Reactions of Some Ammonium Fluorometalates with XeF₂
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Dedicated to Prof. Dr. Drs. h. c. Oskar Glemer on the occasion of his 70th birthday
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Xenon Difluoride Reactions, Ammonium Fluorometalates, Hydrazinium Fluorometalates

The reactions between (NH₄)₂TiF₆, (NH₄)₂ZrF₆, (NH₄)₂HfF₆, (NH₄)₂VF₆, (NH₄)₂CrF₆, NH₄MnF₃, (NH₄)₂FeF₆ and excess xenon difluoride were investigated. The listed ammonium fluorometalates react with xenon difluoride to form corresponding xenon(II) fluorometalates, monoammonium fluorometalates with metal in the same oxidation state, and ammonium fluorometalates with metal in higher oxidation state, respectively.

The reactions between binary fluorides and xenon difluoride or xenon hexafluoride, respectively, yield a series of xenon(II) or xenon(VI) fluorometalates. We have investigated these reactions in detail succeeded to isolate and identify seven xenon(II) and thirteen xenon(VI) fluorometalates [1].

Since in some cases the reaction between binary fluoride and xenon hexafluoride did not proceed at all under the applied reaction conditions, we supposed that the binary fluoride is not reactive enough and that the reaction might proceed if the binary fluoride would be available in a more reactive form. Highly reactive, pure binary fluorides were prepared in this laboratory earlier by reacting hydrazinium fluorometalates with elemental fluorine [2].

It was expected, therefore, that the metal fluoride which is formed in situ during the reaction between hydrazinium fluorometalates and xenon hexafluoride should be in a highly reactive form and should consequently react immediately with excess xenon hexafluoride to form xenon(VI) fluorometalates. We checked our speculation in the reaction between Na₂H₄FeF₆ and xenon hexafluoride. Indeed XeF₄ • FeF₃ was isolated [3], a compound which could not be obtained by other, more conventional ways. This result encouraged us to initiate a systematic study of the reactions between xenon difluoride or xenon hexafluoride on one side and hydrazinium(1⁺) fluorometalates, hydrazinium(2⁺) fluorometalates and metal fluoride adducts with hydrazine on the other side [4–10]. So far the following new compounds, not accessible by other conventional methods, were isolated and characterized:

- XeF₄ • FeF₃ [3]
- XeF₄ • ZrF₄, XeF₄ • HfF₄ [11]
- XeF₄ • 2AlF₃ and XeF₄ • GaF₃ [12]. This study is still being continued.

Following the same basic approach we extended the investigations recently onto reactions between xenon difluoride or xenon hexafluoride and ammonium fluorometalates.

Experimental

Materials

Fluorine was prepared and purified in this laboratory as described elsewhere [13]. Its purity was 99 ± 0.5 vol%. Additional purification, mainly from oxygen, was performed by irradiation of liquefied fluorine with the near UV light at 77 K [14]. The purity of so obtained fluorine was above 99.9 vol%.

Xenon was supplied by l’Air Liquide (Paris, France) in 99.5% purity (the balance was krypton). Xenon difluoride was prepared by photosynthesis using near UV lamp [15]. The purity of xenon difluoride was checked by IR spectrum of the vapours and by the determination of its triple point. (NH₄)₂MF₆ (M = Ti, Zr, Hf) were prepared by crystallization from the water solutions of corresponding fluorometallic acid and ammonium fluoride [16–18].

(NH₄)₂MF₆ (M = V, Cr, Fe) were prepared by crystallization of solutions obtained by dissolving of corresponding metal trifluoride trihydrate in water solution of ammonium fluoride [19–21].

NH₄MnF₃ was prepared by reaction between Mn(NO₃)₂ • 4 H₂O and ammonium fluoride in water solution [22].

General procedure

Reactions were carried out in argon arc welded nickel or copper pressure and weighing vessels equipped with Teflon packed nickel valves. The volume of the reaction vessel was about 100 ml.
Chemical analysis of the products:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calcd [%]</th>
<th>Found [%]</th>
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<tbody>
<tr>
<td>NH₄ZrF₅</td>
<td></td>
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<tr>
<td>NH₄HfF₅</td>
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<tr>
<td>(NH₄)₃VF₈</td>
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<td>NH₄CrF₄</td>
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<td>NH₄MnF₄</td>
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<tr>
<td>NH₄FeF₄</td>
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They were tested hydrostatically up to 200 atm and were designed also for manipulating solid materials. All transfers of materials were carried out either in the atmosphere of a dry box or by distillation under vacuum in a well dried apparatus.

