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Short communication

Elimination of AsF_3 from anhydrous HF using $AgFAsF_6$ as a mediator

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Dedicated to the late Professor Neil Bartlett in recognition of his many achievements in inorganic fluorine chemistry, including transition metal fluorides in high oxidation states.

ABSTRACT

Elimination of the arsenic (III) impurity AsF_3 from anhydrous hydrogen fluoride has been demonstrated using a bench-scale apparatus (~500 mL of HF), with a Ag(II) salt $AgFAsF_6$ as a mediator. In this process, AsF_3 is oxidized by $AgFAsF_6$ to AsF_5. In the next step, AsF_5 is eliminated from HF by reaction with NaF. The oxidizer, $AgFAsF_6$, is reduced to $AgAsF_6$ which is regenerated to $AgFAsF_6$ by F_2 in HF at room temperature. This method can reduce the arsenic content in HF from a few hundred ppm to the industrially required level (<3 ppm). The results for three other methods (distillation, oxidation by F_2 gas, and oxidation by K_2NiF_6) are reported and compared with the $AgFAsF_6$ method in a preliminary examination (using ~4 mL of HF).

1. Introduction

Hydrogen fluoride is the precursor for many fluorine-containing materials and is also used as a fluorinating reagent or a solvent. Hydrogen fluoride is manufactured on a scale of millions of tons per year, mainly by the reaction of fluorite (also called fluorspar) and sulfuric acid, but resources of the high-quality fluorite required for industrial preparation are limited to certain areas, such as China. However, appropriate treatment may reduce impurities in the resulting HF, allowing lower quality fluorite to be used.

The main impurities resulting from the reaction between fluorite and sulfuric acid such as SiF_4 and SO_2 are usually removed by fractional distillation. Impure fluorite can contain arsenic species with an oxidation state of three, which is much more difficult to remove from HF. This is because the As(III) species is converted in anhydrous HF to AsF_3 which has similar physical and chemical properties to HF (*e.g.* boiling point: 19 °C for HF and 57 °C for AsF_3) [1,2]; in addition there is a possibility of interaction between HF and AsF_3 molecules that may impede the separation by distillation. Several techniques have already patented for the removal of AsF_3 from HF [3]. One plausible method would be oxidation of As(III) to As(V) using an oxidizer such as F_2 or H_2O_2. The product AsF_5, as opposed to AsF_3, has completely different physical and chemical properties to those of HF, so it can be more easily removed. However, slow reaction rate, oxidizing reagent recovery, and generation of industrial wastes remain problematic.

In this communication, a new oxidizing pathway for As(III) to As(V), using a silver complex salt $Ag(II)FAsF_6$, is examined to allow effective removal of As impurity from HF. The target As content in HF was below 3 ppm, which represents a sufficient purity for industrial use. The starting As content was adjusted to a few hundred or thousand ppm to reflect HF synthesized from As-containing fluorite such as that produced in Mexico. The oxidizing salt, $AgFAsF_6$, was first reported in 1982 [4], and was characterized by several methods [5–7]. The solid-state structure of $AgFAsF_6$ contains a cationic $(Ag–F)_n$ chain, and an octahedral AsF_6 group cross-linked to the chain via F bridges [5]. On the other hand, $AgFAsF_6$ dissociates into AgF^+ and AsF_6^- in anhydrous HF, resulting in lower oxidizing power than the naked Ag^{2+} cation [7–10]. Following the oxidation of As(III) to As(V), $AgFAsF_6$ can be easily regenerated using F_2 gas at room temperature. Although the oxidation can be performed using other $AgFAF_6$-type compounds (for example, $AgFSbF_6$), $AgFAsF_6$ is preferred because the risk of contamination is lower.

2. Results and discussion

2.1. Preliminary examination

Table 1 summarizes typical preliminary examination results for the removal of As from HF using $AgFAsF_6$, as well as for methods

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Table 1
Summary of As removal results in preliminary examination.[a].

