

The room temperature conversion of nickel difluoride to hexafluoronickelate(IV) salts of alkali cations

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Abstract

NiF_2 was oxidized at $\sim 20^\circ\text{C}$, to NiF_6^{2-} by sunlight- or ultraviolet light-irradiated F_2 in liquid anhydrous hydrogen fluoride (aHF) containing alkali hydrofluorides $\{\text{AF}(\text{HF})_x\}$. Quantitative formation of NiF_6^{2-} can be achieved with strongly basic solutions (e.g., $\text{KF}:\text{HF}$ molar ratio $\sim 1:4$). Li_2NiF_6 , which was previously unknown, is the least aHF soluble of the alkali NiF_6^{2-} salts, and was prepared in high purity. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

An important industrial process for the conversion of organic precursors to fully fluorinated derivatives (perfluorocarbon compounds) is the Simons Process. The Simons Process [1–9] uses an electrochemical cell to oxidize perhydro-organic materials, at a nickel anode, to their perfluoro-relatives. The electrolyte for that process is liquid anhydrous hydrogen fluoride in which sodium fluoride, or other ionizing solutes, are dissolved (the latter, to provide for electrical conductance).

Recently, Bartlett et al. [10] showed that the Simons Process Chemistry could be conveniently simulated at room temperature, and often in high efficiency, using nickel trifluoride (NiF_3), nickel tetrafluoride (NiF_4), or hexafluoronickelate(IV) salts. The thermodynamically unstable fluorides, NiF_3 and NiF_4 , were first established by Žemva et al. [11], the precursor from which both are derived being the commercially available salt potassium hexafluoronickelate(IV), K_2NiF_6 , prepared by an adaptation of the original synthesis of Klemm and Huss [12].

When NiF_3 or NiF_4 (the latter prepared from K_2NiF_6 in situ) are used to fluorinate organic compounds, the solvent (as in the Simons Process) is aHF; this serves to carry even slightly soluble organic precursors [10] to the insoluble NiF_3 or NiF_4 surface, where the organic compounds are efficiently fluorinated at room temperature or below. In these fluorina-

tion reactions, NiF_3 and NiF_4 are reduced to NiF_2 . This is also the reduction product of NiF_6^{2-} salts. The use of these high oxidation-state nickel compounds as fluorination reagents on a large scale would require a simple method for reconvertng NiF_2 to the higher nickel fluorides. In any case, a convenient solution synthesis of NiF_6^{2-} salts is desirable. This paper reports on facile room temperature conversions of NiF_2 to NiF_6^{2-} salts. Included is the new salt, Li_2NiF_6 , prepared in high purity.

2. Experimental details

2.1. Materials

Cylinders of aHF and F_2 were obtained and used as previously described [11]. NiF_2 (Ozark-Mahoning Pennwalt, Tulsa, OK 74107) was fluorinated (F_2 pressure ~ 2000 Torr) at $\sim 250^\circ\text{C}$, to destroy water impurity. The alkali fluorides, dried at 150°C under vacuum, were supplied by Allied Chemical, (B and A quality) Morristown, NJ.

2.2. Apparatus and technique

A metal vacuum, line as previously described [13], provided for the distribution of gaseous reactants, but all of the preparations were carried out in all Teflon/FEP apparatus, isolated from the metal system by a Teflon valve [13] (with Kel-F stem and Teflon tip) closed, except in the transfer of

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Table 1

Conversion of NiF_2 to A_3NiF_6 ($\sim 20^\circ\text{C}$), in liquid anhydrous hydrogen fluoride, with alkali hydrofluoride ($\text{A} = \text{Li, Na, K, Cs}$) and fluorine (at ~ 1 atm partial pressure) in ultraviolet light or sunlight (quantities of reagents in millimoles)

NiF_2	AF	HF	Irradiation time (hr)	NiF_2 to A_3NiF_6 conversion (%) ^a
<i>U.V.</i>				
1.76	LiF, 5.3	25	34	Li_3NiF_6 : 48
0.935	LiF, 2.37	118	46	Li_3NiF_6 : 56
1.102	NaF, 2.80	118	73	Na_3NiF_6 : 71
1.4	KF, 28.7	98.6	78	K_3NiF_6 : 100
1.28	NaF, 3.28	36.6 ^b	83	Na_3NiF_6 : 69
1.12	CsF, 3.01	36.6 ^b	83	Cs_3NiF_6 : 60
<i>Sunlight</i>				
2.7	LiF, 14.5	115	37	Li_3NiF_6 : 31
0.809	LiF, 2.65	70	36	Li_3NiF_6 : 17
0.143	CsF, 2.32	80	20	Cs_3NiF_6 : 43

^aUnreacted NiF_2 (insoluble in aHF) and aHF-soluble components (alkali hydrofluoride and alkali salts of NiF_6^{2-}) were separated by decantation and washing, followed by removal of the aHF in vacuum. Percent conversion was based on the weight of NiF_2 consumed.