In a typical run 3 to 6 mmoles of ammonium fluorometalate was weighed into reaction vessel and dried by pumping upon in a dynamic vacuum for 12 h. Then a corresponding amount of xenon difluoride was added by sublimation. The vessel was then thermostated at predetermined temperature for several hours. After the reaction was completed, the reaction products were separated by fractional sublimation, isolated and identified. Volatiles at 77 K, 193 K, 233 K and at room temperature were characterized by mass spectrometry and infrared spectroscopy. Solids were identified by chemical analysis, X-ray powder diffraction patterns, infrared and Raman spectroscopy and magnetic susceptibility measurements. The stoichiometry of the reactions was followed throughout of experiment by weighing of all reactants and products to ± 5 mg.

General apparatus and techniques

Raman spectra were recorded using a Spex 1401 double monochromator. As exciting radiation, the 515.5 nm line of an Ar⁺ laser or 647.1 nm of a Kr⁺ laser (Coherent Radiation) were used. Powdered samples were loaded into quartz capillaries in a dry box temporarily plugged with Kel-F grease and sealed off by a small flame outside the dry box. Samples were loaded into quartz capillaries in a dry box with Kel-F grease and sealed off by a small flame outside the dry box. The sample was finely powdered and dusted onto silver chloride plates sandwiched in a leak tight brass holder.

IR spectra were recorded using Perkin Elmer 521 and Zeiss UR-20 spectrometers over the range 400 to 4000 cm⁻¹. The sample was finely powdered and sealed in 0.5 mm thin walled quartz capillaries as described under Raman spectra.

Mass spectra were recorded on a Nier type mass spectrometer with an inlet system for the analysis of gases.

Results and Discussion

The reactions between (NH₄)₂TiF₆, (NH₄)₂ZrF₆, (NH₄)₂HfF₅, (NH₄)₃VF₈, (NH₄)₂CrF₄, NH₄MnF₄, (NH₄)₂FeF₄ and excessive xenon difluoride were investigated. The listed ammonium fluorometalates react with xenon difluoride in a three different modes as follows:

1. Ammonium fluorometalate is completely fluorinated by xenon difluoride to corresponding binary fluoride which reacts further with excess of xenon difluoride to form corresponding xenon-(II) fluorometalate.

2. Tri- or di-ammonium fluorometalate is only partially fluorinated by xenon difluoride to form monoammonium fluorometalate with the metal in the same oxidation state.

3. Only metal in ammonium fluorometalate is oxidized while the rest of the compound does not change.

The reaction between (NH₄)₂TiF₆ and xenon difluoride belongs to the first group:

\[(NH_4)_2TiF_6 + nXeF_2 \rightarrow \text{453 K several hours}\]

\[XeF_2 \cdot TiF_4 + zN_2 + 2(1-x)NF_2 + 8HF + 3(2-x)Xe + n(7-3x)XeF_2\]

\[n > 10, \ x > 0.7.\]

The reaction between (NH₄)₂TiF₆ and xenon difluoride starts somewhere around 413 K but is very slow. Even at 433 K with periodic pumping away of all volatile reaction products it takes several days, before the reaction is completed. Normally the reaction was carried out at 453 K. Obviously the related hydrazinium(2+) compound N₂H₄TiF₆ is
much more reactive. It reacts with xenon difluoride already at 393 K forming XeF$_2$·TiF$_4$.

Interestingly enough, also some nitrogen trifluoride was obtained during the reaction. This is, as far as we know, the first chemical reaction where nitrogen trifluoride was prepared by the reaction with xenon difluoride.

The reactions in the analogous systems (NH$_4$)$_2$ZrF$_6$/XeF$_2$ and (NH$_4$)$_2$HfF$_6$/XeF$_2$ belong to the second group:

$$(\text{NH}_4)_2\text{MF}_6 + n\text{XeF}_2 \xrightarrow{\text{423 K}} 36\text{ h}$$

$$\text{NH}_4\text{MF}_5 + 0.5\text{N}_2 + 4\text{HF} + 1.5\text{Xe} + (n - 1.5)\text{XeF}_2$$

$$n > 6, M = \text{Zr, Hf}.$$ 

Also in this case the reaction proceeds at the temperature around 423 K but only to NH$_4$ZrF$_5$ [22] and NH$_4$HfF$_5$ [23], respectively. Both formed compounds are very stable and do not react further with excess of xenon difluoride even at 473 K.

The most interesting reaction in the investigated series of ammonium fluorometalates is the reaction between (NH$_4$)$_3$VF$_6$ and xenon difluoride:

$$(\text{NH}_4)_3\text{VF}_6 + n\text{XeF}_2 \xrightarrow{\text{343 K}} \text{several days}$$

$$(\text{NH}_4)_3\text{VF}_8 + \text{Xe} + (n - 1)\text{XeF}_2$$

$$n > 8.$$ 

The volatiles which were pumped away after reaction, were only pure xenon and excess of xenon difluoride as shown by mass spectrometry and infrared spectroscopy. Neither nitrogen, nor nitrogen trifluoride or any other nitrogen fluoride were found in volatiles. The amount of evolved xenon was equivalent to the oxidation of V$^{3+}$ to V$^{6+}$ by xenon difluoride. As shown by the magnetic susceptibility measurements (NH$_4$)$_3$VF$_8$ is diamagnetic what is also the evidence that vanadium was oxidized to the 5$^+$ oxidation state.

