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Probing the Reactivity of the Potent AgF_2 Oxidizer. Part 2: Inorganic Compounds

Przemysław Malinowski[a], Zoran Mazej[b] and Wojciech Grochala[a,c,*]

[a] Warsaw / Poland, Laboratory of Intermolecular Interactions, Faculty of Chemistry, University of Warsaw
[b] Ljubljana / Slovenia, Department of Inorganic Chemistry and Technology, Jožef Stefan Institute
[c] Warsaw, Poland Laboratory of Technology of Novel Functional Materials, Interdisciplinary Center for Mathematical and Computational Modeling, University of Warsaw

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Dedicated to Professor Zbigniew Galus on his 75th Birthday and in Recognition of his Remarkable Contributions to Inorganic Electrochemistry

Abstract. The reactivity of $Ag^{II}F_2$ towards forty two inorganic compounds containing oxo- and chloro- ligands, has been investigated. Five families of compounds were studied: (i) binary oxides of metals and nonmetals, (ii) ternary salts of inorganic oxo acids, (iii) concentrated or anhydrous oxo- acids, (iv) binary and ternary chlorides and (v) oxochlorides. At low temperatures up to 200 °C AgF_2 readily oxidizes HgO, B_2O_3, PbO_2, As_2O_5, Ag_2SO_4, $LiBO_2$, K_2CO_3, KVO_3, Ag_2WO_4, and $AgMnO_4$ with concomitant oxygen evolution. In the same conditions V_2O_5, CrO_3, MoO_3, WO_3, CuO, Tl_2O_3, I_2O_5, Re_2O_7, K_2SO_4, $HgSO_4$, KSO_3F, KNO_3, $KClO_4$, KIO_4, $BaCrO_4$, $KMnO_4$ and $KReO_4$ resist the action of AgF_2 but many of these compounds get oxidized at higher temperatures (up to nearly 300 °C). Substantial inertness of sulfates, chromates, nitrates, perchlorates, permanganates and perrhenates suggests that one might attempt to synthesize salts of divalent silver with these anions. AgF_2 vigorously reacts with H_2SO_4 (fuming, 30% SO_3), HSO_3Cl (100%), $HClO_4$ (70%), and HNO_3 (fuming, 100%) at room temperature yielding salts of Ag^I and O_2; for $HClO_4$ and HNO_3 pre-cooled to -35 °C metastable perchlorate / nitrate complexes of Ag^{II} are obtained. Anhydrous HSO_3F behaves similar to HSO_3CF_3 (see Part 1 of this series) yielding slow methathetical conversion of AgF_2 without concomitant redox reaction.
Majority of chlorides and oxochlorides studied (AgCl, $AuCl_3$, $KAuCl_4$, WCl_6, $WOCl_4$, $MoOCl_4$, MoO_2Cl_2) react with AgF_2 at temperatures below 160 °C. Reaction with $SiCl_4$ (in contrast to CCl_4) is violent and very exothermic at room temperature. Liquid CrO_2Cl_2 (at room temperature) and solid WO_2Cl_2 (up to 180 °C) are kinetically inert to AgF_2. We do not observe intercalation of AgF_2 with various redox−inert oxo- and chloro- Lewis bases at the experimental conditions.

Keywords: Chlorides; Fluorine; Oxides; Redox reactions; Silver

Introduction

Divalent silver (Ag^{II}) is the most potent oxidizer among all attainable M^{2+} cations [1] whereas its binary fluoride, AgF_2, ranks among the most powerful fluorinating agents known [2]. Inorganic fluorides of chemical elements at their highest oxidation states obviously cannot be oxidized any further, and some of them participate in acid−base reactions involving AgF_2. For example, AgF_2 gradually transfers its F^- anions to a strong Lewis acid:

$$AgF_2 + SbF_5 \rightarrow (AgF^+)(SbF_6) \qquad (1a)$$

$$(AgF^+)(SbF_6) + SbF_5 \rightarrow Ag(SbF_6)_2 \qquad (1b)$$

or gradually accepts F^- anions from a strong Lewis base:

$$AgF_2 + KF \rightarrow (K^+)(AgF_3^-) \qquad (2a)$$

$$(K^+)(AgF_3^-) + KF \rightarrow (K^+)_2(AgF_4^{2-}) \qquad (2b)$$

For Lewis acids and bases of moderate strength reactions (1−2) may stop at the first stage (1a, 2a).

Acid−base chemistry of AgF_2 is interesting and valuable as it might help to generate a novel 2D compound exhibiting superconductivity [1, 3]. Yet, unfortunately, chemistry of Ag^{II} has so far been limited to fluoride connections, leaving rather little room for an advanced crystal−engineering. How can this be changed? May other than F−based ligands be introduced into a coordination sphere of a voracious Ag^{II} oxidizer? Species based on oxygen and chlorine (the most electronegative elements except fluorine) are obvious pretenders.

Recently, thermodynamics of various redox reactions involving AgF_2 has been analyzed based on the data available in the literature [4]. It turns out that as far as thermodynamics is considered, AgF_2 is capable of oxidizing vast majority of binary oxides and chlorides of chemical elements at their highest oxidation states [5]. For example:

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* Dr. Wojciech Grochala
Laboratory of Intermolecular Interactions
Faculty of Chemistry, University of Warsaw, Pasteur 1
PL-02093 Warsaw / Poland
Tel. +48 (22) 5540828; Fax. +48 (22) 5540801
E-mail: wg22@cornell.edu

$$\tfrac{1}{2}\,Li_2O + AgF_2 \rightarrow LiF + AgF + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = -161.7\ \text{kJ/mol}) \quad (3a)$$

$$Li_2O + AgF_2 \rightarrow 2\,LiF + \tfrac{1}{2}\,Ag_2O + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = -289.7\ \text{kJ/mol}) \quad (3b)$$

$$Li_2O + AgF_2 \rightarrow \tfrac{1}{2}\,Li_2O_2 + LiF + AgF \quad (\Delta H^0_r = -158.7\ \text{kJ/mol}) \quad (3c)$$

$$LiCl + AgF_2 \rightarrow LiF + AgF + \tfrac{1}{2}\,Cl_2 \quad (\Delta H^0_r = -52.3\ \text{kJ/mol}) \quad (4)$$

This conclusion has been confirmed by quantum mechanical calculations for discrete molecules and for extended solids containing oxo- and chloro- ligand [5, 6, 7]. Standard enthalpy of reactions analogous to (3−4) is positive or close to null only for the following oxides: HgO, CO_2, N_2O_5, V_2O_5, As_2O_5, SeO_3, MoO_3, WO_3, UO_3, Cl_2O_7, and chlorides: AgCl, $AuCl_3$, NCl_3, and $PbCl_4$. In all cases the entropy factor favours redox process due to evolution of gaseous products, and the standard free enthalpy is positive only for a very few binary substrates.

