# PROBING THE REACTIVITY OF THE POTENT AgF$_2$ OXIDIZER. PART 1: ORGANIC COMPOUNDS

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*Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday and in recognition of his outstanding contributions to the area of organofluorine chemistry.*

The reactivity of Ag(II)F$_2$ towards a variety of organic compounds of a high degree of fluorination has been investigated. AgF$_2$ readily fluorinates P(C$_6$F$_5$)$_3$ to PF$_2$(C$_6$F$_5$)$_3$, and attacks the isothiocyanate functional group, –NCS, yielding Ag$_2$S. Perfluorinated aliphatic nitriles resist the action of AgF$_2$, but aromatic C$_6$F$_5$CN undergoes a radical-initiated oligomerization; byproducts include C$_6$F$_6$CN$^\bullet$ and C$_6$F$_5$N$_2$$^\bullet$ (after intramolecular rearrangement following the bimolecular reaction). AgF$_2$ oxidizes higher fluorosulfonic acids (C$_4$F$_9$SO$_3$H, C$_8$F$_{17}$SO$_3$H) at or close to the room temperature and triflic acid (CF$_3$SO$_3$H) at its boiling point to the corresponding peroxides. CF$_3$COOH and CF$_3$CONH$_2$ are also decomposed in redox reactions, but the gaseous products have not been identified. Surprisingly, AgF$_2$ is kinetically inert to perfluorinated aromatic hydrocarbons and to CCl$_4$, but it decomposes CBr$_4$ with vigorous elimination of Br$_2$. CI$_4$ decomposes explosively in the presence of AgF$_2$. C$_6$F$_5$OH and CF$_3$COOH are readily oxidized with AgF$_2$ but, surprisingly, *t*-C$_4$F$_9$OH is kinetically resistant under similar conditions. Coordination complexes of perfluorinated aza and oxa Lewis bases (including perfluorinated 15-crown-5 ether) and AgF$_2$ are not formed under the experimental conditions.

**Keywords**: Acid-base reactions; Fluorine; Fluorination; Redox reactions; Oxidations; Silver.

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Divalent silver (Ag(II)) is the most potent oxidizer among all attainable $M^{2+}$ cations[1] while its binary fluoride, $AgF_2$, ranks among the most powerful fluorinating agents known[2]. For example, fluorination of $C_{60}$ fullerene with $AgF_2$ at 300 °C leads to $C_{60}F_{44}$ with an impressive 80% yield[3]. Following the Manhattan project, $AgF_2$ was used by Cady[4] as a catalyst of fluorination with gaseous $F_2$ of a variety of organic compounds including aromatic hydrocarbons and alcohols.

$$C_6H_6 + 8\ F_2 \rightarrow c\text{-}C_6F_{12} + 6\ HF \tag{1}$$

$$C_nH_{2n+1}OH + (n + 3/2)\ F_2 \rightarrow C_nF_{2n+1}OF + HF \tag{2}$$

All preceding studies of the reactivity of $AgF_2$ towards organic substances have relied on compounds containing C–H bonds[5]. The C–H bonds are readily fluorinated with $AgF_2$ under ambient conditions

$$C\text{–}H + 2\ AgF_2 \rightarrow 2\ AgF + C\text{–}F + HF \tag{3}$$

but, due to limited reaction times, a mixture of partly fluorinated $(CH_xF_y)$ products was frequently obtained[6], which necessitated laborious chromatographic separation and analysis of the products.

The purpose of this contribution is to summarize the results of our recent investigations of the reactivity of $AgF_2$ towards various perfluorinated organic compounds containing various functional groups.[7] The use of perfluorinated compounds allowed us to systematically study the impact of $AgF_2$ on the functional group without the involvement of secondary reactions due to partial fluorination of the hydrocarbon moiety. Only in some cases, notably for $CCl_4$, $CBr_4$ and $CI_4$, and related compounds, have we used derivatives of other halogens to systematically estimate their propensity to fluorination with $AgF_2$.

### EXPERIMENTAL

All perfluorinated chemicals were purchased from specialized vendors: Fluorochem (U.K.), Sigma-Aldrich (Poland), ABCR (Germany), Alfa-Aesar (Germany), TCI Europe (Belgium), Wako Chemicals (Japan) and Exfluor (Japan) and were typically of 98–99+% purity. $F_3CCBr_3$ was kindly provided by Prof. V. Nenaidenko (Moscow, Russia). $AgF_2$ was freshly prepared by fluorination of $AgNO_3$ in liquid HF; the product was extremely reactive to moisture.

All reactions were carried in pure Teflon® apparatus inside an Ar-filled two-column glovebox (MBraun, Germany, Labmaster DP), operating at <0.1 ppm O$_2$ and <0.1 ppm H$_2$O. In a typical reaction, ca. 70–140 mg of AgF$_2$ was mixed with an excess of the organic compound and the behaviour of the mixture was monitored upon heating for 15–30 min, typically up to 300 °C (except for cases where a violent reaction took place at room temperature).

