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

The Oxidation of Arsenic(III) Fluoride with Bromine and Iodine[1]

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In the presence of almost equimolar amounts of water arsenic(III) fluoride (AsF_3) is oxidized by bromine to give arsenic(III) bromide ($AsBr_3$), hexafluoroarsenic acid ($HAsF_6$) and arsenic acid (H_3AsO_4). The compound tetrabromoarsenic(V) hexafluoroarsenate ($[AsBr_4^+][AsF_6^-]$) was never isolated although evidence for its transitory existence was found. Iodine oxidizes arsenic(III) fluoride in water solution to give arsenic acid. No hexafluoroarsenic acid could ever be identified in the products. Results are compared to those obtained with chlorine and chemical implications are considered.

In an earlier paper[2] it was shown that small amounts of water are essential for the oxidation of arsenic(III) fluoride (AsF_3) by chlorine. The rate of the oxidation and the course of the reaction are determined by the ratio of AsF_3 to water. The tetrachloroarsenic(V) hexafluoroarsenate ($[AsCl_4^+][AsF_6^-]$) was established as a product of the chlorination when only small amounts of water were present.

A reaction between AsF_3 and Br_2 is indicated in the early literature, but the products formed were never identified and the role played by "catalysts" such as antimony(III) fluoride (SbF_3) and antimony(V) fluoride (SbF_5)[3] was mentioned but not established. The work described herein was undertaken in an effort to apply to the AsF_3–Br_2 reaction the information gained from the chlorination study.[2]

The Reaction of Arsenic(III) Fluoride with Bromine.—The bromination reaction parallels the chlorination process in a number of ways. As in the case of chlorine, the water content of the system is a major variable which determines both the rate and the course of the oxidation. Results are classified on the basis of the water content of the AsF_3.

1. Rigorously Anhydrous Conditions.—No reaction between AsF_3 and Br_2 was ever detected under these conditions.

2. Water Present in Small Quantities.—Amounts of water needed to effect the bromination were considerably greater than for the corresponding chlorination process. Threshold AsF_3/H_2O mole ratios for chlorination were about 30 or 40 to 1; for bromination the corresponding ratios were about 5 or 6 to 1. The compound tetrabromoarsenic(V) hexafluoroarsenate, ($[AsBr_4^+][AsF_6^-]$) was never isolated although indirect evidence for its transitory existence was obtained. Systems containing the smallest quantity of water necessary for reaction at a reasonable rate gave complex mixtures. Arsenic(III) bromide ($AsBr_3$), hexafluoroarsenic acid ($HAsF_6$), and arsenic acid (H_3AsO_4), were the principal non-volatile constituents of the mixtures. Side reactions seemed to be complicating the stoichiometry. No representative equation could be written. Attempts to prepare $[AsBr_4][AsF_6]$ by the oxidation of slightly moist AsF_3 with a mixture of Br_2 in liquid $AsBr_3$ gave no solid product. The corresponding process for chlorination works well.

3. Water and Arsenic(III) Fluoride Present in Approximately Equimolar Amounts.—Data obtained from this system were sufficiently reproducible to permit writing of a stoichiometric equation. AsF_3 and Br_2 form a two layer liquid system, the AsF_3 being the upper layer. The Br_2 layer is slowly converted to $AsBr_3$. Although water was added initially to the AsF_3 before the addition of Br_2, further quantities always had to be added, in small increments until the Br_2 which dissolved in the $AsBr_3$ reacted completely. If the Br_2 was not removed completely by its reaction with AsF_3, its final separation from the $AsBr_3$ was almost impossible. Molar ratios for reactants and products in two runs are summarized below.