Ternary oxides and chlorides, which are products of the thermodynamically favourable acid−base reactions between ionic and covalent binary systems ($K_2O + SO_3 \rightarrow K_2SO_4$) are often more resistant to oxidation by AgF_2. For example:

$$\tfrac{1}{2}\,K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{2}\,SO_3 + KF + AgF + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +107.4\ \text{kJ/mol}) \quad (5a)$$

$$K_2SO_4 + AgF_2 \rightarrow SO_3 + 2\,KF + \tfrac{1}{2}\,Ag_2O + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +252.2\ \text{kJ/mol}) \quad (5b)$$

$$K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{2}\,SO_3 + 2\,KF + \tfrac{1}{2}\,Ag_2SO_4 + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +107.7\ \text{kJ/mol}) \quad (5c)$$

$$K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{2}\,K_2O_2 + KF + AgF + SO_3 \quad (\Delta H^0_r = +383.2\ \text{kJ/mol}) \quad (5d)$$

$$K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{2}\,K_2S_2O_8 + KF + AgF \quad (\Delta H^0_r = +68.0\ \text{kJ/mol}) \quad (5e)$$

$$\tfrac{1}{4}\,K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{4}\,SO_2F_2 + \tfrac{1}{2}\,KF + AgF + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +41.5\ \text{kJ/mol}) \quad (5f)$$

$$\tfrac{1}{2}\,K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{2}\,SO_2F_2 + KF + \tfrac{1}{2}\,Ag_2O + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +116.7\ \text{kJ/mol}) \quad (5g)$$

$$\tfrac{1}{8}\,K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{8}\,SF_6 + \tfrac{1}{4}\,KF + AgF + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +40.8\ \text{kJ/mol}) \quad (5h)$$

$$\tfrac{1}{4}\,K_2SO_4 + AgF_2 \rightarrow \tfrac{1}{4}\,SF_6 + \tfrac{1}{2}\,KF + \tfrac{1}{2}\,Ag_2O + \tfrac{1}{4}\,O_2 \quad (\Delta H^0_r = +115.2\ \text{kJ/mol}) \quad (5i)$$

Thus, a range of ternary nitrates, metavanadates, sulfates, chromates, perchlorates, but also oxofluorides MO_2F_2 (M = S, W), MOF_4 (M = W, U), and WO_2Cl_2, yield reactions which are substantially endothermic; for some of these reactions the standard free enthalpy is positive despite the large negative entropy factor.

Analysis of thermodynamics of various redox reactions involving AgF_2 [5] obviously calls for an experimental verification. Are thermodynamic data precise enough? At which temperature redox reaction will proceed for compounds predicted to be redox-inert at ambient conditions? And will some other compounds be *kinetically* resistant to AgF_2 despite favourable thermodynamics of a redox process?

The purpose of the current contribution is to summarize results of our recent experimental investigations of the reactivity of AgF_2 towards various inorganic oxo- and chloro- compounds [8]. This study continues and completes our previous investigations of reactivity of AgF_2 towards *organic* compounds described in Part 1 of this series [9]. It is important to realize that our long−standing goal is to synthesize organic and / or inorganic 2D hybrid compounds based on AgF_2 and on various fluoro-, oxo- or chloro- ligands. Such intercalates should exhibit flat $[AgF_2]$ layers at an elongated octahedral coordination of divalent silver in order to attain unique electronic structure desired for generation of superconductivity in these compounds [1, 3]. Thus, our initial goal was to determine which inorganic oxo- and chloro- compounds are (at least kinetically) inert to AgF_2. In other words, we have treated all compounds scrutinized here as potential reducing agents and we were interested if a redox reaction occurs at ambient or elevated temperature ('Yes'/'No'), as confirmed by presence or absence of Ag(I)F, formed in a generalized reaction:

$$AgF_2 \rightarrow AgF + [F]) \quad (6),$$

without in depth investigating of other products if the reaction has taken place. Cases of 'no reaction', *i.e.* where we could not detect substantial amounts of Ag^IF, have been of most interest for us. Having this in mind, in the present contribution we have not described majority of analytical results which support the final conclusions. Only the most interesting results are discussed in more detail and supported by XRD, spectroscopic or other analytical data [10].

Experimental

Chemicals were purchased from Sigma-Aldrich (Poland), Alfa−Aesar (Germany) or ABCR (Germany) and were typically of 98−99+% purity. AgF_2 was freshly prepared by fluorination of $AgNO_3$ in the HF solvent; the product was extremely reactive to moisture. Chemicals were homogenized before the reaction using agate mortar and a Teflon spatula except for liquids.

All reactions were carried in pure Teflon® apparatus inside of the Ar−filled two-column glovebox (MBraun, Germany, Labmaster DP), typically operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. In a typical reaction, *ca.* 70−140 mg of AgF_2 was mixed up with an excess of inorganic compound, homogenized in the agate mortar, and behaviour of the mixture was systematically monitored upon heating for about 20−30 min, typically up to 300 °C (except for the cases when violent reaction took place at a room temperature). The oxygen level indicator has allowed us to detect evolution of even small amounts of O_2 from the samples.

The reaction products were carefully inspected visually using Leica MZ6 microscop inbuilt in the glovebox chamber at 320-times magnification. In many cases we have detected characteristic dark yellow grains of nonstoichiometric $AgF_{1\pm x}$ among dark−brown grains of native AgF_2 (see Figure 1); presence of Ag^I fluoride obviously heralds the redox (fluorination) reaction. It is important to note that commercially available AgF_2 usually contains small amount of AgF and therefore we have not used commercial product in our investigations. The samples were then analyzed by elemental combustion analysis for F and (wherever applicable) Cl and S content (Schöniger method); typical detectability limit is 0.2 weight %. In addition, we have obtained the X-ray diffractograms

(Bruker D8 Discover, utilizing Cu 1.54 Å radiation; intensity ratio of Kα1 to Kα2 beam is as 0.6538 to 0.3462) for samples sealed inside quartz glass capillaries of 0.3 mm or 1.0 mm diameter (Hilgenberg, Germany), the FT−IR spectra (Bruker, vacuum V80 model) for selected pre- and post-reaction samples in the solid state. Raman spectroscopy was occassionally used (Jobin Yvonne, T64000 spectrometer equipped with an argon/ krypton ion laser (usually using 488.0 nm, 514.5 nm or 647.1 nm excitation) and an optical microscope facility (focal length 50 mm) providing a lateral resolution of the optical image of the examined surface of about 1 mm. Selected samples were subject to thermogravimetry (TGA) / differential scanning calorymetry (DSC) analysis (Netzsch STA 409 PG) with a simultaneous evolved gas analysis (EGA) encompassing FT−IR (Bruker V80) and QMS (Pfeiffer-Vacuum, Aëolos 403 C) of the gaseous products. The spectrometers were connected to the TGA/DSC analyzer using quartz capillary (MS) or Teflon® pipe (FT−IR), both preheated to 200 °C to avoid condensation of solid residues. The samples were exposed to atmosphere for a short time during preparations before elemental analysis and TGA/DSC measurements; in all other cases samples were protected from atmospheric oxygen and moisture.