^bIrradiation of the $\text{NiF}_2/\text{AF}/\text{aHF}$ mixture necessarily results in a decrease in the fluoro-basicity of the solution as $\text{F}(\text{HF})_2^-$ is converted to $\text{NiF}_6^{2-} + 2\text{x HF}$. In these two experiments, a solid hydrofluoride in equilibrium with its saturated aHF solution, placed in the non-irradiated side arm, took up aHF from the irradiated mixture as the quantity of $\text{F}(\text{HF})_2^-$ in that mixture decreased.

the gases. (Severe corrosion of the metal vacuum system occurs if aHF, F_2 , and fluoroacids are simultaneously present in it.) A typical reactor was constructed in T shape (T reactor) from FEP tubing, Teflon Swagelok T, and Teflon valve as previously described [14]. One arm of the T reactor was charged with NiF_2 and alkali fluoride in a DRH AB (Vacuum Atmospheres); aHF and F_2 were introduced from the vacuum line, and that arm was arranged to be nearly horizontal, in order to maximize the F_2 /liquid aHF interface. This nearly horizontal tube was either placed in strong sunlight, with a curved metal reflector behind it, or adjacent to the water-cooled jacket of a 450-W immersion type Hanovia U.V. lamp (Ace Glass) and at the approximate line of focus of a cylindrical metal reflector, surrounding and parallel to the lamp. As the mixture was irradiated, it was mixed by sideways flicking of the tube, by a properly placed rotating arm. Fluorine was replenished (at ~ 1000 Torr partial pressure) as it was consumed. To fully separate the NiF_6^{2-} salt from residual unoxidized NiF_2 after irradiation, the purple-red supernatant solutions in aHF were decanted to the other limb of the T reactor, and the aHF back-distilled to the reaction limb to extract soluble species. Washing of aHF insoluble NiF_2 was repeated as often as necessary to affect the separation.

Interaction of NiF_2 with most of the alkali fluorides, AF ($\text{A} = \text{Li, Na, K, Cs}$) under a variety of aHF concentrations gave the findings listed in Table 1. The conversion to NiF_6^{2-} was found to be most effective (row 4) with a saturated solution of potassium hydrofluoride [i.e., $\text{KF}(\text{HF})_2$] in aHF and a large excess of alkali over NiF_2 . More concentrated alkali fluoride solutions always provided for quicker, more efficient fluorination.

X-ray diffraction powder photographs (XRDP) were routinely obtained with $\text{CuK}\alpha$ (Ni filtered) radiation on each solid, packed as a powder in thin-walled quartz capillaries [11].

2.3. High purity Li_2NiF_6

There is no previous report of Li_2NiF_6 . The highest oxidation-state lithium hexafluoronickelate is $\text{Li}_3\text{Ni}(\text{III})\text{F}_6$, made by Grannec et al. [15] at 500°C and 70-atm F_2 pressure.

The relatively low solubility of Li_2NiF_6 in aHF at 0°C (solubility: 0.50 g/100 g aHF) allowed for its isolation from excess lithium hydrofluoride in the NiF_2/F_2 (U.V.)/LiF/aHF synthesis (see Table 1, row 1); the volume of liquid aHF was reduced by applying a vacuum until the bulk of the Li_2NiF_6 had crystallized. The lithium hydrofluoride-saturated aHF was decanted to the other limb of the T reactor (that containing the unreacted NiF_2 residue). The aHF was back-distilled onto the Li_2NiF_6 for four additional times of washing and decantation. The Li_2NiF_6 , a dark purple-red solid, was dried in vacuum at $\sim 20^\circ\text{C}$. The XRDP showed no LiF, nor LiHF_2 impurity, and the pattern was fully indexed as given in Table 2.

3. Results and discussion

The light-promoted reaction of the aHF-insoluble NiF_2 with F_2 to give NiF_6^{2-} is remarkably efficient in strongly fluorobasic aHF solution. Photodissociation of F_2 to F^\cdot atoms must be the consequence of absorption of the relatively high-energy photons. The absorption maximum of F_2 is close to 3000 Å, with a broad tail into the visible. As is well known [16], this absorption has no band structure, signifying that it is associated with electron promotion from the bonding levels to the σ^* orbital, and hence, dissociation to atoms [17]. The F-atom effective lifetime could be augmented by the formation of species such as $\text{F}_2^{\cdot-}$, or its hydrogen bonded solvates, $(\text{F}_2\text{HF})^\cdot$ or $(\text{F}_2\cdot 2\text{HF})^\cdot$, in the strongly basic aHF. The high effectiveness of strongly basic aHF solutions in generating

