

Metastable fluorides and potent oxidizers

Their preparation in liquid anhydrous HF, at room and lower temperatures

Boris Žemva and Neil Bartlett*

Résumé Préparation à basses températures et en milieu HF anhydre de fluorures métastables, oxydants très puissants

La faible électronégativité d'un degré d'oxydation dans un anion permet l'obtention de cations à hauts degrés d'oxydation, tels que Ni^{IV} , Au^{V} , Ag^{III} . Ces degrés d'oxydation sont facilement atteints en milieu fluorure d'hydrogène anhydre et liquide (aHF) et sont en outre favorisés lorsque du fluor élémentaire est produit *in situ* par photodissociation. Des tubes et récipients réalisés en polymères perfluorés transparents permettent de mener à bien de telles synthèses. Des fluorures binaires faiblement solubles dans aHF peuvent ainsi être obtenus à partir de leurs anions à degré d'oxydation élevé, à l'aide de forts accepteurs d'ions F^- . NiF_4 , NiF_3 et AgF_3 , qui peuvent être préparés de cette manière, sont thermodynamiquement instables par rapport à la perte de fluor. L'électronégativité du degré d'oxydation dans le fluorure binaire est plus élevée que dans l'anion, d'où son état métastable. Lorsqu'un fort accepteur d'ions F^- transforme ce fluorure binaire en une espèce cationique, l'électronégativité est renforcée. Ainsi, les cations Ag^{III} et Ni^{IV} sont-ils des oxydants monoélectroniques supérieurs à KrF^+ . Ils sont capables d'arracher un électron aux anions hexafluorés MF_6^- de tous les métaux de la série du platine. Toute cette chimie est réalisée à température ambiante.

Mots-clés Hauts degrés d'oxydation, fluorure d'hydrogène anhydre, oxydants, électronégativité, métaux de la série du platine.

Abstract The low electronegativity of an oxidation state in an anion enables high oxidation states, e.g. Ni^{IV} , Au^{V} , and Ag^{III} , to be easily attained in liquid anhydrous HF (aHF), made basic with fluoride-ion donors. The oxidation state can be enhanced if elemental fluorine is photo-dissociated. Teflon valves and lines, especially transparent and kinetically stable fluorocarbon containers for the aHF solutions, provide for this. Binary fluorides, that are of low solubility in aHF, can be displaced by stronger F^- acceptors from their high oxidation-state anions. NiF_4 , NiF_3 , and AgF_3 , which can be made in this manner, are thermodynamically unstable with respect to loss of fluorine. The electronegativity of the oxidation state in the binary fluoride is higher than in the anion (hence the metastability) and when a strong F^- acceptor converts the binary fluoride into a cationic species, the electronegativity is further enhanced. Thus cationic Ag^{III} and Ni^{IV} are superior to KrF^+ , as one-electron oxidizers. They are able to remove the electron from all platinum-metal hexafluoro-anions, MF_6^- , to liberate the hexafluorides. All of this chemistry can be achieved at or below room temperature.

Keywords High oxidation states, liquid anhydrous HF, oxidizers, electronegativity, platinum-metals.

As in other aspects of fluorine chemistry, Henri Moissan was a pioneer of the fluorides of the less reactive elements, including the noble metals [1]. The extent of the chemistry of these elements, however, greatly increased in the late forties with the work of Professor Emeléus and his coworkers at Cambridge, with their exploitation of bromine trifluoride as both solvent and fluorinating agent [2]. In particular, A.G. Sharpe's work established several new fluorides of the coinage metals and relatively easy routes to them [3].

More recently, the availability of transparent polyfluorocarbon plastic tubing, and its remarkable kinetic inertness to elemental fluorine and other oxidizers, has provided the means for further extending the range of fluorides, including some that are thermodynamically unstable with respect to loss of fluorine [4]. In addition, with the use of anhydrous hydrogen fluoride (aHF) as solvent, in the fluoropolymer

containers, it has proved possible to prepare the most potent oxidizers yet known to us. This has been achieved with less than one atmosphere of pressure of fluorine, at room temperature or below [5-6].