	As content before treatment (ppm)		As content after treatment (ppm)	
Distillation[b]	(D-1)	1600	(D-2)	1600
Elemental fluorine	(F-1)	1600	(F-2)	18
$AgFAsF_6$	(Ag-1)	489	(Ag-2)	<3
K_2NiF_6	(Ni-1)	464	(Ni-2)	<3

[a] The symbol of each result such as (D-1) refers to the sample name in Section 3.
[b] The As content in the residual HF sample (D-3) was also 1600 ppm.

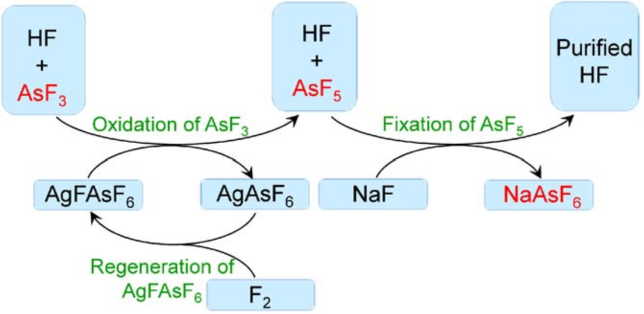

Fig. 1. Concept of the removal of As using $AgFAsF_6$.

using distillation, elemental fluorine, and K_2NiF_6 which were performed for comparison.

2.1.1. *Distillation*

According to the analysis, the As concentration in the original, distilled, and residual HF samples was the same, at 1600 ppm each. The original HF sample was prepared from AsF_3 and HF. The distilled HF sample was produced by distillation into another reactor, and the residual HF sample was that left behind after distillation. If the distillation works, then distillated sample should be poorer in As(III) than original sample, and the residual sample should be richer in As content than original sample. This result means that simple distillation is not effective for reducing the As content in HF.

2.1.2. *Oxidation by elemental fluorine*

The effectiveness of elemental fluorine in removing the As impurity was examined (at room temperature) by introducing F_2 in the gas phase over HF containing AsF_3 (Eq. (1)) and treating with NaF to completely remove the product AsF_5 (Eq. (2)).

$$AsF_3 + F_2 \rightarrow AsF_5 \quad (1)$$

$$AsF_5 + NaF \rightarrow NaAsF_6 \quad (2)$$

According to the patent covering this process, a small amount of F_2 gas is quite effective, even within a short period [3]. However, the results of the current study suggest that F_2 gas treatment under ambient conditions does not decrease As concentration to the target level ($As < 3$ ppm). This is presumably due to the low solubility of F_2 gas in HF, although different experimental conditions, such as water impurity and the agitation method used, may have affected the results.

2.1.3. *Oxidation by K_2NiF_6*

Removal of As was also performed via oxidation by K_2NiF_6, which is a very strong oxidizer of Ni(IV) [11,12]. The process is based on the following equation (Eq. (3)).

$$AsF_3 + K_2NiF_6 \rightarrow KAsF_6 + NiF_2 + KF \quad (3)$$

Further treatment to fix AsF_5 was not necessary, since it was trapped in the reactor as nonvolatile $KAsF_6$. The final sample was obtained by distilling HF from the K_2NiF_6 reactor to another reactor.

This treatment is effective for reducing the As content from a few hundred ppm to a value below 3 ppm. The high solubility of K_2NiF_6 in HF is thought to facilitate the fluorination of AsF_3 even under ambient conditions. However, the supply of costly K_2NiF_6 is a drawback since the regeneration of the products to K_2NiF_6 requires fluorination by elemental fluorine at a high temperature.

2.1.4. *Oxidation by $AgFAsF_6$*

The use of $AgFAsF_6$ as an oxidizer to remove As from HF is based on the following reaction (Eq. (4)).

$$AsF_3 + 2AgFAsF_6 \rightarrow AsF_5 + 2AgAsF_6 \quad (4)$$

The reaction proceeds readily since $AgFAsF_6$ has sufficient solubility into HF. In this case treatment with NaF is necessary for fixing AsF_5 (Eq. (2)). However, the concentration of AsF_5 after the first cycle was low even before treating with NaF. This is because of the high solubility of AsF_5 into the residual HF in the reactor. Repetitive $AgFAsF_6$ treatments gave increasingly more AsF_5 in the distilled HF. After NaF treatment, the final HF had less than 3 ppm of As, compared to a starting concentration of a few hundred ppm. Unlike oxidation by elemental fluorine, this method does not require removal of F_2 from the anhydrous HF product and continuous oxidation is possible as long as $AgFAsF_6$ exists in the system.