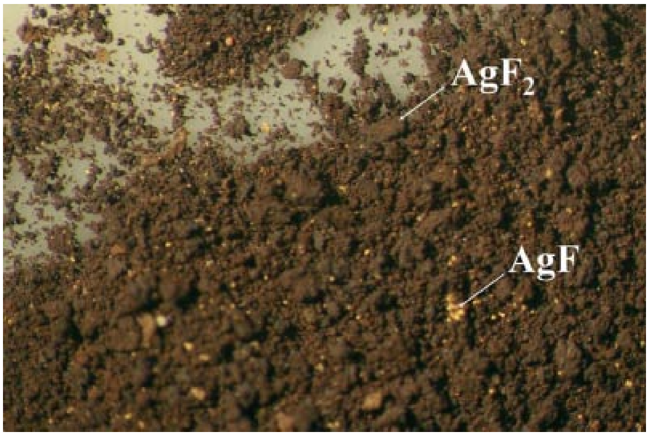

Fig. 1 Dark yellow grains of nonstoichiometric $AgF_{1\pm x}$ amongst dark−brown grains of native AgF_2.

NOTE! Reaction between $SiCl_4$ and AgF_2 is vigorous and very exothermic, generating sparks of hot gases even if mg amounts of chemicals are used. Care is advised while performing this reaction.

Results and Discussion

1 Compounds Studied

The forty two inorganic compounds studied here may be categorized into five distinct classes:

1. Binary oxides of metals and nonmetals (V_2O_5, CrO_3, MoO_3, WO_3, Re_2O_7, CuO, HgO, B_2O_3, Tl_2O_3, PbO_2, As_2O_5, I_2O_5).
2. Ternary salts of oxo- acids ($LiBO_2$, K_2CO_3, KVO_3, KNO_3, K_2SO_4, Ag_2SO_4, $HgSO_4$, KSO_3F, $BaCrO_4$, Ag_2WO_4, $KClO_4$, KIO_4, $AgMnO_4$, $KReO_4$).
3. Concentrated and anhydrous oxo- acids (H_2SO_4 fuming 30% SO_3, HSO_3Cl 100%, $HClO_4$ 70%, HNO_3 fuming, yellow 100%, HSO_3F 100%).
4. Binary and ternary chlorides of metals and nonmetals (AgCl, $AuCl_3$, WCl_6, $SiCl_4$, $KAuCl_4$).
5. Oxochlorides of transition metals ($WOCl_4$, WO_2Cl_2, $MoOCl_4$, MoO_2Cl_2, CrO_2Cl_2).

The set of compounds studied in this work thus encompasses five binary oxides and two binary chlorides, previously predicted to be substantially inert to AgF_2 (HgO, V_2O_5, As_2O_5, MoO_3, WO_3, AgCl, $AuCl_3$) [5]. For various reasons, we have not studied other binary oxides and chlorides anticipated to be markedly resistant to AgF_2, such as gaseous CO_2 and N_2O_5, very toxic SeO_3, radioactive UO_3, and four explosive or significantly thermally unstable compounds: Cl_2O_7, Mn_2O_7, NCl_3 and $PbCl_4$. Instead, we have extended our study to these systems, for which the thermodynamic data was either unavailable, incomplete, subject to large error or showed severe discrepancies in various sources [5]. Thus, in addition to HgO we have studied other oxides of heavy elements with substantial relativistic stabilization of the 6s valence orbital (Tl_2O_3, PbO_2), aside MoO_3 and WO_3 we have also studied related CrO_3, instead of explosive Cl_2O_7 and Mn_2O_7 we have used much more stable Re_2O_7, in addition to systems predicted to be quite inert to AgF_2 we have also looked at these, which were thought to be oxidized easily (B_2O_3, $LiBO_2$, K_2CO_3 etc.), and so on.

Forty one compounds scrutinized contain oxide (O^{2-}) and/or chloride (Cl^{1-}) ligands attached to isoelectronic Lewis acids of varying strength (for example: Hg^{II}, Tl^{III}, Pb^{IV}, or: B^{III}, Si^{IV}, As^{V}, etc.) and at varying acidity of a chemical environment (B_2O_3 *vs.* $LiBO_2$, Re_2O_7 *vs.* $KReO_4$ etc.). Chemical elements, to which these anions are attached, are usually at their highest attainable oxidation states ranging from II (for Hg) to VII (for Re). Such approach has allowed us to systematically study reducing properties of oxide and chloride ligands confronted with the potent AgF_2 oxidizer, and also evaluate prospect for novel oxo- and chloro- derivatives of divalent silver.

2.1 Binary oxides of metals and nonmetals

Oxides from this family may be tentatively divided to these, which are quite reactive towards AgF_2 (B_2O_3, PbO_2, As_2O_5, and HgO) and those which are quite inert (CuO, Tl_2O_3, V_2O_5, I_2O_5, CrO_3, MoO_3, WO_3, and Re_2O_7). B_2O_3, PbO_2 and As_2O_5 react with AgF_2 at a temperature as low as 90−100 °C, while red (orthorhombic) HgO is markedly stable at 100 °C and it requires somewhat stronger thermal activation at temperatures up to 140 °C. Reaction proceeds before any of the substrates is melted (the corresponding melting temperatures for AgF_2, B_2O_3, PbO_2, As_2O_5 and HgO are: T_m = 690 °C (with decomposition), 460 °C, 290 °C (with decomposition), 315 °C (with decomposition), and 500 °C (with decomposition)). In all reactions evolution of O_2 has been detected by sensitive oxygen analyzer. Reaction products in all cases contain dark yellow AgF (and sometimes also small amounts of black Ag_2O), as additionally evidenced by XRD (Figure 2). Formation of metal peroxides is unlikely except for mercury, which is known to form metastable peroxide [11]. Facile oxidation of oxides in question is not surprising provided that the calculated standard enthalpy (per 1 mol of AgF_2) for the thermodynamically most favoured reactions involving B_2O_3, PbO_2, As_2O_5 or HgO is either negative or slightly positive (−11.0 kJ/mol, −10.7 kJ/mol, +34.0 kJ/mol, and −1.7 kJ/mol, respectively [5]). Recollect, even a modest positive standard enthalpy may be overcome by the negative entropy factor for these reactions, since the (−SΔT) factor for gaseous dioxygen is as large as −61.1 kJ/mol at room temperature. For example [5]:

$$^{1}/_{2}\ HgO + AgF_2 \rightarrow {}^{1}/_{2}\ HgF_2 + AgF + {}^{1}/_{4}\ O_2 \quad (\Delta H^0_r = -1.7\ kJ/mol,\ \Delta G^0_r \approx -17.0\ kJ/mol) \quad (7).$$

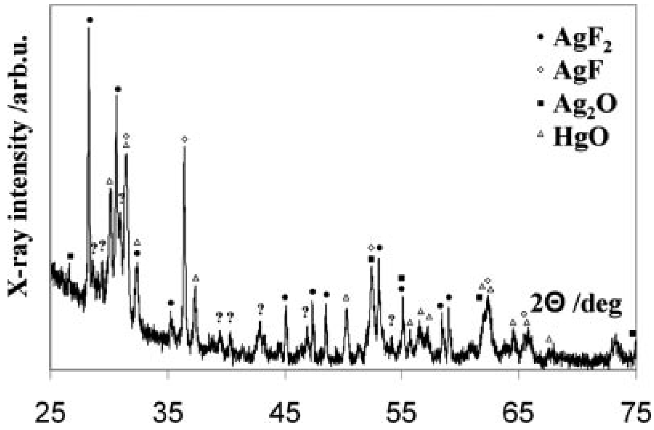

Fig. 2 The XRD pattern of the products of reaction at 140 °C between AgF_2 and HgO (red). Peaks from unidentified product(s) have been marked with '?'

We anticipate that redox reactions in question are spontaneous even at room temperature and that heat is needed mostly to enhance transport of the solid substrates at the intragrain boundary. Silica may be added to the set of compounds, which undergo oxidation by AgF_2; recollect, AgF_2 may be kept in quartz capillaries for short times in moisture−free atmosphere, but surface etching of silica is seen for longer times of reaction and even at room temperature.

The remaining binary oxides studied are quite resistant to action of AgF_2. For V_2O_5 very little reduction of AgF_2 to AgF is seen at the temperature as high as 250 °C, Tl_2O_3 behaves similarly undergoing only a very slow reaction at 270−285 °C, while Re_2O_7 is quite stable even above its melting temperature (T_m = 220 °C) and slow reaction begins around 275 °C. The oxides of heavy hexavalent elements studied (MoO_3, WO_3) do not undergo oxidation to any appreciable degree despite prolonged heating at 260−285 °C. Reaction for CrO_3 could not be conducted above 196 °C, since anhydrous CrO_3 decomposes at this temperature, but we noticed that CrO_3 resists presence of AgF_2 at 170 °C. The inertness of MO_3 (M = Mo, W) is of a purely kinetic nature; the calculated standard enthalpy of the most facile redox reactions is only slightly positive [5]:

$$^{1}/_{4}\ MO_3 + AgF_2 \rightarrow {}^{1}/_{4}\ MOF_4 + AgF + {}^{1}/_{4}\ O_2 \quad (\Delta H^0_r = +13.5\ kJ/mol\ for\ Mo,\ +14.4\ kJ/mol\ for\ W) \quad (8),$$

and it is certainly overcome by entropy factor at temperatures close to ambient and higher.

The cases of CuO and I_2O_5 are interesting; these compounds constitute important exceptions in our set of binary oxides, since Cu and I, respectively, are not at their highest attainable oxidation states (+4 for Cu [12], +7 for I). Despite that, CuO is not oxidized by AgF_2 even at 250 °C, while I_2O_5 may be melted at 200 °C in the presence of AgF_2 without noticeably undergoing a redox reaction. We anticipate that lack of thermodynamic stability of a possible product, scarce CuF_3 (CuF_3 loses F_2 at −40 °C in KHF_2−rich aHF [13]) is largely responsible for the observed lack of susceptibility of CuO towards fluorinative oxidation. But I_2O_5 is a different story, since both IF_7, IF_5 and various oxofluorides of I^{VIII} (such as for example IOF_5) and I^{V} are known and quite stable thermodynamically [14]. Thus, the following reactions:

$$^{1}/_{14}\ I_2O_5 + AgF_2 \rightarrow {}^{1}/_{14}\ IF_{7(g)} + AgF + 5/28\ O_{2(g)} \quad (9)$$

$$^{1}/_{2}\ I_2O_5 + {}^{7}/_{2}\ AgF_2 \rightarrow IF_{7(g)} + {}^{7}/_{4}\ Ag_2O + 3/4\ O_{2(g)} \quad (10)$$

are supposed to have negative ΔH^0_r and even more negative ΔG^0_r due to favourable entropy term. The remarkable inertness of I_2O_5 towards AgF_2 thus must be of a purely kinetic nature.

2.2 Ternary salts of oxo- acids

Similar to the binary oxides (see preceding section), also the ternary oxides may be tentatively divided to these, which are reactive towards AgF_2 ($LiBO_2$, K_2CO_3, KVO_3, Ag_2WO_4, $AgMnO_4$) and those which are rather inert (KNO_3, $KMnO_4$, $KReO_4$, KIO_4, $KClO_4$, K_2SO_4, Ag_2SO_4, $HgSO_4$, KSO_3F, $BaCrO_4$).

Glassy $LiBO_2$ reacts with AgF_2 at very small thermal activation (65−80 °C), K_2CO_3 and KVO_3 require slightly higher temperature (130 °C, reactions are very fast at higher temperatures), while Ag_2WO_4 gets oxidized at 145−150 °C. $AgMnO_4$ also reacts at 145−150 °C and the result is unambiguous since this dark salt does not decompose thermally even at 200 °C if heated alone. All reactions proceed with the evolution of substantial amount of O_2 and the reaction products contain dark yellow AgF, as evidenced by XRD. Facile oxidation of these oxo- salts is not very surprising since the calculated standard enthalpy (per 1 mol of AgF_2) for the thermodynamically most favoured reactions involving KBO_2, K_2CO_3, and $NaVO_3$ is either substantially negative or at best close to null (−108.3 kJ/mol, −65.1 kJ/mol, and +3.6 kJ/mol, respectively [5]). Thus, ΔG^0_r is certainly negative for reactions involving K_2CO_3, $LiBO_2$ and KVO_3.