In the P.L. Robinson research group at Newcastle, M.A. Hepworth was a mentor to N. Bartlett. They made the first samples of PdF_2 free of elemental palladium. This initiated Bartlett's interest in noble-metal chemistry: PdF_2 was shown to be the first high-spin Pd^{II} compound [7]. This is in harmony with its rutile structure [8]. It is of historical interest that a subsequent fruitless search for PtF_2 [9] led to the discovery of O_2PtF_6 [10]. That, in turn, led to XePtF_6 [11]. Sharpe had previously shown that when PdBr_2 was dissolved in BrF_3 , an adduct $\text{BrF}_3 \cdot \text{PdF}_3$ was obtained, pyrolysis of which gave black paramagnetic PdF_3 [3] (later shown to be $\text{Pd}^{\text{II}}\text{Pd}^{\text{IV}}\text{F}_6$ [12]). Yet he also observed that when PdBr_2 was

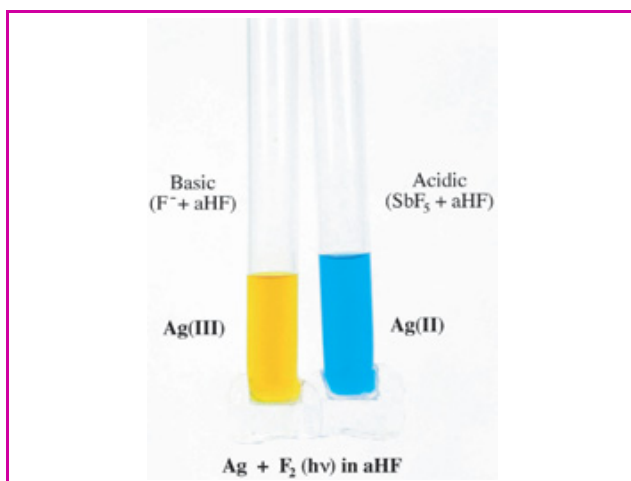


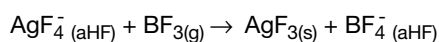
Figure 1 - Photo-fluorination of silver gives: 1) in basic aHF, orange $\text{AgF}_4^-_{(\text{aHF})}$ (left), and 2) in acidic aHF, blue $\text{Ag}^{2+}_{(\text{aHF})}$ (right).

dissolved in BrF_3 made basic with good F^- donors, yellow diamagnetic Pd^{IV} salts were formed [3]. This impact of bases on the making of Pd^{IV} was reinforced by the finding of W.J. Quail, that even selenium tetrafluoride (the reducing agent used to make PdF_2 , and a relatively weak base) was basic enough to make $[\text{PdF}_6]^{2-}$ salts [13]. Eventually it was realized that the reason for this ease of formation of $[\text{PdF}_6]^{2-}$ salts lay in the lower electronegativity of an oxidation state when in an anion. The difficulty that P.R. Rao had in making PdF_4 , and the ease of its reduction [14], contrasted with the ready synthesis of $[\text{PdF}_6]^{2-}$ salts. This was consistent with the electronegativity of Pd^{IV} being higher in the binary fluoride than in the anion. Of course this implied that a cationic oxidation state should have the highest electronegativity. Such interpretations had important consequences in our later work.

Exploiting anhydrous HF (aHF) as a solvent

Our interest in the nature of “silver trifluoride” as first reported [15], coincided with the centennial celebration of the discovery of elemental fluorine by Moissan, and disclosure of the first chemical route to elemental fluorine, as demonstrated by K.O. Christe at that meeting [16]. It was immediately evident to us that polymeric acid fluorides ought to be precipitated from solution in aHF, by good F^- acceptors. AgF_3 was expected to be isostructural with AuF_3 [17], and therefore polymeric. The long, low-temperature liquid range, and high dielectric constant of aHF [18], made it especially attractive as a solvent, for the preparation of what were likely to be thermodynamically unstable binary fluorides.