Since the validity of the $AgFAsF_6$ treatment was confirmed in the preliminary examination, this method was scaled up as shown in the next section.

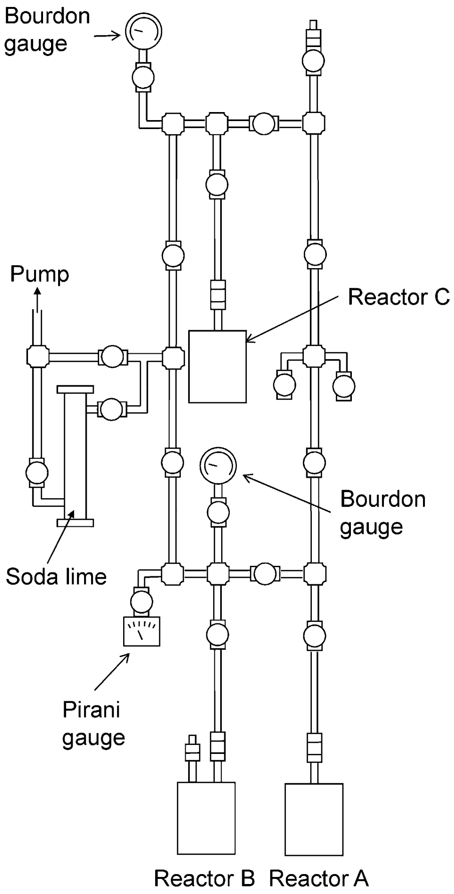

Fig. 2. Schematic illustration of the reaction line used in the bench-scale demonstration.

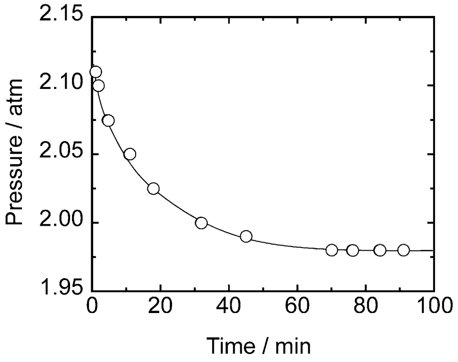

Fig. 3. Time dependence of the pressure in the reactor during fluorination of $AgAsF_6$ by F_2 gas in the bench-scale demonstration.

2.2. Bench-scale demonstration

The concept of As removal using $AgFAsF_6$ at an industrial level is shown in Fig. 1. A schematic illustration of the reaction line for the bench-scale demonstration is shown in Fig. 2. A photograph of the PFA (poly(tetrafluoroethylene-*co*-perfluoro(alkyl vinyl)ether)) reactor used in the bench-scale demonstration can be seen in Fig. S1 (Supplementary material).

The oxidizing reagent $AgFAsF_6$ was prepared from $AgAsF_6$ in 70 mL of aHF, by fluorination with diluted F_2 gas (F_2:N_2 = 30:70), under vigorous agitation in Reactor (B) (Eq. (5)).

$$2AgAsF_6 + F_2 \rightarrow 2AgFAsF_6 \tag{5}$$

Diluted F_2 gas was used because it is less corrosive than 100% elemental fluorine, so it is the preferred choice in industrial application. Fig. 3 shows the time dependence of the pressure in the reactor during fluorination, where the gas phase consists of the diluted F_2/N_2 gas and HF vapor. The solution began to turn blue within a few minutes of introducing fluorine gas, and the pressure showed a steep decline during the first 20 min. The decrease in pressure ceased within 90 min. At this stage, the color of the HF solution was dark blue. The yield of $AgFAsF_6$, calculated using the uptake of F_2 gas and the initial amount of $AgAsF_6$ was 87%. It should be noted that the amount of F_2 gas consumed in the first minute of the reaction could not be measured, as the pressure in the reactor had not yet stabilized. The yield can be increased by adding this amount of F_2 gas.