	Reactants used				Products found		
Run	AsF_3	Initial H_2O	Final H_2O	Br_2	$HAsF_6$	$AsBr_3$	H_3AsO_4
1	1	0.39	1.0	0.44	2.09	2.44	1
2	1	1	1.9	0.45	1.82	1.95	1

For reasons outlined above the water content is listed as initial and final. The mass balance on the arsenic is poor because the system was opened from time to time and significant amounts of AsF_3 escaped. The ratios of *non-volatile* products are of major significance, however, in establishing the following equation for the over-all process.

$$5AsF_3 + 4H_2O + 3Br_2 \longrightarrow 2HAsF_6 + 2AsBr_3 + H_3AsO_4 + 3HF \quad (1)$$

4. Large Excess of Water with Arsenic(III) Fluoride.—A mixture of AsF_3 and excess water (H_2O/AsF_3 mole ratio in *excess* of 10 to 1) is oxidized quantitatively by Br_2 in accordance with the equation

$$AsF_3 + 4H_2O + Br_2 \longrightarrow 2HBr + H_3AsO_4 + 3HF \quad (2)$$

No $HAsF_6$ was ever found under these conditions. A comparison of the results for runs number 1 and 2 shows a decrease in the relative amounts of $AsBr_3$ and $HAsF_6$ and an increase in H_3AsO_4 as the amount of water in the system is increased. Such an observation is consistent with the implications of eq. 1 and 2 above.

The Reaction of Arsenic(III) Fluoride with Iodine.—Elemental I_2 will not oxidize AsF_3 until enough water has been added to cause almost complete hydrolysis of the halide

$$AsF_3 + 3H_2O \longrightarrow As(OH)_3 + 3HF \quad (3)$$

The usual iodometric oxidation of H_3AsO_3 then results

$$H_3AsO_3 + I_2 + H_2O \rightleftarrows H_3AsO_4 + 2HI \quad (4)$$

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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] H. M. Dess, R. W. Parry and G. Vidale, THIS JOURNAL, **78**, 5730 (1956).

[3] O. Ruff and H. Graf, *Ber.*, **39**, 67 (1906); O. Ruff, K. Stauber and H. Graf, *Z. anorg. Chem.*, **58**, 325 (1908).

The above reaction has been well studied in the past.[4] Neither AsF_6^- nor AsI_3 was ever detected as reaction products of the AsF_3–I_2 system.

If the water content was increased enough to give reaction 4, the only arsenic compound formed as a product was H_3AsO_4.

Discussion

Since Br_2 and I_2 are weaker oxidizing agents than chlorine, either a higher concentration of the oxidizable species (*i.e.*, AsF_2OH) or a more readily oxidizable molecule ($AsF(OH)_2$ or $As(OH)_3$) must be present if reaction is to occur with these halogens. This means that the amount of water necessary to obtain oxidation of AsF_3 increases from none with the strong oxidizing agent F_2, to a large excess of water with the weak reagent I_2. The complete absence of $HAsF_6$ and AsI_3 in the I_2 reaction suggests that only completely hydrolyzed AsF_3 (*i.e.*, $As(OH)_3$) is oxidized by iodine.

An analogy between the Cl_2 oxidation scheme and the Br_2 process suggests the following reaction sequence for the bromination. The equations in each case represent types of processes which are assumed to occur in the oxidation. They do not represent a unique mechanism.

$$\text{(a) } AsF_3 + H_2O \longrightarrow AsF_2OH + HF \qquad (5)$$

$$\xrightarrow{H_2O} AsF(OH)_2 \xrightarrow{H_2O} As(OH)_3$$

$$\text{(b) } As(OH)_3 + Br_2 + H_2O \longrightarrow H_3AsO_4 + 2HBr$$

$$\text{(c) } AsF_2OH + Br_2 \longrightarrow AsF_2BrOH$$

$$\text{(d) } 2AsF_2Br_2OH + 2AsF_3 \longrightarrow [AsBr_4^+][AsF_6^-] + 2AsF_2OH$$