The reaction products were carefully examined visually at 320 times magnification using a Leica MZ6 microscope in the glovebox chamber. In many cases we detected characteristic dark yellow grains of nonstoichiometric AgF$_{1\pm x}$ among dark-brown grains of native AgF$_2$; the presence of Ag(I) fluoride obviously indicates a redox (fluorination) reaction. The samples were then analyzed by elemental analysis for H, C, N (Vario EL III, Elementar and Perkin–Elmer analyzer type 240) and (wherever applicable) F, Cl, Br, I or S content (Schöniger method); the typical detectability limit was 0.2 wt.%. In addition, we obtained X-ray diffractograms (Bruker D8 Discover, 1.54 Å radiation) for samples sealed in quartz glass capillaries of 0.3 or 1.0 mm diameter (Hilgenberg, Germany), FT-IR spectra (Bruker, vacuum V80 model) for selected pre- and post-reaction samples in the solid state, and MS spectra with EI ionization or, occasionally, by ESI technique (AMD 604, AMD Intectra and Mariner Biospectrometry Workstation by PerSeptive Biosystems, respectively) for a few solid and liquid samples. Raman spectroscopy was sometimes used (Jobin Yvonne, T64000 spectrometer equipped with an Ar/Kr ion laser (488.0, 514.5 or 647.1 nm excitation) and an optical microscope (focal length 50 mm), providing a lateral resolution of the optical image of the examined surface of 1 mm. Selected samples were subjected to thermogravimetry (TGA) and differential scanning calorimetry (DSC) analysis (Netzsch STA 409 PG) with a simultaneous analysis of evolved gas (EGA) encompassing FT-IR (Bruker V80) and QMS (Pfeiffer-Vacuum, Aëolos 403 C) of gaseous products. The spectrometers were connected to a TGA/DSC analyzer using a quartz capillary (MS) or Teflon® pipe (FT-IR), both preheated to 200 °C to avoid condensation of solids. The samples were exposed to atmosphere for a short time before high-resolution MS, elemental analysis and TGA/DSC measurements; in all other cases samples were protected from atmospheric oxygen and moisture.

*NOTE. CBr$_4$ and in particular CI$_4$ are thermodynamically unstable. Reactions of these compounds with AgF$_2$ may result in explosion even if milligram amounts of the chemicals are used. Utmost care is advised while performing these reactions. The violent reaction of the CF$_3$COOK and AgF$_2$ mixture also generates large amounts of gases upon heating and should not be performed in a tightly closed container.*

Standard enthalpies of chemical reactions have been calculated using data available in the literature[8].

## RESULTS AND DISCUSSION

### Compounds and Functional Groups Studied

The forty six highly-fluorinated or perfluorinated organic compounds studied can be categorized into several distinct classes:

*1*. Aromatic hydrocarbons: benzene (C$_6$F$_6$).

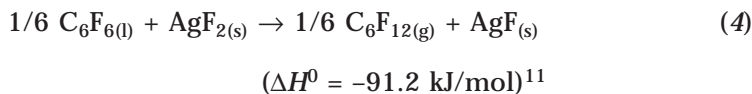*2*. Aliphatic and aromatic aza, oxa and phosphorus Lewis bases:

*2a*. aza bases: pyridine ($C_5F_5N$), *p*-bromopyridine (4-Br-$NC_5F_4$), 1,3,5-tri-azine ($C_3F_3N_3$), triethylamine ($(C_2F_5)_3N$);

*2b*. phosphorus bases: triphenylphospine ($(C_6F_5)_3P$);

*2c*. oxa bases: 2-*tert*-butyltetrahydrofurane ($C_8F_{16}O$), 15-crown-5 ether ($C_{10}F_{20}O_5$).

3. Halogenated aliphatic and aromatic hydrocarbons:

   *3a*. fluoro derivatives (*c*-$C_{12}F_{24}$, *n*-$C_{12}F_{26}$, *n*-$C_{14}F_{30}$);

   *3b*. chloro derivatives ($CCl_4$, $C_2Cl_4$, $C_2Cl_6$, *c*-$C_6Cl_6$, $C_5Cl_5N$);

   *3c*. bromo and mixed bromo-chloro derivatives ($CBr_4$, $CBrCl_3$, $Br_3CCF_3$, 1,4-$Br_2$-*n*-$C_4F_8$, *p*-$C_6F_4$-$Br_2$);

   *3d*. iodo derivatives ($CI_4$, 1,4-$I_2$-*n*-$C_4F_8$, *p*-$C_6F_4$-$I_2$).

