HIGHER FLUORIDES OF NICKEL: SYNTHESES AND SOME PROPERTIES OF Ni_2F_5[†]

Melita Tramšek and Boris Žemva*

Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

[†] Dedicated to the memory of fluorine chemist and friend dr. Karel Lutar (d. September 2, 2000)

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Abstract

Ni_2F_5 was prepared by thermal decomposition of *R*-NiF_3 at 373 K or by reduction of *R*-NiF_3 with xenon or XeF_2. Reaction of Ni_2F_5 in anhydrous HF (aHF) acidified with AsF_5 yielded $Ni(AsF_6)_2$ and F_2 while Ni_2F_5 disproportionated in aHF made basic with KF yielding NiF_2 and K_2NiF_6. Ni_2F_5 is able to oxidize xenon to XeF_2 and fluorinate C_3F_6 to C_3F_8. Ni_2F_5 is most probably playing an important role in the electrochemical fluorination.

Introduction

Higher binary fluorides of nickel have been a subject of investigation since the development of electrochemical fluorination of organic compounds (Simon´s process ECF).[1,2] This process is particularly efficient if nickel is used as an anode.[2] Several authors[3,4] were convinced that higher nickel fluorides are formed at the anode during electrochemical fluorination and that these nickel fluorides have the major role in the fluorination of organic compounds by Simon´s process. Even more, some authors[5,6] tried to prepare higher nickel fluorides using electrochemical fluorination.

Court and Dove[7,8] tried to prepare higher nickel fluorides with the reaction between K_2NiF_6 and Lewis acid (e.g. AsF_5, BF_3) in anhydrous hydrogen fluoride (aHF) but their material was always heavily contaminated with co-produced potassium salts (KBF_4, $KAsF_6$). The oxidation state of their mostly brown precipitates was always lower than +3. It is surprising that they did not observe NiF_4 or isolate the relatively long-lived NiF_3, which is thermally stable at 293 K as dry solid.

It was not until 1989[9] that in joint efforts of researchers from the University of California, Berkeley and “Jožef Stefan” Institute, Ljubljana the evidence for the existence of NiF_4 was provided. In the next years[10] three forms of NiF_3 have been prepared, their structures identified and the oxidizing properties described. The existence of Ni_2F_5 was also mentioned and the X-ray powder diffraction patterns of Ni_2F_5 prepared by different synthetic routes were given.[10]

In this paper the efforts to synthesize pure Ni_2F_5 are described together with its characterization and some of its properties.

Results and discussion

1. Synthetic routes to Ni_2F_5

Ni_2F_5 is red brown solid with negligible vapour pressure at room temperature. It is stable when dry and in an inert atmosphere. It slowly decomposes at room temperature in the suspension of aHF to NiF_2 and fluorine. Among all higher nickel fluorides it is the most stable binary fluoride of nickel.

Ni_2F_5 could be prepared from *R*-NiF_3 by thermal decomposition or by reduction with xenon or xenon(II) fluoride. *R*-NiF_3 is the most thermodynamically unstable of all three forms of NiF_3 and it loses F_2 at temperatures higher than 312 K.[10] Thermal decomposition at 312 K is very slow process therefore for the preparation of Ni_2F_5 higher temperatures between 353 to 373 K are used. The mass balance is in accordance with the reaction:

$$2R\text{-}NiF_3 \xrightarrow{373\ \mathrm{K}} Ni_2F_5 + 1/2F_2$$

The chemical analysis of the obtained product is giving the molar ratio Ni:F=1:2.47. X-ray powder diffraction pattern matches X-ray powder diffraction pattern of the product NiF_x ($2<x<3$).[10] The crystallinity of the product obtained by thermal decomposition is usually not good therefore thermal decomposition of *R*-NiF_3 at 313 K in fluorine atmosphere ($P = 10^5$ Pa) was tried besides recrystallization of the obtained product in supercritical NF_3. The crystallinity of these products was not improved.