$$\text{(e) } [AsBr_4^+][AsF_6^-] + HBr \longrightarrow AsBr_3 + HAsF_6 + Br_2$$

The tetrabromoarsenic(V) ion should be even more sensitive to hydrolysis than the easily hydrolyzed tetrachloroarsenic(V) ion. Furthermore the reduction of the $[AsBr_4^+]$ by Br^- must go much more readily than the parallel reaction in the chlorine system since the bromide ion is known to be a stronger reducing agent than the chloride and since normal periodic relationships indicate that $[AsBr_4^+]$ should be a stronger oxidizing agent than $[AsCl_4^+]$.[5] These arguments coupled with the necessity for a larger amount of water in the system, justify the fact that $[AsBr_4^+][AsF_6^-]$ could never be isolated from the reaction but that $AsBr_3$ and $HAsF_6$ always appeared together in the products. The foregoing equations indicate that $AsBr_3$ and $HAsF_6$ should be present in a one to one ratio. In practice the $AsBr_3$ was also produced by an independent side reaction thus resulting in a mole ratio of $AsBr_3$ to $HAsF_6$ somewhat greater than 1:1. It was found that if HBr gas was bubbled through AsF_3 which contained very small quantities of water, the following exothermic reaction ensued immediately

$$AsF_3 + 3HBr \xrightarrow{H_2O} AsBr_3 + 3HF \qquad (6)$$

By this process $AsBr_3$ can be produced without a corresponding amount of $HAsF_6$. In separate tests the corresponding reaction between AsF_3 and HCl was scarcely detectable.

In light of the foregoing statements it is now possible to rationalize the observations of Ruff[3] which are summarized in the equation

$$AsF_3 + Br_2 + 2SbF_5 \longrightarrow AsF_5 + \text{Residue} \qquad (7)$$

Ruff apparently had enough water in his system to obtain AsF_6^- as an oxidation product. Addition of SbF_5 would then result in an acid–base reaction

$$SbF_5 + AsF_6^- \longrightarrow SbF_6^- + \overline{AsF_5} \qquad (8)$$

Ruff identified only the AsF_5, not the solid residue which would contain SbF_6^-.

The foregoing interpretation is supported by another reaction reported by Ruff.[3]

$$SbF_5 + NOF\text{-}AsF_5 \longrightarrow NOF\text{-}SbF_5 + \overline{AsF_5} \qquad (9)$$

By an application of coördination theory this process becomes

$$[NO][AsF_6] + SbF_5 \longrightarrow NO[SbF_6] + \overline{AsF_5} \qquad (10)$$

In terms of the Lewis theory SbF_5 appears to be a stronger acid than AsF_5, a conclusion consistent with eq. 8.

In its simplest terms the oxidation of AsF_3 by a halogen is dependent upon the amount of water present. The limiting cases $AsF_3 >> H_2O$ and $AsF_3 << H_2O$ are characterized by two distinctly different types of reaction

$$2AsF_3 + 2X_2 \xrightarrow[\text{trace}]{H_2O} [AsX_4^+][AsF_6^-] \qquad \text{(I)}$$

$$AsF_3 + 4H_2O + X_2 \xrightarrow[\text{excess}]{H_2O} 2XH + H_3AsO_4 + 3HF \qquad \text{(II)}$$

The first reaction shows an interesting variation as X_2 is changed from Cl_2 to Br_2 to I_2. In the Cl_2–AsF_3 system $[AsCl_4^+][AsF_6^-]$ has been isolated and characterized. In the Br_2–AsF_3 system the compound $[AsB_4^+][AsF_6^-]$ could not be isolated but evidence was found for its transitory existence. In the I_2–AsF_3 system no evidence of any type was ever found for the existence of $[AsI_4^+]$-$[AsF_6^-]$, so much water being required for the iodometric oxidation that eq. 1 degenerated into eq. 2.

In the presence of an excess of water Cl_2, Br_2 and I_2 all react in accordance with eq. 2.

