarrow NH_4Cl + 3Cl_2 \quad (17)$$

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

$$PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl \quad (18)$$

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 $Mg(ClO_4)_2$. 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 $(NH_4)_2SO_4$; 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 Ŧ 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 $Mg(ClO_4)_2$ 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 Ŧ 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

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[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 $AgF < AgCl < AgBr < AgI$. 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).

[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 $[AsCl_4][AsF_6]$

Sample	Treatment	As^{+5} not as fluoride complex, %	As^{+5} 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 $[AsCl_4][AsF_6]$. 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 chlorine 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 $[AsCl_4][AsF_6]$ 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 $[AsCl_4][AsF_6]$ of about 96% purity if the impurity is assumed to be $[AsCl_3OH][AsF_6]$.

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 $[AsCl_4][AsF_6]$ began to precipitate from the liquid phases. The $[AsCl_4][AsF_6]$ 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 $[AsCl_4][AsF_6]$: 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 nitron[19] or by tetraphenylarsonium chloride. The latter reagent gave a precipitate of better physical properties than the former. The complex $[AsF_6^-]$ 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 (α = 1.542 Å.) was used. Exposure time was one hour.

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