The remaining oxo- salts studied are pretty resistant to AgF_2, even at elevated temperatures. KNO_3 yields to AgF_2 only at 275 °C, $KReO_4$ at 290 °C, KIO_4 at 300 °C, while $KClO_4$ resists prolonged heating at 300 °C in the presence of AgF_2. $KBrO_4$ has not been studied here; this compound is not available commercially and difficult to prepare in a pure state but one obviously expects that its inertness to

AgF_2 should be substantial and similar to the KIO_4 and $KClO_4$. Interestingly, K_2SO_4, Ag_2SO_4, $HgSO_4$, KSO_3F, and $BaCrO_4$, also resist oxidizing action of AgF_2 at temperatures close to 250−300 °C; $KMnO_4$ is inert up to 290 °C. These results confirm conclusions obtained previously from the assessment of the thermodynamic parameters for various redox reactions involving AgF_2 [5] (compare also Eqs.(5a-i)). Inertness of many of these salts is not just of kinetic but also of thermodynamic nature.

The results obtained here are important in context of possible synthesis of novel oxo- derivatives of divalent silver. Specifically we expect that synthesis of $Ag^{II}MO_4$ (M = S, Cr), $Ag^{II}(MO_4)_2$ (M = Cl, Br, I, Mn, Re) and $Ag^{II}(NO_3)_2$ should be feasible and the products could be (meta)stable at slightly decreased or even at ambient temperature. These as yet unknown salts would add to the small set of pseudobinary oxo- compounds of divalent silver encompassing to date only $Ag^{II}(SO_3X)_2$ (X = F, CF_3) [15, 16]. However, it is not entirely clear on which synthetic route these new compounds might be obtained since the corresponding peroxides (hypothetical Cl_2O_8, N_2O_6, etc.) are not stable and thus unavailable as possible reagents. The only metastable peroxo species, $S_2O_8^{2-}$ (known from peroxodisulfates in the solid state) could in principle be used:

$$2\ AgF + K_2S_2O_8 \rightarrow 2\ KF + 2\ AgSO_4 \qquad (11),$$

but it is difficult to find a solvent which would permit separation of the products without simultaneous decomposition of $Ag^{II}SO_4$ or oxidation of the solvent. Performing of this reaction at elevated temperature must also be excluded since $K_2S_2O_8$, like all peroxodisulfates, decomposes at temperatures as low as *ca.* 100 °C.

Another interesting route towards oxo- salts of Ag^{II} might be a methathetical reaction, *e.g.*:

$$Ag(SbF_6)_2 + K_2SO_4 \rightarrow 2\ KSbF_6 + AgSO_4 \qquad (12),$$

but it is not straightforward in which solvent this reaction should be carried out. $HF_{(l)}$ is a solvent of choice when it comes to strong oxidizers, such as Ag^{II} species, but unfortunately HF is also known to hydrolyze many oxo salts in the acid − base reactions, for example [17]:

$$K_2SO_4 + HF_{(l)} \rightarrow KHF_{2(HF)} + KSO_3F \qquad (13).$$

Despite these difficulties, novel thermodynamically stable or metastable oxo- derivatives of Ag^{II} seem to constitute an interesting synthetic target.

2.3 Concentrated and anhydrous oxo- acids

Mineral oxo- acids such as H_2SO_4, $HClO_4$, HNO_3 and HSO_3F (and related organic perfluorinated sulfonic acids) are often considered to be inert to oxidation; indeed, some of these acids themselves oxidatively dissolve various precious metals at ambient or elevated temperature. Such behaviour predominates their chemistry, but as we will show it may be bent under certain circumstances.

Fig. 3 The progress of reaction between AgF_2 and fuming H_2SO_4 (top) and the products of reaction (bottom). Dense colourless H_2SO_4 x SO_3 is added drop by drop to the reaction vessel containing brown AgF_2.

Fuming H_2SO_4 saturated with SO_3 (30% SO_3), HSO_3Cl (100%), concentrated $HClO_4$ (70%) and yellow fuming HNO_3 (100%) all react vigorously and quite exothermally with AgF_2 at ambient temperature (Figure 3) while evolving large amounts of oxygen. Colourless salts of Ag^I, crystalline (Figure 3) or dissolved in their parent acid, constitute final products of these reactions. In the case of H_2SO_4, small amount of black residue (Figure 3) is also observed. Oxidation of H_2SO_4 by AgF_2 is not surprising; the reaction:

$$H_2SO_4 + AgF_2 \rightarrow {}^1/_2\ SO_3 + 2\ HF + {}^1/_2\ Ag_2SO_4 + {}^1/_4\ O_2 \qquad (14a)$$

is favoured thermodynamically ($\Delta G^0_r = -48$ kJ/mol), despite the fact that ΔH^0_r is in fact positive (+71.6 kJ/mol) [5]. The black product is supposedly '$Ag^{II}(SO_4)$' or $Ag^I_2S_2O_8$, since it can be decomposed thermally at *ca.* 120 °C (with a concomitant O_2 evolution) yielding a colorless disulfate salt of monovalent silver:

$$2\ \text{'}Ag^{II}(SO_4)\text{'} \rightarrow Ag^I_2S_2O_7 + {}^1/_2\ O_2 \qquad (14b)$$

At higher temperatures disulfate releases SO_3 and yielding Ag_2SO_4:

$$Ag^I_2S_2O_7 \rightarrow Ag^I_2SO_4 + SO_3 \qquad (14c)$$

To best of our knowledge reactions (14b-c) have not been reported so far.