4. Aliphatic and aromatic nitriles: (*n*-$C_8F_{17}CN$, $C_6F_5CN$, $CCl_3CN$).

5. Alcohols and phenols: ($(CF_3)_3COH$, $C_6F_5OH$).

6. Carboxylic acids: ($CF_3COOH$).

7. Sulfonic acids: ($CF_3SO_3H$, *n*-$C_4F_9SO_3H$, *n*-$C_8F_{17}SO_3H$).

8. Amides and imides of carboxylic and sulfonic acids: ($CF_3CONH_2$, $(CF_3SO_2)_2NH$).

9. Potassium salts of carboxylic and sulfonic acids and of their imides: ($CF_3COOK$, $(CF_3)_3COK$, $CF_3SO_3K$, *n*-$C_8F_{17}SO_3K$, $(CF_3SO_2)_2NK$).

10. Quinones: (*p*-$C_6F_4O_2$, *p*-$C_6F_4[=C(CN)_2]$, $[=C(CN)_2]_2$).

11. Other compounds: ($C_6F_5NO_2$, *n*-$C_8F_{17}SO_2F$, $C_6F_5NCS$).

It should be realized that we have accessed reactions between $AgF_2$ and organic compounds from the point of view of inorganic chemistry. We are searching for organic ligands which might, under certain conditions, form organic-inorganic hybrid compounds with $AgF_2$, similar to those prepared for uranium and thorium fluorides (UFO and TFO)[9]. Thus our major goal was to determine which functional groups are (at least kinetically) inert to $AgF_2$. We treated all the organic compounds studied here as potential reducing agents and were interested in whether $AgF_2$ can be reduced at ambient or elevated temperature ('Yes'/'No') without further investigation of the organic products if indeed the reaction took place; the cases of 'no reaction' were of most interest to us. Therefore, in this contribution we have not described a majority of the analytical results that support the final conclusions; only the most interesting results are discussed in more detail[10].
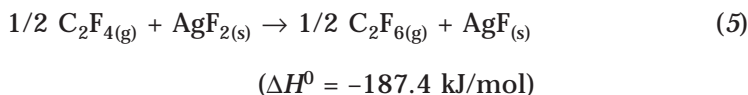
*1*. Aromatic Hydrocarbons: Benzene ($C_6F_6$)

Liquid $C_6F_6$ is inert to $AgF_2$ and it may be distilled over it without undergoing decomposition to a noticeable degree. The inertness of $C_6F_6$ is of purely
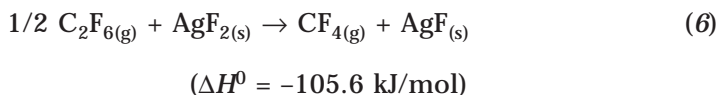
kinetic nature; the calculated standard enthalpy of the fluorination reaction is negative and large.

$$1/6 \ C_6F_{6(l)} + AgF_{2(s)} \rightarrow 1/6 \ C_6F_{12(g)} + AgF_{(s)} \qquad (4)$$

$$(\Delta H^0 = -91.2 \ \text{kJ/mol})[11]$$

Indeed, analysis of thermodynamic parameters suggests that AgF$_2$ should be capable of fluorinating not only C$_6$F$_6$, but also any unsaturated perfluorinated hydrocarbon

$$1/2 \ C_2F_{4(g)} + AgF_{2(s)} \rightarrow 1/2 \ C_2F_{6(g)} + AgF_{(s)} \qquad (5)$$

$$(\Delta H^0 = -187.4 \ \text{kJ/mol})$$

and, which is even more impressive, of any perfluorinated aliphatic hydrocarbon.

$$1/2 \ C_2F_{6(g)} + AgF_{2(s)} \rightarrow CF_{4(g)} + AgF_{(s)} \qquad (6)$$

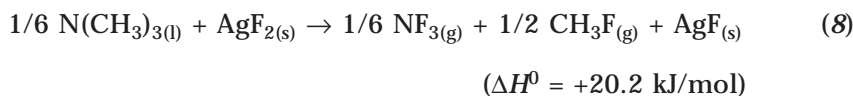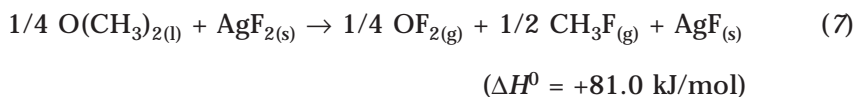$$(\Delta H^0 = -105.6 \ \text{kJ/mol})$$

The behavior of AgF$_2$ contrasts surprisingly with that of Ni$_2$F$_5$, which is a weaker oxidizing agent, and yet is capable of generating a radical cation from C$_6$F$_6$, and of quantitative fluorination of CF$_2$=CF–CF$_3$ [12]. This finding also suggests that further tests of the redox properties of AgF$_2$ could involve not only perfluorinated aliphatic but also perfluorinated aromatic compounds, without high risk of attack of AgF$_2$ on an aromatic moiety. As we will see from the next sections, our surmise is supported in all cases but one.