In the next step, approximately 430 mL of a mixture of HF and AsF_3 was prepared in Reactor (A) and transferred into Reactor (B) by distillation. Arsenic trifluoride was oxidized by $AgFAsF_6$ in Reactor (B) and the resulting HF sample was transferred to Reactor (C) by distillation, where AsF_5 was trapped by NaF as $NaAsF_6$. The final HF was sampled from Reactor (C) by distillation. This 500 mL-scale demonstration successfully reduced the As impurity from a few hundred ppm in the original HF to a concentration below 3 ppm. The solution in Reactor (B) became less and less blue as the $AgFAsF_6$ treatment was repeated, and finally became colorless. Regeneration of $AgFAsF_6$ from $AgAsF_6$ was performed in the same manner as its preparation above. In practical processes, accumulating $NaAsF_6$ must be removed from the reactor after a certain number of treatments. If $AgFAsF_6$ regeneration or $NaAsF_6$ removal is time-consuming, a second reactor may need to be installed in parallel to the first.

3. Experimental

3.1. General experimental procedure

Moisture-sensitive materials were handled in a glove box under a dry Ar atmosphere. Volatile materials were handled in a reaction line made of stainless steel pipes (SUS-316, 1/2-in. o.d.) which were connected by stainless steel unions and valves with Kel-F tips. The line was connected to a rotary vacuum pump through a soda lime chemical trap, which was connected in series to a liquid nitrogen trap. Occasionally, direct pumping was performed through the liquid nitrogen trap only, in order to obtain a high vacuum ($1 <$ Pa). The pressure and vacuum of the line were monitored by Bourdon and Pirani gauges.

3.2. Reagents

For bench-scale demonstration, anhydrous hydrogen fluoride (Stella Chemifa, purity >99%) was used as supplied, but for the small-scale demonstration it was treated with K_2NiF_6 prior to use. Arsenic trifluoride was prepared by reaction of As_2O_3 and HF according to the literature method [13] and stored over NaF. Diluted F_2 gas was prepared by mixing F_2 (Daikin Industries) and N_2 (extra pure grade, Japan Air Gases) in a ratio of 30–70 prior to use.

3.3. Reactions in the preliminary examination

Unless otherwise specified, the term "distillation" is taken to mean the transfer of volatile compounds from a reactor at room temperature to another reactor at −196 °C. An h-shaped PFA reactor, equipped with a stainless steel valve at the top and with a PFA valve at the side arm, was used for the preliminary reactions (Fig. S2 in Supplementary data). The PFA reactor, HF container, and AsF_3 container were connected via a three-way PFA connector. To prepare HF with the AsF_3 impurity, AsF_3 was distilled into the main arm of the h-shaped reactor, and about 4 mL of HF was distilled on it. The amount of AsF_3 was roughly estimated using the volume of the reaction line. The mixture was then warmed up to room temperature and stirred for a few minutes.

3.3.1. Removal of As impurity by distillation

Approximately 4 mL of HF with AsF_3 impurity was prepared in the main arm of an h-shaped reactor, using the method described in Section 3.3. Half of the sample was poured into the side arm and the PFA valve was closed. The other half in the main arm was distilled onto ~4 mL of frozen H_2O to give Sample D-1. Half of the mixture in the side arm was distilled onto ~4 mL of frozen H_2O in another PFA reactor and collected as Sample D-2 and the remainder was distilled onto ~4 mL of frozen H_2O in one more PFA reactor (Sample D-3). These samples provide the As content in three states: the original HF (Sample D-1), the distilled HF (Sample D-2), and the residual HF (Sample D-3), as shown in Table 1.