Reaction of AgF_2 with 70% $HClO_4$ is very interesting; at the end it also yields a corresponding Ag(I) salt, but at the first stage of reaction gas bubbles evolve (HF ↑) and a dark black solution forms; its colour then slowly decays, within 24 hrs, via light yellow to colourless. If the reaction is performed for reagents, which have been pre-cooled at −35 °C, dark colour persists for several days without any noticeable fading away. Such behaviour suggests the presence of metastable perchlorate complexes of Ag^{II}, such as $Ag(ClO_4)_2$ or $[Ag(ClO_4)_3]^-$ and reconfirms our earlier surmise that similar complexes could be synthesized rather easily. A tentative simplified reaction sequence may be proposed:

$$2\ HClO_4 + AgF_2 \rightarrow 2\ HF + Ag(ClO_4)_2 \qquad \text{(fast)} \quad (15a)$$

$$Ag(ClO_4)_2 + {}^1/_2\ H_2O_{[HClO4]} \rightarrow AgClO_4 + HClO_4 + {}^1/_4\ O_2 \qquad \text{(slow)} \quad (15b)$$

Use of anhydrous 100% $HClO_4$ might allow for elimination of step (9b); however, we have decided not to perform reaction of AgF_2 with anhydrous $HClO_4$ (or, similarly, with anhydrous HNO_3) due to highly explosive nature of these species.

Reaction between AgF_2 and concentrated HNO_3 is spontaneous even if conducted for reagents pre-cooled to −35 °C and leads to gradual worming up of the liquid; after 12 hrs only white $AgNO_3$ can be isolated. Emission of dark brown oxides of nitrogen is not observed, which suggests that colourless N_2O_5 (which dissolves in HNO_3), HF and O_2 are the only gaseous products. However, if the reaction is conducted at −35 °C it results in dark gray solution; colour persists at low temperature for several days without any noticeable fading away, similar as for reaction between AgF_2 and $HClO_4$. Our surmise is that isolation of pure $Ag(NO_3)_2$ may prove equally challenging as that of $Ag(ClO_4)_2$.

Reaction between AgF_2 and anhydrous HSO_3F (100%) takes a very different route than those for other mineral acids studied in this work as no immediate redox reaction is observed. Instead, the acid becomes slightly yellow (which suggests that redox reaction leading to yellowish $(SO_3F)_2$ takes place only to a very small degree), the brown AgF_2 solid becomes black in appearance and it increases volume about twofold with respect to the fluoride substrate. The observations suggest that either a partial or more likely a full methathetical reaction takes place, leading, respectively, to $(AgF)(SO_3F)$, or to $Ag(SO_3F)_2$ [18], although a mixed−valence Ag^I/Ag^{II} fluorosulfate or a mixed fluorosulfate/fluoride phases cannot be completely rule out. The ligand exchange reaction is quite slow at a room temperature (similar to reaction between AgF_2 and HSO_3CF_3 [9]) and a full conversion takes place only after one month. The characteristic most intense peaks of AgF_2, AgF and $Ag^I(SO_3F)$ cannot be detected in the complex XRDP of the black product (Figure 4) reconfirming that redox reaction is unlikely. Grinding of this seemingly black compound in agate mortar shows it is dark brown in fact, similar to $Ag(SO_3F)_2$ reported by *Leung* and *Aubke* some thirty years ago [15].

Reaction between AgF_2 and HSO_3Cl takes very different route from that between AgF_2 and HSO_3F. HSO_3Cl is oxidized very easily by AgF_2 even if reagents are pre-cooled to −35 °C. Evolution of very small amounts of O_2 is seen (in contrast to reaction between AgF_2 and H_2SO_4) which suggests that this is the S−Cl bond which undergoes fluorination.

In conclusion of this section, strong mineral oxo- acids undergo facile oxidation by AgF_2 at room temperature, $HClO_4$ and HNO_3 resist action of AgF_2 at −35 °C, while HSO_3F is the most resistant to oxidation (similarly to related HSO_3CF_3) [9]. There is good prospect for so far unsynthesized $Ag(ClO_4)_2$ and $Ag(NO_3)_2$.

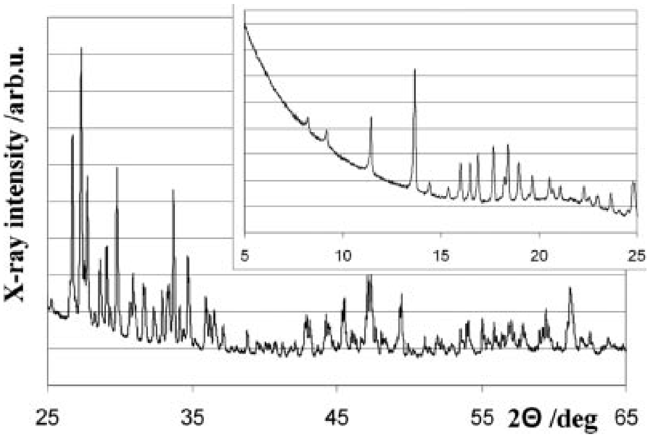

Fig. 4 The XRD pattern of the solid product of reaction at 25 °C between AgF_2 and HSO_3F. No peaks from AgF_2, AgF or $AgSO_3F$ can be identified.

2.4 Binary and ternary chlorides of metals and nonmetals

Having studied a range of oxo- derivatives, we have turned to simple compounds containing chloro- ligands. Chlorides are known to be quite resistant to oxidation but the standard redox potential of the [Cl_2 / 2 Cl^-] couple equals +1.36 V in the acidic aqueous environment, and thus it is 0.4 V smaller than the corresponding value for the [H_2O_2, 2 H^+/ 2 H_2O] couple (+1.76 V) [19]. However, E^0 of the [Cl_2 / 2 Cl^-] couple is simultaneously much closer to the E^0 value for the [1/2 O_2, 2 H^+/ H_2O] couple (+1.23 V). Concerning the above it is expected that oxidation of chlorides may be equally facile, or even easier than of the corresponding oxides, depending on the reaction path.[5]

First, $SiCl_4$ has been tested as an example of chloride which, at least in thermodynamic terms, should easily undergo oxidation by AgF_2 [5]. Another reason for studying $SiCl_4$ was a surprising kinetic inertness towards AgF_2 of its lighter analogue, CCl_4, described in the first part of the series [9].

It turns out that reaction between AgF_2 and $SiCl_4$ conducted in Ar atmosphere is vigorous (Figure 5), even in the reagents were pre-cooled to −35 °C; hot gases (Cl_2? ClF_x?) are readily generated in form of yellow sparks. The idealized reaction equation:

$${}^1/_4\ SiCl_4 + AgF_2 \rightarrow {}^1/_4\ SiF_4 + AgF + {}^1/_2\ Cl_2 \qquad (\Delta H^0_r = -76.6\ \text{kJ/mol})^5 \quad (16)$$

certainly does not describe the factual course of this reaction, since we see formation of large amounts of dark orange compound (AgF_xCl_{1-x}: compare reaction between AgF_2 and AgCl below) and of unidentified black products (amorphous Si?) (Figures 5 and 6). The XRD pattern of the solid products reveals presence of the peaks which might be indexed based on a cubic F23 cell with the unit cell vector of 5.057 Å. This value is only slightly larger than the unit cell vector of AgF (4.934 Å), which suggests that some incorporation of larger chloride anions has taken place. Thus, crystalline $Ag(F_{1-x}Cl_x)$ is the main product of reaction between AgF_2 and $SiCl_4$ along with some unidentified amorphous products.