*2.* Aliphatic and Aromatic Aza, Oxa and Phosphorus Lewis Bases

Perfluorinated pyridine (C$_5$F$_5$N), p-bromopyridine (*p*-Br-NC$_5$F$_4$), 1,3,5-triazine (*c*-C$_3$F$_3$N$_3$), triethylamine ((C$_2$F$_5$)$_3$N), 2-*tert*-butyltetrahydrofurane (C$_8$F$_{16}$O) and 15-crown-5 ether (C$_{10}$F$_{20}$O$_5$) do not react with AgF$_2$ under experimental conditions. These aza and oxa Lewis bases are thus much more inert than the inorganic nitride and oxide derivatives; the latter are vigorously oxidized with AgF$_2$ [13,14]. The inertness of the Lewis bases studied here is due to (i) a large induction effect of the electron-withdrawing CF$_n$ groups and (ii) an inherent resistance of the C–O and C–N bonds to fluorination;

cleavage of these bonds leads to the thermodynamically unstable $OF_2$ and to the moderately stable $NF_3$ derivative.

$$1/4 \; O(CH_3)_{2(l)} + AgF_{2(s)} \rightarrow 1/4 \; OF_{2(g)} + 1/2 \; CH_3F_{(g)} + AgF_{(s)} \quad (7)$$

$$(\Delta H^0 = +81.0 \text{ kJ/mol})$$

$$1/6 \; N(CH_3)_{3(l)} + AgF_{2(s)} \rightarrow 1/6 \; NF_{3(g)} + 1/2 \; CH_3F_{(g)} + AgF_{(s)} \quad (8)$$

$$(\Delta H^0 = +20.2 \text{ kJ/mol})$$

It is disappointing that these ligands do not form any coordination complexes with $AgF_2$ under experimental conditions. This may be partly due to slow kinetics, since such reactions involve destruction of the 3D network of solid $AgF_2$ with its large lattice energy of 2942 kJ/mol [15].

Perfluorinated triphenylphosphine is a completely different story. This compound sublimes at about 116 °C (white fumes) and simultaneously reacts with $AgF_2$ in an exothermic reaction yielding a grayish solid residue. The mass spectrum of the product (Fig. 1) reveals the presence of peaks which can be assigned to $(C_6F_5)_3PF$ and $(C_6F_5)_2PF_2$ radicals and to their fragmentation products. The lone pair at soft trivalent phosphorus proves to be too susceptible to oxidation to resist the action of $AgF_2$.

Although $(C_6F_5)_3P$ is fluorinated via an attack of $AgF_2$ on the lone pair at trivalent P, the complete reaction leading to $(C_6F_5)_3PF_2$

$$1/2 \; P(C_6F_5)_{3(g)} + AgF_{2(s)} \rightarrow 1/2 \; F_2P(C_6F_5)_{3(g)} + AgF_{(s)} \quad (9)$$
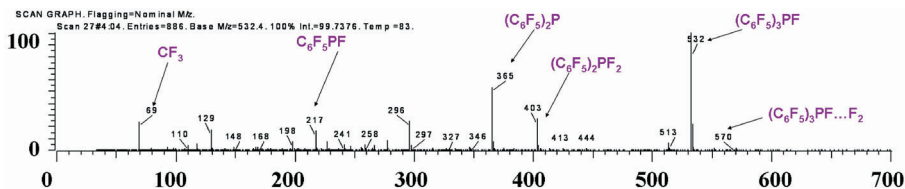


FIG. 1
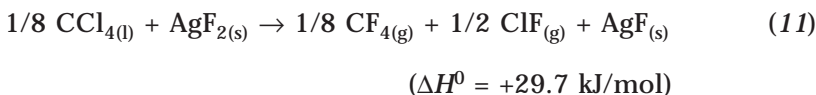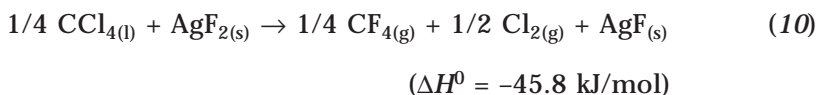The EI mass spectrum of the solid product of the reaction between $P(C_6F_5)_3$ and $AgF_2$

is probably prohibited due to large steric hindrance of P. This poses an interesting question whether hypothetical $F_2P(C_6F_5)_3$ might be stable and possess an ionic nature, $[F^-\cdots FP^+(C_6F_5)_3]$ analogous to $PMe_4F$ [16] and in contrast to the well known $PF_5$.