The preparation of genuine AgF_3 was soon achieved in Ljubljana. In that work we took advantage of the local expertise in making and handling the potent oxidizers KrF_2 [19] and XeF_6 . With the latter acting as base, and the former as the oxidizer, room temperature preparation of aHF-soluble $\text{XeF}_5^+\text{AgF}_4^-$ [20] from AgF_2 was made in high purity. Addition of BF_3 precipitated the bright red solid AgF_3 [21]:



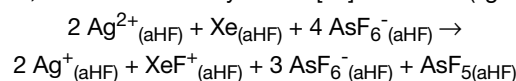
It was easily washed free of $\text{XeF}_5^+\text{BF}_4^-$, which is highly soluble in aHF. The synthesis of NiF_4 and the three forms of NiF_3 quickly followed [22]. These, and AgF_3 , are all thermo-

dynamically unstable with respect to loss of elemental fluorine. But the reagents KrF_2 and XeF_6 are costly and dangerous except in experienced hands, so efforts were soon made to find simpler and easier routes to such high oxidation state species.

It was quickly realized that the fluorocarbon containers withstood photochemical activation of F_2 (sunlight sufficed) and that, in combination with strongly basic aHF, made high oxidation-state anionic species such as AgF_4^- , and NiF_6^{2-} accessible, at room temperature or below [5-6]. With this approach, it was even possible to make salts such as Li_2NiF_6 [6] for which the original high temperature, high fluorine pressure approach, of W. Klemm and E. Huss [23] did not work.

A practical problem in the synthesis of the thermodynamically unstable binary fluorides from their alkali (A) salts is the generally low solubility of byproduct salts, such as AEF_4 and AEF_6 , in aHF, with E = B, As, Ge. Usually A_2EF_6 salts have higher aHF solubility. By using GeF_4 as F^- acceptor, the thermodynamically unstable binary fluorides such as AgF_3 and the nickel fluorides, prepared from their potassium salts, could be easily freed from contaminants [5] at low temperatures.

Because of the higher electronegativity of an oxidation state in a cation it was soon realized that by using acidified aHF, it should be possible to generate lower oxidation states. This is nicely indicated (figure 1) where photo-fluorination of silver in basic aHF generates AgF_4^- salts, whereas in acidic aHF the oxidation limit is Ag^{II} . Similarly, it proved possible to make [24] true paramagnetic Au^{II} salts by maintaining strongly acidic conditions during the fluorination of metallic gold in aHF. Oxidation of silver was also limited in acid (to Ag^{II}) but in accord with its high electronegativity, this Ag^{II} was shown to be a potent oxidizer, as its reduction by xenon [25] illustrates (figure 2):



This is consistent with the second ionization potential of silver (21.5 eV), which is the highest of any metal (other than alkali metals). O_2 (which has a similar first ionization potential to Xe (~ 12 eV) [26] is less polarizable, and therefore less soluble in aHF than Xe. For similar reduction of $\text{Ag}^{2+}_{(\text{aHF})}$ by O_2 , it is necessary to cool the solution to ~ 210 K [27].

The potent oxidizing properties of $\text{Ag}^{2+}_{(\text{aHF})}$ stimulated interest in achieving cationic Ag^{III} , which, it was believed, could be an oxidizer of unsurpassed power. It had already been noticed that the dissolution of AgF_3 in acidified aHF, to give Ag^{II} salts [21, 27], occurred with slow evolution of F_2 , this hinted that cationic Ag^{III} might be living long enough to be an efficient oxidizer. G.M. Lucier quickly showed [27] that acidified AgF_3 in aHF was able to efficiently liberate PtF_6