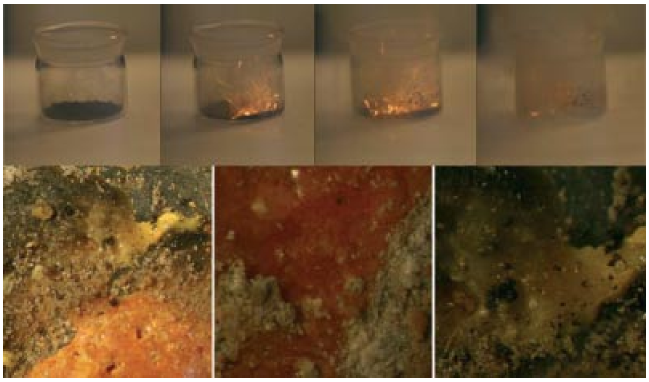

Fig. 5 The progress of reaction (bottom) between AgF_2 and $SiCl_4$ conducted in the inert gas atmosphere (Ar) and various phases found in the reaction products (top). Liquid colourless $SiCl_4$ is added drop by drop to the reaction vessel containing brown AgF_2.

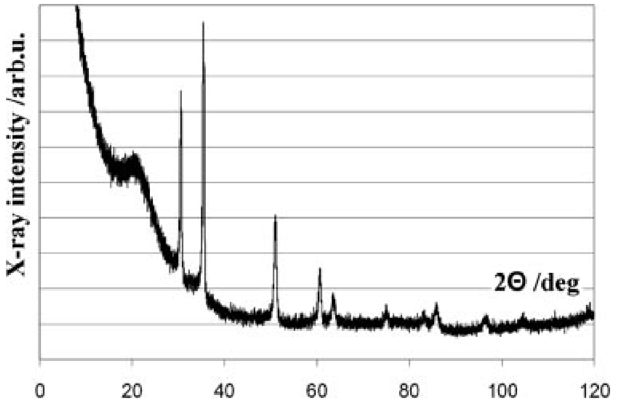

Fig. 6 The XRD pattern of the solid product of reaction between AgF_2 and $SiCl_4$. Only the peaks from $Ag(F_{1-x}Cl_x)$ could have been identified.

The thermodynamic driving force for reaction between AgF_2 and $SiCl_4$ is so large that reaction proceeds simultaneously along several independent channels. Combustion analysis reveals that the solid product contains 10,38−10,45 % F and 6,47−6,73 % Cl. Large Cl content is consistent with presumed incorporation of chloride ligands into the lattice of nonstoichiometric AgF_{1-x}.

In addition to $SiCl_4$, we have also tested WCl_6, AgCl, $AuCl_3$, and $KAuCl_4$. WCl_6 was presumed to yield a slightly exothermic reaction with AgF_2 (−22.2 kJ/mol)[5], while AgCl and $AuCl_3$ were predicted to be inert to AgF_2 at room temperature. Analysis of the following reactions:

$$AgCl + AgF_2 \rightarrow 2\,AgF + {}^{1}/_{2}\,Cl_2 \quad (\Delta H^0_r = +77.8\ \text{kJ/mol},\ \Delta G^0_r = +44.1\ \text{kJ/mol}) \qquad (17)$$

$${}^{1}/_{3}\,AuCl_3 + AgF_2 \rightarrow {}^{1}/_{3}\,AuF_3 + AgF + {}^{1}/_{2}\,Cl_2 \quad (\Delta H^0_r = +73.4\ \text{kJ/mol},\ \Delta G^0_r = +41.3\ \text{kJ/mol}) \qquad (18)$$

has revealed that in contrast to all other chlorides examined, AgCl and $AuCl_3$ should not undergo oxidation up to 380−415 °C. It was anticipated that the fate of ternary $KAuCl_4$ salt might be similar to that of the more acidic $AuCl_3$.

However, our experiments show something qualitatively different. $AuCl_3$ reacts with AgF_2 at the temperature as low as 105−125 °C, AgCl and $KAuCl_4$ at 150−155 °C, while WCl_6 at 160 °C. Our surmise is that the tabulated thermodynamic parameters of AgF_2 and/or other reactants are not very precise, and stability of these substrates is probably somewhat overestimated.

Reaction between AgCl and AgF_2 yields mainly a solid product of intense orange colour dissimilar to a typical dark yellow nonstoichiometric $AgF_{1\pm x}$ but very similar to the main product of reaction between AgF_2 and $SiCl_4$ (see above). XRDP of the product mixture (Figure 7) reveals presence of AgF as well as of several strong peaks which may be assigned to a cubic cell (systematic extensions correspond to F23 symmetry class) with the unit cell vector of 5.065 Å. Again, increase of the unit cell dimension indicates that small amount of chloride anions have been incorporated in crystallographic positions occupied by smaller fluoride anions. Assuming an approximate formula of the product as $Ag(F_{1-x}Cl_x)$ and applicability of the linear relationship between the unit cell vector and the Cl content (unit cell vector for AgCl is 5.546 Å [20]), one obtains x = 0.21. Such stoichiometry would correspond to the following product composition: Ag 82.8 %, F 11.5 %, Cl 5.7 %. Elemental combustion analysis, however, yields F and Cl content of 13.3 % and 1.7 % which corresponds to the formula $AgF_{0.889}Cl_{0.061}$ (x = 0.06). The discrepancy between these two results can be explained considering that substantial amounts of AgF are also found amongst the reaction products. It would be very interesting to study ionic conductivity of the defected salt $Ag(F_{1-x}Cl_x)$ (if obtained in the pure form).