### 3. Halogenated Aliphatic and Aromatic Hydrocarbons

The fluorocarbons $c$-$C_{12}F_{24}$, $n$-$C_{12}F_{26}$ and $n$-$C_{14}F_{30}$ sublime at 51, 75 and 103 °C, respectively, and no reaction with AgF$_2$ can be detected. Interestingly, and despite the 2D puckered-sheet nature of AgF$_2$, these inert fluorocarbons cannot be incorporated between the AgF$_2$ sheets to form an inorganic-organic hybrid compound.
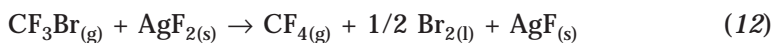
Aliphatic and unsaturated chloro derivatives ($CCl_4$, $C_2Cl_6$, $C_2Cl_4$) behave similarly to the fluoro analogues and do not react with AgF$_2$ to any appreciable extent[17]; $CCl_4$ and $C_2Cl_4$ can be boiled over AgF$_2$ while $C_2Cl_6$ can be melted at 195 °C in its presence. The inertness of these compounds is certainly of kinetic nature, since thermodynamics favours the following reactions.
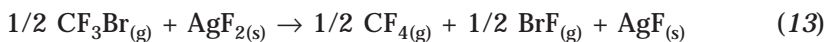
$$1/4\ CCl_{4(l)} + AgF_{2(s)} \rightarrow 1/4\ CF_{4(g)} + 1/2\ Cl_{2(g)} + AgF_{(s)} \tag{10}$$

$$(\Delta H^0 = -45.8\ \text{kJ/mol})$$

$$1/8\ CCl_{4(l)} + AgF_{2(s)} \rightarrow 1/8\ CF_{4(g)} + 1/2\ ClF_{(g)} + AgF_{(s)} \tag{11}$$

$$(\Delta H^0 = +29.7\ \text{kJ/mol})$$

These reactions are favoured due to the beneficial entropy factor, which drives $\Delta G^0$ negative (–13.9 kJ/mol) for reaction (*11*). Thermodynamic parameters for analogous reactions involving the $CF_3Cl$ substrate are similar to those for $CCl_4$; the monochloro perfluorinated hydrocarbons are expected to behave similarly to $CCl_4$.

Aromatic chloro derivative ($C_6Cl_6$) is more susceptible to fluorination and it reacts with AgF$_2$ at 150 °C before its melting temperature (227 °C) is reached. The yellow-orange AgF results together with colorless organic products; the latter have not been studied in detail (color suggests that aromaticity is preserved and no radical cations are generated). In contrast to $C_6Cl_6$, $NC_5Cl_5$ may be melted at 122 °C in presence of AgF$_2$ without noticeable decomposition.

Perfluorinated bromo derivatives ($Br_3CCF_3$, 1,4-$Br_2$-$n$-$C_4F_8$, $p$-$C_6F_4$-$Br_2$) are not reactive to $AgF_2$ in contrast to non-fluorinated ones[5]. 1,4-$Br_2$-$n$-$C_4F_8$ can be boiled over $AgF_2$ (at 96 °C), while $p$-$C_6F_4$-$Br_2$ and $Br_3CCF_3$ can be melted in the presence of $AgF_2$ ($T_m$ = 80 and 157 °C, respectively). As in the case of the chloro derviatives, the kinetic inertness works here against favourable thermodynamics of fluorination reactions.

$$CF_3Br_{(g)} + AgF_{2(s)} \rightarrow CF_{4(g)} + 1/2\ Br_{2(l)} + AgF_{(s)} \tag{12}$$

$$(\Delta H^0 = -64.3\ \text{kJ/mol})$$

$$1/2\ CF_3Br_{(g)} + AgF_{2(s)} \rightarrow 1/2\ CF_{4(g)} + 1/2\ BrF_{(g)} + AgF_{(s)} \tag{13}$$

$$(\Delta H^0 = -15.9\ \text{kJ/mol})$$

$CBr_4$ in the solid state is a distinct case as it spontaneously evolves characteristic red fumes of $Br_2$ when mixed with $AgF_2$ at room temperature. The reaction which takes place at the solid–solid interface, is largely due to the lack of thermodynamic stability of $CBr_4$. $CBr_4$ is composed of sterically crowded molecules and it tends to decompose to $C_2Br_6$ and $Br_2$ upon heating or a photochemical excitation[18]. The spontaneous decomposition reaction may require radical initiation, and $Ag^{2+}$ with its $4d^9$ electronic configuration, serves excellently for this purpose. The mixed bromo-chloro derivative $BrCCl_3$ shares a similar fate to $CBr_4$; the organic liquid immediately becomes dark red when poured over $AgF_2$. The organic products of both fluorinations have not been studied.