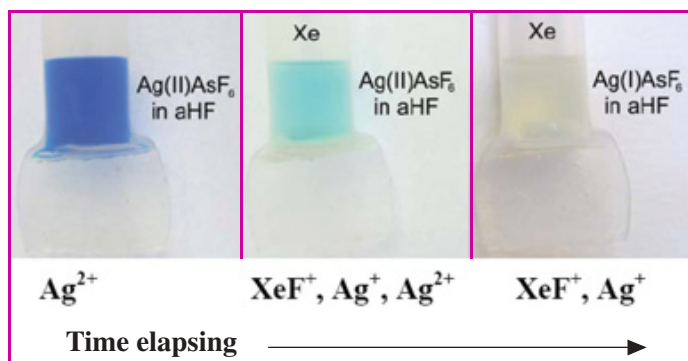


Figure 2 - Reduction of blue $\text{Ag}^{2+}_{(\text{aHF})}$ to colorless $\text{Ag}^+_{(\text{aHF})}$ by xenon at ~ 20 °C.

(~ 72%) and RuF_6 (~ 50%) from their MF_6^- salts. It was even possible to achieve low yields (~ 18%) of RhF_6 , which is otherwise extremely difficult to make [28]. The generation of the red gas PtF_6 by room temperature oxidation with cationic Ag^{III} (possibly $\text{AgF}_2^+(\text{aHF})$) is shown (figure 3):

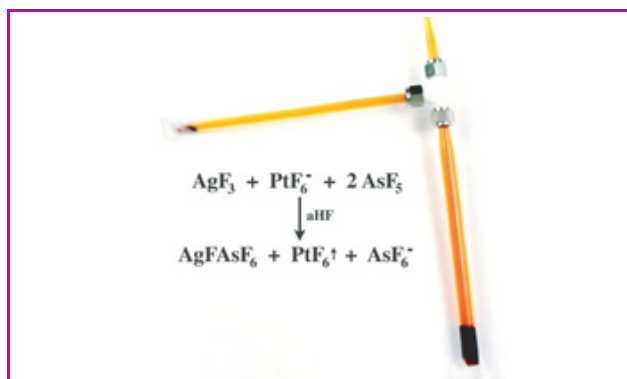
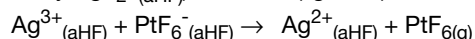


Figure 3 - Oxidation of $\text{PtF}_6^-(\text{aHF})$ by $\text{Ag}^{\text{III}}(\text{aHF})$, in acidic aHF, to PtF_6 (red vapor), at ~ 20 °C.

Although neither this oxidizer nor cationic Ni^{IV} was able to liberate AuF_6 from its monoanion [29], we can be sure that these reagents are the most potent oxidizers yet made. Hitherto, KrF^+ has had that distinction [30], but as R.J. Gillespie, and G.J. Schrobilgen found [31], the compound $\text{KrF}^+\text{PtF}_6^-$ does not release PtF_6 , but decomposes with loss of Kr, and F_2 , and formation of PtF_5 .

Experimental

It was essential to avoid components able to reduce the high oxidation state species. Metals were excluded. Valves, as illustrated previously [32], were of Teflon. Because Kel-F is attacked by oxidizers like PtF_6 , the Kel-F stem is protected by a Teflon tip. Fluorocarbon tubing used for containers was drawn, blown or sealed after being softened in a small non-luminous Bunsen flame. T-shaped decanters, joined by way of a valve to the vacuum line by a length of fluorocarbon tubing, were made using Swagelock Teflon T's. The aHF solvent was dried using K_2NiF_6 . Apparatus was pretreated with F_2 and dry aHF.

Acknowledgements

Research support from the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the US Department of Energy under Contract nr DE-AC-03-76SF00098, and the Slovenian Research Agency are gratefully acknowledged. The authors also thank Gašper Tavčar for figure 2.

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B. Žemva

Boris Žemva

est directeur du Département de Chimie Inorganique & Technologie de l'Institut Jožef Stefan (Ljubljana, Slovénie)*.

Neil Bartlett

est professeur émérite à l'Université de Californie (Berkeley, E.-U.)**.



N. Bartlett

* Jožef Stefan Institute, Jamova 39, 1000 Ljubljana (Slovenia).
E-mail: boris.zemva@ijs.si

** Chemical Sciences Division, Lawrence Berkeley National Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720 (USA).
E-mail: nbartlett@LBL.gov