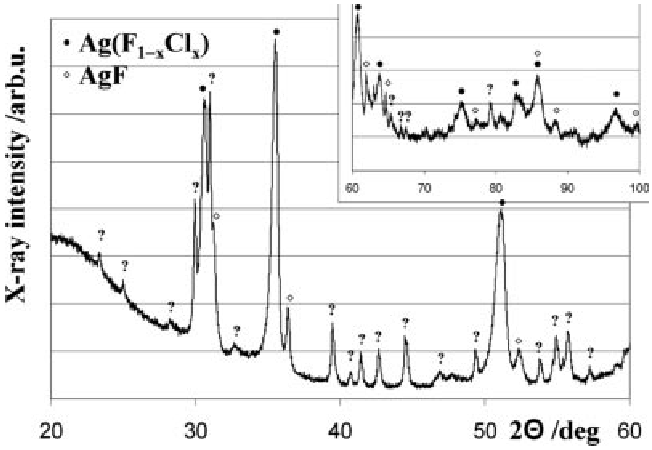

Fig.7 The XRD pattern of the solid product of reaction between AgF_2 and AgCl. Peaks from AgF, $Ag(F_{1-x}Cl_x)$ and from unidentified product(s) '?' are observed.

Analyzing XRDP one may notice presence of over twenty peaks which cannot be assigned to AgF or to $Ag(F_{1-x}Cl_x)$. Attempts to index these peaks have failed, possibly because they belong to more than one crystalline phase. Considering the oxidizing environement, presence of $AgCl^{I}F_2$ (similar to the known $CsClF_2$ [21]) and/or $AgCl^{III}F_4$ (similar to the known $CsClF_4$ [22]) may be expected.

In conclusion, reaction between AgCl and AgF_2 is very complex and, despite previous predictions [5], does not proceed according to Eq.(17). All chloride derivatives are fairly susceptible to oxidation by AgF_2.

2.5 Oxochlorides of transition metals

The thermodynamic data for majority of oxochlorides are not available in the literature and therefore enthalpy of various redox reactions has been evaluated only for SO_2Cl_2, WO_2Cl_2 and $WOCl_4$ [5]. The data suggested that reaction between AgF_2 and WO_2Cl_2 is endothermic, this for $WOCl_4$ is slightly exothermic, while that for SO_2Cl_2 is substantially exothermic.

We have conducted test reactions for AgF_2 homogenized with $WOCl_4$ and WO_2Cl_2, and also for related $MoOCl_4$, MoO_2Cl_2, and CrO_2Cl_2. As expected, orange−red $WOCl_4$ reacts with AgF_2 at rather low temperatures (slowly at 100 °C, much faster at 155 °C) yielding, *inter alia*, AgF and some colourless crystals (WOF_4?). Taking into account larger reactivity of chlorides than of oxides (see the preceding sections) we anticipate that these are chloride and not oxide anions which have been oxidized in $WOCl_4$. WO_2Cl_2 is much more resistant to AgF_2 than $WOCl_4$, and at even 180 °C no reaction is observed. The analogous compounds of Mo are much less resistant to action of AgF_2. Characteristic lemon yellow MoO_2Cl_2 reacts vigorously at 105 °C (well below its melting temperature of 184 °C) yielding white fumes and light yellow products. Dark green $MoOCl_4$ reacts violently with AgF_2 upon melting at 100 °C, and the process is probably exothermic since large volume of dark brown gas (vapour of $MoOCl_4$?) is generated. It is interesting to note that tetrachloro- monooxo- derivative of W^{6+} (with its relativistic, stabilized nominally empty 6s set) is less susceptible to oxidation than the corresponding compound of lighter Mo^{6+} (here, relativistic effects for the 5s set are much less pronounced). This effect is due to a more acidic nature of the 6s set for W, and the concomitant decrease of electron density at the neighbouring chloride anions.

Dark red CrO_2Cl_2, liquid at room temperature, is inert to AgF_2 at ambient condition and may be evaporated over AgF_2 without decomposition, leaving off a strongly electricized dark brown AgF_2 residue. It is unclear is this behaviour is of a purely kinetic nature (as for CCl_4) or it is also due to unfavourable thermodynamics. Reaction with CrO_2Cl_2 was not conducted at higher temperatures (the boiling temperature being 117 °C) due to extremely aggressive nature of vapours of this compound.

Conclusions

Divalent state is by many ways an unusual oxidation state of silver (reader is referred to Ref.1, where properties and structures of higher fluorides of silver have been reviewed). In this work we have scrutinized reactions between AgF_2, the most stable representative amongst binary Ag^{II} compounds, and 42 distinct inorganic chemicals, mostly in the solid state. Twenty of these reagents are capable of reducing AgF_2 at ambient or modest temperature (up to 200 °C, some of them at their melting point), while nineteen do so only at more elevated temperatures (> 250 °C), or are simply inert to AgF_2 at prolonged heating at 280−300 °C. O_2 evolution and production of $Ag^{I}F$ is observed for oxo- derivatives, testifying the occurrence of the redox process; by analogy, elemental Cl_2 or various chlorine fluorides are probably evolved in the case of chloro- derivatives. In general, chloro- derivatives are much more susceptible to oxidation by AgF_2 than the oxo- ones.

The remaining three compounds, $HClO_4$, HNO_3 and HSO_3F, behave differently in their reactions with AgF_2 since a methathetical ligand exchange is seen. $HClO_4$ and HNO_3 are borderline cases: acid−base reaction competes with redox process at ambient temperature; the latter may be slowed down considerably at −35 °C. On the other hand, HSO_3F is the most unsusceptible to a redox reaction amongst all acids studied and formation of Ag^{I} derivatives is negligible at ambient temperature.

It is suspected, base on previous analysis of thermodynamical reaction parameters, that inertness of sulfates, chromates, nitrates, perchlorates, but also periodates, permanganates and perrhenates towards AgF_2 is of a thermodynamic rather than a kinetic nature; whichever is the case, good prospect opens for synthesis of (meta)stable salts of divalent silver with these oxidation−resistant anions. These as yet hypothetical species would enrich the short list of pseudo-binary oxo- derivatives of genuine Ag^{II}, so far limited to fluorosulfate and triflate of silver(II) [15, 16].

AgF_2 has a layered structure and various oxidation−resistant species might be intercalated between the $[AgF_2]$ sheets. Interestingly, none of oxo- or chloro- Lewis bases studied, such as for example CrO_2Cl_2, forms novel coordination compounds with AgF_2 at the conditions of experiment. New approaches are needed to generate AgF_2−based two−dimensional inorganic hybrid materials of desired electronic and magnetic properties, similar to those formed by selected uranium (UFO) [23] and thorium fluorides (TFO) [24].

Note added in proof: While this paper was in proof we have confirmed that SO_2Cl_2 and $VOCl_3$ liquids are inert to AgF_2 at ambient temperature whereas VOF_3 sublimes over AgF_2 without noticeable decomposition at 300 °C [25].

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