Other synthetic routes for the preparation of Ni_2F_5, which were tested, are the reduction of *R*-NiF_3 with elemental xenon and XeF_2.

$$4R\text{-}NiF_3 + nXe \xrightarrow{295\text{ K}} 2Ni_2F_5 + XeF_2 + (n\text{-}1)Xe$$

$$4R\text{-}NiF_3 + nXeF_2 \xrightarrow{295\text{ K}} 2Ni_2F_5 + XeF_4 + (n\text{-}1)XeF_2$$

The obtained products were even less crystalline as the product obtained by thermal decomposition. Their X-ray powder diffraction patterns were the same and they match the X-ray powder diffraction pattern of NiF_x ($2<x<3$) prepared by the reaction between *R*-NiF_3 and Xe without solvent.[10] Mass balances of the reactions with Xe and XeF_2 (see Experimental section, 2.) indicate that it is possible that *R*-NiF_3 oxidize XeF_2 further to XeF_6. In the presence of the base XeF_6 remaining *R*-NiF_3 disproportionates into Ni(II) and Ni(IV). The latter could form with XeF_6 salts of the type $XeF_5^+(Ni_xF_{4x+1})^-$ ($x = 1,2,3...$), which have no vapour pressure and can not be removed from the sample by pumping on the vacuum line. No further characterization of these by-products was done due to their low quantities in the products. According to chemical analysis the best Ni_2F_5 is obtained by thermal decomposition of pure *R*-NiF_3 (without co-product e.g. KBF_4).

2. Characterization of Ni_2F_5 by infrared spectroscopy

Structural features of *R*-NiF_3 were published few years ago.[11,12] Authors suggested that *R*-NiF_3 has a mixed valence composition Ni(II)Ni(IV)F_6. Neutron diffraction study at 2 K indicates the formulation of mixed valence composition but values obtained at 295 K allow that F-ligand may be slightly less unsymmetrically placed; indicative perhaps, of slightly more electron transfer from Ni(II) to Ni(IV).[12] On the basis of the structural data of *R*-NiF_3 we could presume that Ni_2F_5 can be written as $Ni(II)_3Ni(IV)F_{10}$, but so far we were not able to determine the structure of the compound.

Infrared spectra of NiF_2 and *R*-NiF_3 are shown together with Ni_2F_5 on Fig. 1. Ni atoms in NiF_2[13] and in NiF_3[10] have octahedral environment of fluorine atoms. The only difference between NiF_2 and NiF_3 is the positive charge 2+ and 3+ on nickel atom. Therefore weaker bond in the case of NiF_2 (423 cm^{-1}) and stronger bond in the case of NiF_3 (630 cm^{-1}) is expected. In the case of Ni_2F_5 the infrared spectrum has two bands: 623 cm^{-1} which could be assigned to Ni(III)-F bond and at 428 cm^{-1} which probably belongs to vibration of Ni(II)-F bond.