Experimental

1. **Reagents.**—(a) AsF_3.—The preparation of the pure dry AsF_3 has been described elsewhere.[2]

(b) Br_2 and I_2.—Commercial C.P. reagents were used.

2. **The Reaction of the Halogen with Arsenic(III) Fluoride.**—The reactions were carried out in 125-ml. glass-stoppered Erlenmeyer flasks. The AsF_3 and Br_2 form a two layer liquid system, the AsF_3 being the upper layer. Small additional quantities of water always were added during the reaction. In the final separation of products the system was warmed to about 35° (in order to liquefy the $AsBr_3$) and the upper layer was pipetted from the lower. Upon completion of the reaction it was found that the lower layer had been converted from Br_2 to almost pure $AsBr_3$. Analysis showed: As^{+3}, 24.0; Br^-, 75.5. Theory: As^{+3}, 23.8; Br^-, 76.2.

To study the bromination of AsF_3 in the presence of excess water 0.1 mole of AsF_3 was mixed with one mole of water and an excess of Br_2 was added slowly. Air evaporation of the resultant solution, at 100°, gave a viscous, colorless sirup. Analysis showed the following: As^{+5}, 40.4; F^-, 5.3; Br^-, 0; AsF_6^-, 0. A concentrated solution of H_3AsO_4 containing some HF seems probable.

3. **Analytical Methods.** (a).—Bromide and iodide were determined gravimetrically as the silver salt.

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(4) Gmelin, "Arsen," System-Nummer 17, Verlag Chemie, Weinheim, 1952, p. 309–310.

(5) The ability of the halogens to stabilize higher valence states usually decreases from fluorine to iodine.

(**b**).—All other analytical procedures have been described elsewhere.[2]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. VIII. On the Reaction of Iodine Halides with Aluminum Halides[1]

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Spectrophotometric and electrolytic study of the several systems $AlCl_3$–ICl, $AlBr_3$–IBr, $AlCl_3$–IBr and $AlBr_3$–ICl has been made in acetonitrile solutions. The results obtained indicate that aluminum halide, solvated by acetonitrile, undergoes ionization according to the equation $AlX_3 \cdot nCH_3CN \rightleftarrows AlX_m \cdot nCH_3CN^{+3-m} + (3-m)X^-$ with $m = 2$, 1 or 0. The addition of iodine monochloride or iodine bromide leads to the formation of the corresponding polyhalogen anion $IClX^-$ or $IBrX^-$. A hitherto unreported solid compound $AlBr_3 \cdot 2CH_3CN$ has been prepared during this investigation.

Introduction

The reaction of iodine monochloride with aluminum chloride was studied mainly by Fialkov and his co-workers.[2] Physico-chemical measurements such as viscosity, melting point diagrams, electrical conductance and electrical transference were carried out on the iodine monochloride–aluminum chloride system directly, or on concentrated solutions of these compounds in nitrobenzene. The authors report that they have obtained evidence for the formation of the 1:1 addition compound $AlCl_3 \cdot ICl$. Where highly concentrated solutions of the $AlCl_3 + ICl$ mixtures were electrolyzed, aluminum was shown to be migrating to the anode, and iodine, partially, to the cathode. It was postulated that the initial 1:1 addition compound dissociates to I^+ and $AlCl_4^-$. With increasing amount of iodine monochloride in the solution, the former adds to the chloride coördinated to the aluminum, giving a series of addition compounds culminating in $I^+ [Al(ICl_2)_4]^-$. Throughout this series the cation is the positive iodine while aluminum forms part of the anion.

Indications that this reaction mechanism is not the only possible one were obtained by Gutmann in his study of iodine monochloride as an ionizing solvent.[3] This author reports that most covalent halides, such as $SnCl_4$, $SbCl_5$, VCl_4, etc., when dissolved in liquid iodine monochloride, form solvo-acid type of complexes with an iodine cation, such as $(I^+)_2(SnCl_6)^=$, $I^+(SbCl_6)^-$, $(I^+)_2(VCl_6)^=$, etc., and can be titrated conductometrically with a solvo-base such as potassium chloride. It is interesting to note that such conductometric titrations failed to reveal the presence of $I^+(AlCl_4)^-$.