Table 2

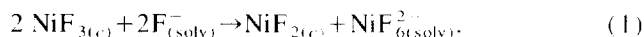
X-ray powder diffraction data (CuK α radiation, Ni filter) for Li₂NiF₆ (hexagonal unit cell: $a_0 = 8.321(4)$, $c_0 = 4.598(2)$ Å; $V = 275.7(1)$ Å³, $z = 3$)

$1/d_{hkl}^2 \times 10^4$						$1/d_{hkl}^2 \times 10^4$					
h, k, l obs.	Obs.	Calc.	h	k	l	h, k, l obs.	Obs.	Calc.	h	k	l
v-w	480	473	0	0	1	m	5970	5987	3	0	3
v-s	578	578	1	1	0	vw	7401	7406	6	0	-
ms*	664	666	1	0	1	w	7500	7511	5	2	0
w	1053	1051	1	1	1	vw	7547	7563	0	0	4
n*	1245	1245	2	0	1	vw	8148	8141	1	1	4
w*	1811	1824	2	1	1	mw	8820	8824	6	0	2
w	1892	1891	0	0	2	vw	9236	9244	4	4	0
v-s	2205	2206	3	0	1	vw	9878	9874	2	2	4
v-v	2309	2311	2	2	0	vw	11183	11187	6	0	3
w	2473	2469	1	1	2	vw	11611	11607	4	1	4
v-	3632	3624	3	0	2	vw	12612	12606	6	3	1
n	4045	4044	4	1	0	w	12765	12763	3	3	4
v-s	4206	4202	2	2	2	w	12859	12868	7	1	2
w	4519	4517	4	1	1	m	14025	14024	6	3	2
s	5204	5200	3	3	0	w	1080	15074	5	2	4
v-w*	5608	5605	2	1	3	vw	15599	15599	9	0	0
ms	5937	5935	4	1	2	vw	16322	16334	5	5	2

*With the omission of these broad lines, the data can be indexed on the hexagonal formula-unit cell ($z = 1$) with $a_0 = 4.804(2)$, $c_0 = 4.598(2)$ Å.

NiF₆²⁻ could be a consequence of that augmentation (compare the results of row 7 with those of row 8, Table 1, and note the 100% yield for row 4). The charged species, F_{2(g)}^{•-}, or its HF solvates, because of like charge repulsion, are less likely than the neutral F[•] to quickly regenerate F₂. Since the electron affinity of F_(g)[•] is 3.399 eV [18] and that of F_{2(g)}^{•-} is 3.10 eV [19], the F_{2(g)}^{•-} species must be less bound than F_(g)[•] by 0.299 eV; therefore, this, or its HF solvates, may be a more effective fluorine atom source than F₂ itself. In addition, and in contrast to F[•] and F₂, such F₂^{•-} species would also be nucleophilic.

In the syntheses carried out in sunlight, it was observed that the particles of the aHF-insoluble pale yellow-green NiF₂ became black, *before* any coloring of the aHF solution occurred. This suggests that the NiF₂ is first fluorinated to NiF_{2+ δ} (with $\delta \leq 1$) [11], followed, as δ approaches 1, by reaction with solvated F⁻ to generate NiF₆²⁻ by disproportionation, as previously described [11], e.g.:



Electron transfer within the Ni(III)F₃, yielding Ni(II)Ni(IV)F₆, probably provides the basis for this conversion. It should, however, be noted that even with $\delta < 1$, disproportionation in basic aHF to generate NiF₆²⁻ could occur. The high effectiveness of aHF saturated with potassium hydrofluoride could be due to that solution promoting disproportionation at low δ values.

X-ray diffraction photography (XRDP) of the K₂NiF₆ and Cs₂NiF₆ products in these syntheses showed that they were identical to the products of the thermal methods, each having the cubic antiperovskite structure previously reported [12,20]. The Na₂NiF₆ made in the present work was always contaminated with sodium bifluoride, and an XRDP confirmed that

mixture, the pattern of Na₂NiF₆ being that given by Fleischer and Hoppe [21]. No attempt was made to separate this mixture. On the other hand, the separation of Li₂NiF₆ from its accompanying LiHF₂ was easily achieved by washing out the lithium hydrofluoride (solubility: 18 g LiF/100 g aHF at 0°C) from the slightly soluble Li₂NiF₆ (solubility: 0.50 g/100 g aHF at 0°C). XRDP of the latter (see Table 2) showed it to have a primitive hexagonal unit cell indicative of the Na₂SiF₆-type structure [22,23]. The formula unit volume of Li₂NiF₆ (91.9 Å³) is the smallest for any known A₂MF₆ structure except Li₂SiF₆ (88.9 Å³). This is consistent with the low-spin d^6 configuration of Ni(IV) and the high effective nuclear charge of Ni(IV) in that configuration [11].

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