The iodo derivatives are supposed to be the most susceptible to $AgF_2$ amongst all organic halo derivatives. Indeed, liquid 1,4-$I_2$-$n$-$C_4F_8$ spontaneously reacts with $AgF_2$ at room temperature yielding orange product(s), while $p$-$C_6F_4I_2$ does so upon moderate heating to its melting temperature (85 °C). Non-stoichiometric $Ag(F_xI_{1-x})_{\sim1}$ is formed in both cases as an inorganic product, as confirmed by XRDPs. A noticeable depletion of iodine content can be noticed which suggest that some I-carrying volatile product is generated (IF, $IF_3$?). Perfluorination of the organic backbone is not sufficient to prevent the soft iodine atom from being attacked by the $AgF_2$ oxidizer. Fluorination of the lone pairs on I as well as the cleavage of the C–I bond are viable scenarios; the C–I bond is known to undergo a facile cleavage ($C^\bullet + I^\bullet$) if catalyzed thermally or by copper species, which is utilized in C–C coupling reactions[19].

CI$_4$ (Fig. 2B), the heavier and thermodynamically unstable analogue of CBr$_4$ [18] reacts vigorously with AgF$_2$ without additional thermal initiation (Fig. 2D). Use of the freshly prepared AgF$_2$ leads to an explosion with evolution of characteristic violet fumes of I$_2$. It is anticipated that, similarly to CBr$_4$, CI$_4$ may auto-decompose if triggered by the Ag$^{2+}$ radical. The reaction product (Fig. 2C) contains a mixture of black carbon deposits, and yellowish-orange nonstoichiometric Ag(F$_x$I$_{1-x}$)$_{\sim 1}$.

Use of surface-contaminated or partly-decomposed (less reactive) AgF$_2$ results in a milder and slower reaction, the substrates being converted within one day to nearly colorless slightly yellowish products (AgF, C$_2$I$_6$?) and despite the fact that reaction may occur exclusively via slow diffusion of reagents at the solid-solid interface.

## 4. Aliphatic and Aromatic Nitriles

The perfluorinated aliphatic nitrile, $n$-C$_8$F$_{17}$CN, does not react with AgF$_2$ to a detectable extent, even if boiled over AgF$_2$ at ca. 160 °C. This is interesting, since analysis of the thermodynamic parameters for two model reactions between CH$_3$CN and AgF$_2$ is following
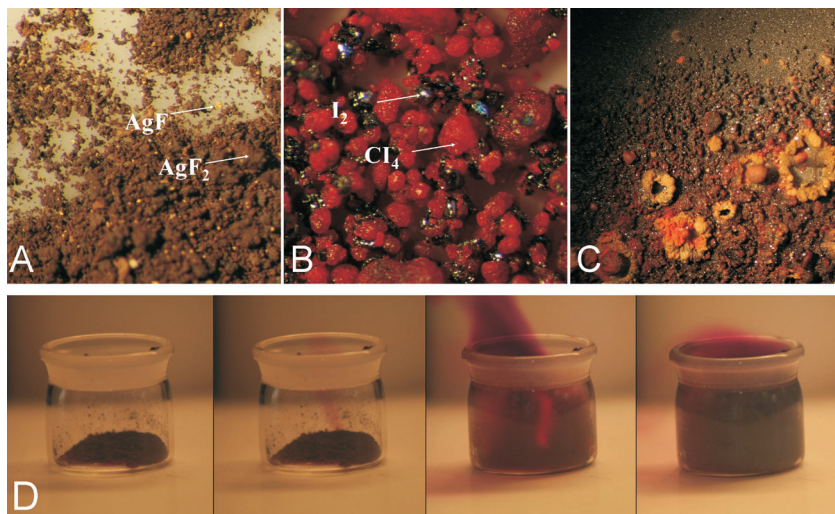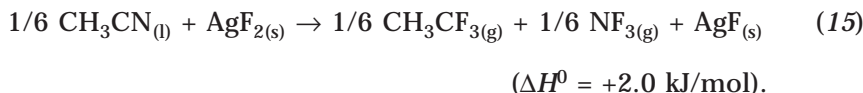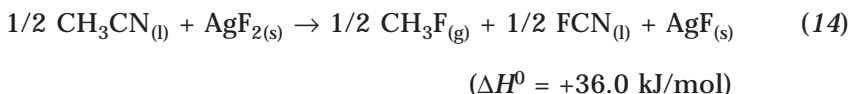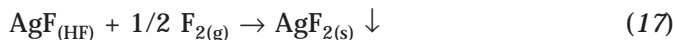