3.3.2. Removal of As impurity using elemental fluorine

Approximately 4 mL of HF with AsF_3 impurity was prepared in the main arm of an h-shaped reactor, using the same method described in Section 3.3. Half of the HF sample was poured into the side arm, and the PFA valve was closed. The other half was distilled onto ~4 mL of frozen H_2O in another PFA reactor (Sample F-1). The contents of the side tube were then distilled into a separate PFA reactor (~80 mL in volume) equipped with a stainless steel valve. Approximately 0.4 atm of F_2 gas was introduced into the gas phase at room temperature, followed by vigorous agitation for 40 min. The fluorine gas was pumped off under vacuum at −85 °C for a few minutes, and the HF sample was distilled into a PFA reactor containing 100 mg of NaF. The solution was warmed up to room temperature and stirred for 5 min, during which time the NaF completely dissolved. Most of the resulting HF was distilled onto ~4 mL of frozen H_2O in another PFA reactor to give Sample F-2. Complete transfer of HF was difficult at this stage, due to the strong HF-absorption ability of NaF (forming $Na(FH)_nF$ [14,15]). Sample F-

1 provided the As content of the original HF, and Sample F-2 provided that of the HF treated with F_2 as shown in Table 1.

3.3.3. *Removal of As impurity using K_2NiF_6*

Approximately 4 mL of HF containing AsF_3 impurity was prepared as described in Section 3.3. Half of the HF sample was poured into the side arm of the h-shaped tube and the PFA valve was closed. The HF in the main tube was distilled onto ~4 mL of frozen H_2O in a PFA reactor (Sample Ni-1). The contents of the side tube were then distilled onto K_2NiF_6 (128 mg) in a PFA reactor equipped with a stainless steel valve. A red-purple HF solution of K_2NiF_6, obtained by warming up the mixture to room temperature, was stirred for 5 min. Most of the resulting HF sample was distilled onto ~4 mL of frozen H_2O in another PFA reactor to give Sample Ni-2. The As content of the original HF (Sample Ni-1) and the K_2NiF_6-treated HF (Sample Ni-2) were obtained, as shown in Table 1.

3.3.4. *Removal of As impurity using $AgFAsF_6$*

Approximately 4 mL of HF with AsF_3 impurity was prepared as described in Section 3.3. Half of the HF sample was poured into the side arm of the h-shaped tube and the PFA valve was closed. The HF in the main tube was distilled onto ~4 mL of frozen H_2O in another PFA reactor (Sample Ag-1). The contents of the side arm were distilled onto $AgFAsF_6$ (100 mg) in a PFA reactor equipped with a stainless steel valve. A blue solution, obtained by warming up to room temperature, was stirred for 5 min. This sample was distilled onto 100 mg of NaF in another PFA reactor, warmed up to room temperature, and stirred for 5 min. Most of the resulting HF sample was distilled onto ~4 mL of frozen H_2O in a PFA reactor to give Sample Ag-2. These samples provide the As content of the original (Sample Ag-1) and $AgFAsF_6$-treated HF (Sample Ag-2).

3.4. *Reactions in the bench-scale demonstration*

3.4.1. *Preparation and regeneration of $AgFAsF_6$ in the bench-scale demonstration*

The starting compound $AgAsF_6$ (8.222 g, 0.02867 mol) was loaded in a PFA reactor (~1 L in volume, Fig. S1) under a dry Ar atmosphere, and the reactor was connected to the reaction line (Fig. 2) as Reactor (B). Approximately 70 mL of anhydrous HF was distilled onto the $AgAsF_6$ in Reactor (B) from a storage vessel. Tanks (A) and (B), each containing 1 L of diluted F_2 gas (F_2:N_2 = 30:70), were connected to the reaction line. The gas in Tank (A) was introduced to Reactor (B) and the valve of Tank (A) was closed once pressure equilibrated. The gas in Tank (B) was also introduced to Reactor (B), but its valve was kept open during the reaction. This led to a volume of ~2.1 L for the gas phase contained in Reactor (B), Tank (B), and the connecting portion. The HF solution was vigorously agitated during the reaction, and the end point was confirmed by a change in color and pressure.