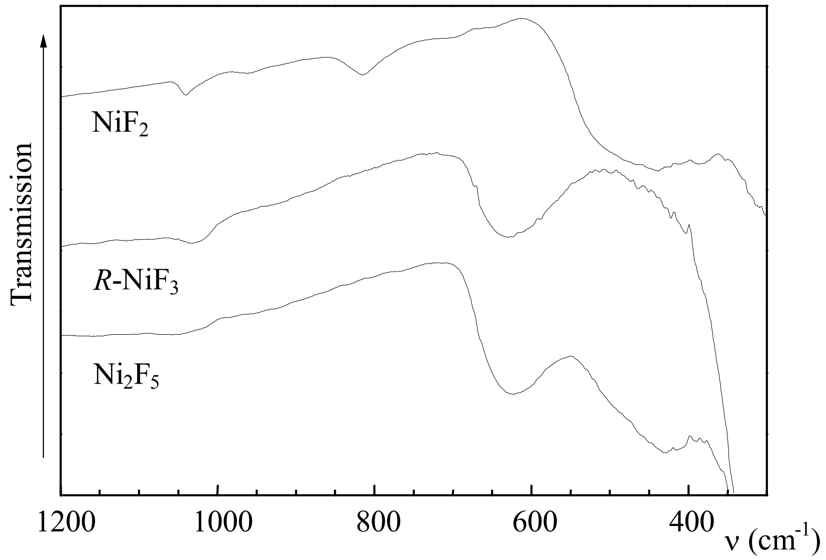

Figure 1: Infrared spectra of NiF_2, Ni_2F_5 and *R*-NiF_3

3. The reactions of Ni_2F_5

3.1. Oxidation of Ni_2F_5 by KrF_2

It is possible to oxidize Ni_2F_5 to *R*-NiF_3 by using strong oxidant e.g. KrF_2 in aHF. The reaction time at 273 K was four days. The reaction was performed at lower temperature 273 K to prevent the decomposition of *R*-NiF_3 in aHF.

$$2Ni_2F_5 + nKrF_2 \xrightarrow[aHF]{273\ K} 4R\text{-}NiF_3 + (1+z)Kr + zF_2 + (n-1-z)KrF_2$$

n is excess of KrF_2

z is the amount of KrF_2 which decomposes in aHF

Ag_3F_8 is an other example of mixed valence compound ($Ag(II)Ag(III)_2F_8$) and it cannot be oxidized to AgF_3 by KrF_2 in aHF at room temperature. Pure AgF_3 can be synthesized only by the method for the preparation of thermodynamically unstable binary fluorides.[9,14] From these results it could be concluded that Ni_2F_5 is less stable against oxidation than Ag_3F_8.

3.2. The reaction of Ni_2F_5 in acidic aHF

Ni_2F_5 is slowly decomposing already in aHF yielding NiF_2 and elemental fluorine. In acidified aHF e.g. when AsF_5 is present in the aHF, the decomposition is finished in 10 minutes transforming red-brown solid Ni_2F_5 into yellow solution $Ni(AsF_6)_2$ and elemental fluorine.

$$Ni_2F_5 + 4AsF_5 \xrightarrow[\text{aHF}]{\text{273 K}} 2Ni(AsF_6)_2 + 1/2F_2$$

The same reaction proceeds also with *R*-NiF_3. Fluoride ion affinity of AsF_5 is high enough (481 kJ/mol)[15] to remove F^- from Ni(III) in Ni_2F_5 generating NiF_2^+ cation which is highly electronegative and electron capture and release of elemental fluorine is expected. Cationic species in acidic aHF (e.g. AgF_2^+, NiF_3^+, NiF_2^+) are the strongest oxidizers known today.[16]

3.3. The reactions of Ni_2F_5 in basic aHF

Ni_2F_5 slowly reacts with excess of Lewis base (e.g. KF) in aHF at 273 K according to the following reaction:

$$2Ni_2F_5 + 2KF \xrightarrow[\text{aHF}]{\text{273 K}} 3NiF_2 + K_2NiF_6$$

The decomposition of Ni_2F_5 in aHF at the reaction temperature (273 K) is practically negligible and only disproportionation is taking place. NiF_2 and K_2NiF_6 were characterized by X-ray powder diffraction patterns of the solids when aHF was pumped away. K_2NiF_6 was shown also by red colour of the aHF solution and Raman spectrum showing its characteristic bands at 560 cm^{-1}, 518 cm^{-1} and 308 cm^{-1}. The reaction between *R*-NiF_3 and good fluoride ion donor (e.g. KF, XeF_6) at room temperature was very quick but there besides of disproportionation also some decomposition of *R*-NiF_3 in aHF was taking place.[10]

4. Oxidizing properties of Ni_2F_5

Reaction of Ni_2F_5 with excess of Xe in aHF at room temperature shows that the fluorinating and oxidizing abilities of the compound are still high. The mass balance of the reaction is in accordance with the following equation:

$$2Ni_2F_5 + nXe \xrightarrow[\text{aHF}]{\text{295 K}} 4NiF_2 + XeF_2 + (n\text{-}1)Xe$$