FIG. 2
The progress of reaction (D) between AgF$_2$ (A) and CI$_4$ (B); the reaction products (C)

$$1/2 \ CH_3CN_{(l)} + AgF_{2(s)} \rightarrow 1/2 \ CH_3F_{(g)} + 1/2 \ FCN_{(l)} + AgF_{(s)} \quad (14)$$

$$(\Delta H^0 = +36.0 \ \text{kJ/mol})$$

$$1/6 \ CH_3CN_{(l)} + AgF_{2(s)} \rightarrow 1/6 \ CH_3CF_{3(g)} + 1/6 \ NF_{3(g)} + AgF_{(s)} \quad (15)$$

$$(\Delta H^0 = +2.0 \ \text{kJ/mol}).$$

The reactions are thermodynamically feasible due to the beneficial entropy factor of gaseous reagents ($\Delta G_0$ equals –17.7 and –36.2 kJ/mol, respectively). It is unclear whether perfluorination may result in an inductive effect large enough to turn $\Delta G^0$ of reactions (*14*) and (*15*) positive. Unfortunately, the thermodynamic data for $CF_3CN_{(g)}$ required to verify this hypothesis are not available in the literature. Similarly to perfluorinated aza and oxa Lewis bases (Section *2.*), we did not observe formation of coordination compounds of a nitrile with $AgF_2$. This may be due to reduced ligation capability of a perfluorinated nitrile compared to the non-fluorinated one[20], as well as due to substantial kinetic barriers for reactions involving bulk $AgF_2$. It would be interesting to check inertness of perfluorinated nitriles and dinitriles towards fluorination and their capacity to form organic/inorganic hybrids with $AgF_2$, using an in situ generated $AgF_2$. Regrettably, simple reactions leading to this valuable reagent

$$Ag(SbF_6)_{2(s)} + 2 \ KF_{(HF)} \rightarrow K_2SbF_{6(HF)} + AgF_{2(s)} \downarrow \quad (16)$$

$$AgF_{(HF)} + 1/2 \ F_{2(g)} \rightarrow AgF_{2(s)} \downarrow \quad (17)$$

are most often performed in anhydrous liquid HF, which efficiently reacts with nitriles according to Eq. (*18*)

$$R-C \equiv N + 2 \ HF \rightarrow R-CF_2-NH_2 . \quad (18)$$

The perfluorinated aromatic nitrile, $C_6F_5CN$, reacts with $AgF_2$ at room temperature, i.e. behaves very differently from the aliphatic analogue. The originally colorless liquid becomes cloudy and a white gel residues formed with the simultaneous evolution of small amounts of an unidentified gas.

The white product becomes light pink or yellow when the reaction is allowed to take place over several hours. The solid product does not evaporate at elevated temperatures which suggests that its molecular mass is much higher than that of the low-boiling organic substrate (b.p. 107 °C). The physical appearance and color of the product crucially depends on the reagent ratio and temperature, which suggests that a free-radical polymerization takes place. Indeed, peaks at *m/z* 195 and 212 have been detected in the mass spectra of the post-reaction mixture (Fig. 3). They may be ascribed to the radicals C$_6$F$_6$CN$^{\bullet}$ and C$_6$F$_5$N$_2$$^{\bullet}$, respectively.

The presence of C$_6$F$_6$CN$^{\bullet}$ amongst the reaction products is not surprising, since facile fluorination of organic nitriles in the α position is well known (Fig. 4)[21]. However, the appearance of a strong signal assigned to C$_6$F$_5$N$_2$$^{\bullet}$ (a species with two N atoms) suggests that substantial intramolecular rearrangement takes place (the carbon atom from the nitrile group is expelled from the molecule, Fig. 4) following the bimolecular reaction.

The complex reaction between AgF$_2$ and C$_6$F$_5$CN is possibly of interest to organic chemists; for our purposes it suffices to know that perfluorinated aromatic nitriles cannot be used for construction of organic-inorganic hybrids featuring AgF$_2$ and, therefore, we have not studied this reaction in more detail.
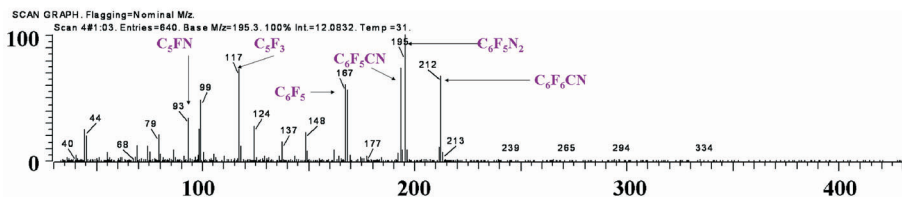


FIG. 3
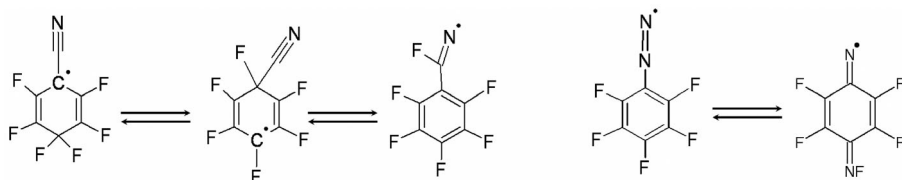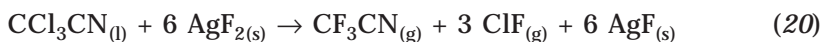The EI mass spectrum of the solid product of the reaction between C$_6$F$_5$CN and AgF$_2$