The formation of VF$_8^{3-}$ anion should be very unlikely but some of the experimental results collected so far indicate vanadium atom has co-ordination of fluoride ions above six. Xenon difluoride is electrophilic agent, therefore we would expect its attack on the anion rather than on a cation.

The symmetrical (V–F) stretching mode in Raman spectrum of NH$_4$VF$_6$, which contains isolated octahedra of VF$_6^{-}$, appears at 660 cm$^{-1}$ [25]. The corresponding band in the Raman spectrum of our compound is at 612 cm$^{-1}$ indicating higher coordination number of fluorine around vanadium than six. The compound decomposes in X-ray beam and it turns very quickly from a white colour with a pink cast to a green colour. This behaviour also rules out the potential possibility of having a mixture of ammonium fluoride and NH$_4$VF$_6$ as the reaction product. Both components are white and very stable in X-ray beams. Quite interesting is also the comparison with the analogous reaction of (NH$_3$)$_2$VF$_6$ and xenon difluoride. In this case NH$_4$VF$_6$ [25] was obtained besides of nitrogen, hydrogen fluoride, xenon and excess of xenon difluoride. It should be mentioned here that in this case ammonium hexafluorovanadate(III) and hydrazinium hexafluorovanadate(III) appear to be approximately equally stable. The reason for this is that vanadium is in 3$^+$ oxidation state what is not the stable oxidation state of vanadium in xenon(II) fluorovanadates consequently the oxidation of the metal takes place. At higher temperatures (about 400 K or higher) the reaction between (NH$_3$)$_2$VF$_6$ or (NH$_4$)$_3$VF$_6$ and xenon difluoride proceeds in both cases to XeF$_2$·VF$_3$.

Reactions between NH$_4$MnF$_3$, (NH$_4$)$_2$CrF$_6$ and (NH$_4$)$_3$FeF$_6$ and xenon difluoride yield corresponding NH$_4$MF$_4$ compounds. All three compounds are isomorphous as shown by X-ray diffraction patterns.

$$(\text{NH}_4)_2\text{MnF}_3 + n\text{XeF}_2 \xrightarrow{\text{333 K}} \text{several hours}$$

$$(\text{NH}_4)_2\text{MnF}_4 + 0.5\text{Xe} + (n - 0.5)\text{XeF}_2$$

$$n > 6.$$ 

$$(\text{NH}_4)_3\text{CrF}_6 + n\text{XeF}_2 \xrightarrow{\text{393 K}} \text{several hours}$$

$$(\text{NH}_4)_3\text{CrF}_4 + \text{N}_2 + 8\text{HF} + 3\text{Xe} + (n - 3)\text{XeF}_2$$

$$n > 7.$$ 

$$(\text{NH}_4)_3\text{FeF}_6 + n\text{XeF}_2 \xrightarrow{\text{393 K}} \text{several hours}$$

$$(\text{NH}_4)_3\text{FeF}_4 + \text{N}_2 + 8\text{HF} + 3\text{Xe} + (n - 3)\text{XeF}_2$$

$$n > 7.$$ 

It is somewhat surprising that NH$_4$MnF$_3$ is oxidized to NH$_4$MnF$_4$. The product formed at
analogous reaction between \((N_2Hs)_2MnF_4\) and xenon difluoride would namely suggest formation of \(NH_4MnF_5\) [25] specially so since \(Mn^{4+}\) is the only known oxidation state in the xenon(II) and xenon(VI) fluorometalates. Interestingly enough, the reaction between \(NH_4MnF_3\) and xenon hexafluoride proceeds to the formation of \(NH_4^+XeF_5^{2-}\) [29].

Ammonium hexafluorochromate(III) and -ferrate(III) reacted with xenon difluoride according to our expectation. \(NH_4CrF_4\) was obtained also by the reaction of hydrazinium fluorochromate(III) with xenon difluoride, while in a similar reaction \(N_2H_6FeF_5\) yielded iron trifluoride.

As expected, ammonium fluorometalates react with xenon difluoride less readily than the corresponding hydrazinium fluorometalates. This is specially true if the oxidation state of a metal in the starting compound is the same or higher than the usual oxidation state of a metal in corresponding xenon(II) fluorometalates (e.g. Ti\(^{4+}\), Zr\(^{4+}\), Cr\(^{4+}\), V\(^{5+}\) etc.). If the oxidation state of a metal in the starting compound is lower than already mentioned (e.g. Mn\(^{2+}\), V\(^{3+}\)) than the reactivity of such an ammonium fluorometalate is comparable with the reactivity of the corresponding hydrazinium fluorometalate. This system offers a convenient way for the syntheses of ammonium fluorometalates with a metal in higher oxidation state.

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