Ni_2F_5 is the least potent oxidizer among all higher binary fluorides of nickel. This is understandable because the amount of Ni(III) is the smallest among all higher Ni fluorides. Ni_2F_5 is still enough strong oxidizer to fluorinate some organic compounds. The reaction between C_3F_6 vapour and excess of solid Ni_2F_5 is very rapid and exothermic although there is no carbon-carbon bond cleavage. Infrared spectrum of the obtained gaseous product is showing perfluoropropane without even traces of CF_4.

$$C_3F_6 + 2Ni_2F_5 \xrightarrow{\text{295 K}} C_3F_8 + 4NiF_2$$

According to Sartori and his coworkers[17,18] Simon´s process proceeds in two stages. Fluorination of organic molecules takes place by chemical reaction between organic molecules and higher nickel fluorides formed on the anode. Higher nickel fluorides on the anode are formed by electrochemical process. Bartlett and his coworkers[19] suggest that nickel fluoride formed on the anode is not *R*-NiF_3 but less potent form of nickel fluoride. They explain this statement by the fact that MeCOF is efficiently perfluorinated in the Simon´s process while the reaction between MeCOF and *R*-NiF_3 is giving very little CF_3COF but mostly decomposition products CF_4 and COF_2.

Ni_2F_5 is the most stable higher nickel fluoride therefore we believe that nickel fluoride formed on the Ni anode during electrochemical fluorination in the Simon´s process is Ni_2F_5.

Conclusions

Higher binary fluorides of nickel, including Ni_2F_5, have been studied previously.[10] In this paper we report about different synthetic routes for the preparation of Ni_2F_5. On the basis of the obtained results it could be concluded that the best synthetic approach for the preparation of Ni_2F_5 is thermal decomposition of *R*-NiF_3 at higher temperature (373 K). According to infrared spectra two nickel species are present in the compound: Ni(II) and Ni(III). Further it was shown that the oxidizing and fluorinating abilities of Ni_2F_5 are still high and that it is able to oxidize xenon in aHF to XeF_2. The most important feature is that by our opinion it is involved in electrochemical fluorination in the Simon's process. In comparison with *R*-NiF_3 the advantages of Ni_2F_5 are its thermal stability and its fluorinating ability.

Experimental

1. Apparatus, technique and reagents

Apparatus - A nickel vacuum line and Teflon vacuum system were used as previously described.[20] Non-volatile materials, which were very sensitive to traces of moisture, were handled in the dry argon atmosphere of a glove box with maximum content of 0.1 ppm of water vapour (Mbraun, Garching, Germany). The reactions with aHF were carried out in reaction vessels constructed from PFA (Polytetra, Germany) tubes (16 mm i.d. x 19 mm o.d.) equipped with Teflon valves or in reaction vessels constructed from two PFA tubes (16 mm i.d. x 19 mm o.d.) each drawn down to 8 mm i.d. ×10 mm o.d., joined at right angles by a Teflon Swagelok T compression fitting and joined to a Teflon valve.[10] Metal reaction vessels with inner Teflon coating (volume 5-6 ml) were used for thermal decomposition of *R*-NiF_3 at temperatures around 373 K. Vessels were constructed at the Institute Jožef Stefan and equipped with modified valve. All reaction vessels were prior use pretreated with elemental fluorine.

Technique- X ray diffraction powder patterns (XRPP) were obtained by using the Debye-Scherrer camera (143.2 mm diameter), Ni filtered CuKα radiation. Powdered samples were filed in 0.3 mm quartz capillaries. Infrared spectra were taken on a FTIR spectrometer (Perkin Elmer 1710) on samples powdered between AgCl windows in a leak tight brass-cell. A 10 cm nickel cell with AgCl windows was used for volatile samples. Raman spectra of powder samples in sealed quartz capillaries were taken on a Renishaw Ramanscope dispersive instrument (System 1000) with the exiting line at 632.8 nm of a He-Ne laser.