3.4.2. *Oxidation of AsF_3 in the bench-scale demonstration*

Approximately 430 mL of HF was condensed from a storage cylinder to Reactor (A) at $-90\ ^\circ C$. Reactor (B) contained $AgFAsF_6$, prepared as described in Section 3.4.1, and Reactor (C) contained NaF (2.2 g, 0.05 mol). An amount of AsF_3 estimated from the volume of the reaction line was condensed onto the HF in Reactor (A) at $-90\ ^\circ C$. The mixture was warmed up to room temperature and stirred for 5 min. Approximately 4 mL of the HF in Reactor (A) was distilled onto ~4 mL of frozen H_2O in a PFA tube (Sample Bench-1). The rest was distilled onto 70 mL of HF in Reactor (B) at $-90\ ^\circ C$. The solution was warmed up to room temperature, stirred for 5 min, and distilled into Reactor (C), where AsF_5 was trapped by NaF as $NaAsF_6$. Approximately 4 mL of the final HF in Reactor (C) was distilled onto ~4 mL of frozen H_2O in another PFA tube (Sample Bench-2).

3.5. *Analysis*

The HF sample distilled onto H_2O in a PFA reactor for all the treatments above was diluted with more H_2O, and sent for analysis as 3–10% hydrofluoric acid. The concentration of As in the sample was measured by ICP-AES (SPS3000, Seiko Instruments Inc.), and the concentration of HF was measured by titration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.04.006.

References

[1] H. Russell, R.E. Rundle, D.M. Yost, J. Am. Chem. Soc. 63 (1941) 2825.
[2] J. Simons, J. Am. Chem. Soc. 46 (1924) 2179.
[3] For example: Japanese Patents 16407 (1972), 151002 (1986), 502277 (1990), 146401 (1991), 205304 (1991), 263406 (1994), and 504149 (1995), US Patents 4,032,621 (1977), 4,083,941 (1978), 4,424,067 (1984), 4,491,570 (1985), 4,668,497 (1987), 4,756,899 (1988), 4,960,580 (1990), 4,954,330 (1990), 4,990,320 (1991), 5,108,559 (1992), 5,100,639 (1992).
[4] B. Frlec, D. Gantar, J.H. Holloway, J. Fluorine Chem. 20 (1982) 385.
[5] D. Gantar, B. Frlec, D.R. Russell, J.H. Holloway, Acta Cryst. C 43 (1987) 618.
[6] W. Grochala, R. Hoffmann, Angew. Chem. Int. Ed. 40 (2001) 2742.
[7] B. Žemva, R. Hagiwara, W.J. Casteel, K. Lutar, A. Jesih, N. Bartlett, J. Am. Chem. Soc. 112 (1990) 4846.
[8] N. Bartlett, G. Lucier, C. Shen, W.J. Casteel, L. Chacon, J. Munzenberg, B. Žemva, J. Fluorine Chem. 71 (1995) 163.
[9] G. Lucier, C. Shen, W.J. Casteel, L. Chacón, N. Bartlett, J. Fluorine Chem. 72 (1995) 157.
[10] B. Žemva, K. Lutar, A. Jesih, W.J. Casteel, A.P. Wilkinson, D.E. Cox, R.B. Von Dreele, H. Borrmann, N. Bartlett, J. Am. Chem. Soc. 113 (1991) 4192.
[11] L. Stein, J.M. Neil, G.R. Alms, Inorg. Chem. 8 (1969) 2472.
[12] B. Žemva, K. Lutar, L. Chacón, M. Fele-Beuermann, J. Allman, C. Shen, N. Bartlett, J. Am. Chem. Soc. 117 (1995) 10025.
[13] G. Brauer (Ed.), Handbuch der Präparativen Anorganischen Chemie, Ferdinand Enke Verlag, Stuttgart, 1954.
[14] R.L. Adamczak, J.A. Mattern, H. Tieckelmann, J. Phys. Chem. 63 (1959) 2063.
[15] G.A. Bottomley, J.B. Farrow, F.J. Lincoln, Aust. J. Chem. 36 (1983) 649.