Since iodine monochloride has a very characteristic absorption spectrum in the visible and the ultraviolet spectral regions, a spectrophotometric study of the iodine monochloride–aluminum chloride system in an appropriate solvent should give some indication as to the nature of addition compounds formed. Also, this technique permits the study of dilute solutions where the reaction mechanism might be quite different from the one found by Fialkov. In this study the measurements were made in acetonitrile solutions since the latter is a polar solvent, has good transparency in the ultraviolet region, and is fairly stable to halogenation. The investigation also has been extended to include aluminum bromide–iodine bromide, aluminum chloride–iodine bromide and aluminum bromide–iodine monochloride systems.

Experimental Part

Reagents.—The preparation of iodine monochloride, iodine bromide and the purification of acetonitrile have been described in a previous publication.[4]

Aluminum chloride was Baker and Adamson resublimed product. It dissolved in acetonitrile with large evolution of heat and upon careful concentration of the resulting solution a solid compound of the formula $AlCl_3 \cdot 2CH_3CN$ crystallized out. This compound was previously reported by Perrier.[5] The best method of preparation consists of the addition of aluminum chloride to 200–300 ml. of acetonitrile until saturation, decanting the clear liquid from the excess salt and then concentrating the former by evaporation of the solvent at room temperature in a vacuum desiccator until a crop of white crystals is obtained. The crystals are ground in a dry box, vacuum-dried, and stored in a desiccator. *Anal.* of the product. Calcd. for $AlCl_3 \cdot 2CH_3CN$: Al, 12.52; Cl, 49.37; C, 22.40; H, 2.81; N, 13.00. Found: Al, 12.60, 12.62; Cl, 49.26, 49.43, 49.30; C, 22.11; H, 3.23; N, 12.17. Analysis for chloride was carried out by the Volhard method using the improved procedure of Caldwell and Moyer.[6] The aluminum was determined by precipitation with 8-hydroxyquinoline. Carbon, hydrogen and nitrogen were determined by the familiar semi-micro-combustion methods. While Perrier reports a melting point of 50–55°, followed by decomposition at 60°, the product obtained in this investigation had no melting point and did not show any decomposition until 90°.

Aluminum trichloride diacetonitrile is stable and does not lose acetonitrile at ordinary temperatures and pressures. It is hygroscopic, but appears much less reactive to atmospheric moisture than the aluminum chloride itself. It was kept in a desiccator and was used in all subsequent work as a weighing form of aluminum chloride. An analysis for aluminum and chloride carried out on an eight month old sample gave identical results as for the freshly prepared compound.

Aluminum bromide was a laboratory preparation[7] and was obtained as a pure white crystalline solid, with analytical

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[1] Abstracted in part from the Ph.D. Thesis of Francis B. Stute, State University of Iowa, February, 1957.

[2] (a) Ya. A. Fialkov and K. Ya. Kaganskaya, *Zhur. Obshchei Khim*, **16**, 1961 (1946); (b) **18**, 289 (1948); (c) Ya. A. Fialkov and O. I. Shor, *ibid.*, **19**, 1787 (1949); (d) *ibid.*, **23**, 357, 363 (1953).

[3] V. Gutmann, *Z. anorg. Chem.*, **264**, 151 (1951).

[4] A. I. Popov and N. E. Skelly, THIS JOURNAL, **77**, 3277 (1955).

[5] M. G. Perrier, *Compt. rend.*, **120**, 1423 (1895).

[6] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

[7] "Inorganic Syntheses," McGraw-Hill Book Co., Vol. III, New York, N. Y., p. 33.