Reagents - Fluorine (Solvay, 99.9%), BF_3 (Ucar), perfluoropropene (Aldrich Chemical Company, 99%), xenon (L'Air Liquide, 99.95%) were used as supplied. Anhydrous HF (Praxair, 99.9%) was purified by treatment with K_2NiF_6 for at least 24 hours. K_2NiF_6 (Ozark-Mahoning Pennwalt, 99.5%), which was used for the syntheses of *R*-NiF3, was heated in F_2 ($1.5 \cdot 10^6$ Pa) at 573 K for at least 24 hours. To extract KF impurity and to remove in aHF insoluble impurity a method described elsewhere was used.[10] XeF_2 was prepared in the photochemical reaction between Xe and F_2 at room temperature.[21] KrF_2 was prepared by irradiation of liquefied mixture of F_2 and Kr with near UV light at 77 K.[22] AsF_5 was synthesised by the reaction of As_2O_3 with elemental fluorine under high pressure at 573 K.[23] KF (Merck, anhydrous, p.a.) was heated at 573 K and at the same time pumped in a dynamic vacuum.

2. Syntheses of Ni_2F_5:

Rombohedral NiF_3 (R-NiF_3) was a starting material for the preparation of Ni_2F_5. It was synthesised by the reaction between K_2NiF_6 and BF_3 in aHF as described previously.[10]

Thermal decomposition of R-NiF_3: (5.53 mmol) *R*-NiF_3 was heated at 395 K and thermal decomposition was completed in several days. During decomposition elemental fluorine was pumped away several times. Ni_2F_5 (2.73 mmol) was characterized by XRPP (Table 1) and chemical analysis: calculated for Ni_2F_5: F: 55.28%; Ni: 44.72%; found: F: 53.7%, Ni: 42.9%, K: 1.5% and B: 1.0%. Infrared spectra of Ni_2F_5, *R*-NiF_3 and NiF_2 were recorded (Fig. 1)

Reaction of R-NiF$_3$ with Xe: solid, dry *R*-NiF$_3$ (3.51 mmol) was put into PFA reaction vessel, excess of gaseous Xe (2.79 mmol) at 293 K was added tensiometricaly. The change in colour from black *R*-NiF$_3$ to red-brown Ni$_2$F$_5$ was noticeable in approximately 24 hours. The excess of Xe was pumped away at 193 K. XeF$_2$, which was formed (0.45 mmol, calc.: 0.88 mmol), was pumped away at room temperature through the infrared cell for volatile samples and checked by IR spectroscopy. Ni$_2$F$_5$ (2.15 mmol, calc.: 1.755 mmol) was determined by XRPP (Table 1).

Reaction of R-NiF$_3$ with XeF$_2$: *R*-NiF$_3$ (2.31 mmol) and excess of solid XeF$_2$ (3.56 mmol) were put into PFA reaction vessel in a glove box. Reaction at 293 K was finished in several days. Formed XeF$_4$ and the unreacted XeF$_2$ were pumped out at room temperature and checked by recording their infrared spectra. Red-brown Ni$_2$F$_5$ (1.40 mmol, calc.: 1.155 mmol) was determined by XRPP (Table 1). Results of chemical analyses were: F: 40.6%, Ni: 42.9%, together: 83.5%.

Table 1: X-ray Powder Diffraction Data for Ni$_2$F$_5$

d (pm) [a]	I/I$_0$	d (pm) [b]	I/I$_0$	d (pm) [c]	I/I$_0$
355	w				
261	w	249	w	248	w
245	s				
214	vs	217	s	216	s
164	vs	166	s	166	s
141	s	143	vw	143	vw

a.) Ni$_2$F$_5$ synthesised with thermal decomposition of *R*-NiF$_3$

b.) Ni$_2$F$_5$ synthesised with reaction of *R*-NiF$_3$ with Xe

c.) Ni$_2$F$_5$ synthesised with reaction of *R*-NiF$_3$ with XeF$_2$

Intensities of the lines were estimated visually (vs-very strong, s-strong, w-weak, vw-very weak).

3. The reactions of Ni_2F_5:

Oxidation of Ni_2F_5 with KrF_2: Ni_2F_5 (1.13 mmol) reacted with large excess of KrF_2 (approximately 8 mmol) in aHF at 273 K in PFA reaction vessel. Reaction was finished after four days. Fluorine, which is the product of thermal decomposition of KrF_2 had to be pumped away during the reaction several times at 77 K. Kr, product of the reaction and from thermal decomposition of KrF_2, was also pumped away at 213 K. Black R-NiF_3 (2.16 mmol) was characterised by XRPP.

Reaction of Ni_2F_5 with AsF_5 in aHF: AsF_5 (4.7 mmol) was added to the suspension of Ni_2F_5 (0.87 mmol) in aHF. Product of the reaction at 273 K was yellow solution, from which $Ni(AsF_6)_2$ (1.64 mmol, calc.: 1.74 mmol) was isolated (determined by XRPP). The reaction was very quick even at 273K (10 minutes).

Reaction of Ni_2F_5 with KF in aHF: Ni_2F_5 (1.16 mmol) was weight in one arm of PFA vessel and KF (1.88 mmol) into another one. Anhydrous HF was condensed in the arm with Ni_2F_5 and thermostated for several hours at 273 K. The solution above solid Ni_2F_5 was completely colourless. Than KF dissolved in aHF which was decanted from the arm with Ni_2F_5 was added to the Ni_2F_5. Reaction between soluble KF and insoluble Ni_2F_5 was running for three days at 273 K. We noticed presence of K_2NiF_6 by red colour of the solution. Soluble KHF_2 and K_2NiF_6 (mass of the soluble products was 0.199 g, calc.: 0.202 g) were separated from NiF_2 (2.20 mmol, calc.: 1.74 mmol) by decantation of aHF solution. Washing procedure was repeated several times before aHF was pumped away and products of he reaction were checked by XRPP. K_2NiF_6 was also determined by Raman spectroscopy.

Oxidation of Xe in aHF: excess of gaseous Xe (approximately 1.2 mmol) was added in the suspension of Ni_2F_5 (0.75 mmol) in aHF at room temperature. After 17 hours of the reaction all Ni_2F_5 was reduced to NiF_2 (1.61 mmol, calc.: 1.50 mmol) and Xe was oxidized to XeF_2 (0.35 mmol, calc.: 0.375 mmol). Unreacted Xe and aHF were pumped out at 238 K and XeF_2 was pumped out at 293 K and checked by infrared spectroscopy.

Ni_2F_5 like fluorinating agent: excess of solid and dry Ni_2F_5 (0.78 mmol) was exposed to perfluoropropen vapor ($1.2.10^4$ Pa). Rapid reaction at room temperature was

exothermic and yellow solid NiF_2 and gaseous C_3F_8, as was shown by infrared spectroscopy, were the only products.

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Povzetek

Ni_2F_5 lahko pripravimo s termičnim razkrojem *R*-NiF_3 pri 373 K in z redukcijo R-NiF_3 s Xe oziroma XeF_2. Termični razkroj je najprimernejša metoda sinteze. Produkta reakcje v kislem HF (AsF_5) sta $Ni(AsF_6)_2$ in F_2. Pri reakciji v bazičnem HF (KF) pa Ni(III) v Ni_2F_5 disproporcionira in dobimo NiF_2 in K_2NiF_6. Ni_2F_5 je še vedno dovolj močan oksidant in

fluorirno sredstvo da lahko oksidira ksenon do XeF_2 in fluorira C_3F_6 do C_3F_8. Zaradi tega je njegova vloga pomembna v procesu elektrokemijskega fluoriranja.