FIG. 4
Various constitutional isomers of C$_6$F$_6$CN$^{\bullet}$ (left) and of C$_6$F$_5$N$_2$$^{\bullet}$ (right)

The perchlorinated acetonitrile $CCl_3CN$ is another interesting case. This liquid reacts instantly with $AgF_2$ with noticeable gas evolution. The reaction is exothermic, and even if reagents are cooled to –37 °C, the evolved heat may lead to boiling of the reaction mixture. The solution becomes orange-red and, after some time, an orange deposit of the insoluble non-stoichiometric $Ag(F_xCl_{1-x})_{\sim 1}$ forms. However, the mother liquor remains orange-red, which suggests the presence of a colored organic product. There is a significant depletion of N and Cl from the post-reaction $CCl_3CN$-containing mixture; its composition varies between $C_2N_{0.75}Cl_{1.55}$ and $C_2N_{0.75}Cl_{2.20}$ in two independent experiments (the F content was not determined) which suggests evolution of volatile nitrogen- and chlorine-containing products. It is very likely that the C–Cl bonds are cleaved by $AgF_2$ together with the C–C bond, since the C:Cl ratio is significantly decreased in this reaction. Two simplified (limiting) reaction equations

$$CCl_3CN_{(l)} + 2\ AgF_{2(s)} \rightarrow CCl_3F_{(g)} + FCN_{(l)} + 2\ AgF_{(s)} \tag{19}$$

$$CCl_3CN_{(l)} + 6\ AgF_{2(s)} \rightarrow CF_3CN_{(g)} + 3\ ClF_{(g)} + 6\ AgF_{(s)} \tag{20}$$
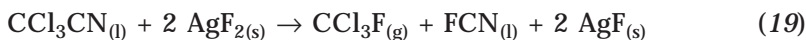
may be proposed to account for the experimental observations. It is interesting to note that AgF is not capable of fluorinating $CCl_3CN$ under the same conditions.

## 5. Alcohols and Phenols

$C_6F_5OH$ vigorously reacts with $AgF_2$ upon melting at 34 °C, resulting in an oily yellow-liquid and a solid yellowish-gray residues, which are not reactive to humidity, and in contrast to $AgF_2$ is soluble in MeOH. The MS analysis did not allow to identify organic substances other than the parent volatile $C_6F_5OH$, but the presence of $C_6F_5$–O–O–$C_6F_5$ peroxide or $C_6F_5O^•$ radical[22] cannot be ruled out (their fragmentations should yield similar MS peaks to those for $C_6F_5OH$). Concluding, a redox reaction takes place and monovalent silver is generated along with unidentified organic product(s).

$(CF_3)_3COH$, one of the few perfluorinated aliphatic alcohols stable under ambient conditions[23], exhibits an unusual inertness and it can be kept for a prolonged time, or boiled over $AgF_2$, without appreciable decomposition (b.p. 45 °C). The fluorination leading to $(CF_3)_3COF$ might be thermo-

dynamically feasible but very slow due to steric hindrance at the quaternary C atom.

*6. Carboxylic Acids*

Anhydrous CF$_3$COOH is readily attacked by AgF$_2$ under ambient conditions; the reaction leads to gas evolution (HF?) and to a colorless solid product, which is determined by elemental analysis and XRD to be CF$_3$COOAg. A simplified reaction equation may be proposed.

$$2 \text{ CF}_3\text{COOH}_{(l)} + \text{AgF}_{2(s)} \rightarrow \text{CF}_3\text{COO}^{\bullet}{}_{(g)} + 2 \text{ HF}_{(g)} + \text{CF}_3\text{COOAg}_{(s)} \quad (21)$$

It is unclear whether there are subsequent rearrangements and/or reactions involving CF$_3$COO$^{\bullet}$ radical and whether the C–C bond of CF$_3$COOH is also cleaved during these reactions. Formation of trifluoroacetic fluoride, CF$_3$COOF, cannot be excluded despite lack of thermodynamic stability of this species.
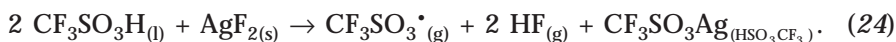
$$\text{CF}_3\text{COOF} \rightarrow \text{CF}_4 + \text{CO}_2 \quad (22)$$
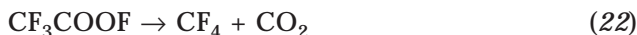
*7. Sulfonic Acids*

Perfluorinated sulfonic acids rank among the most redox-inert organic compounds known. AgF$_2$, however, is capable of oxidizing these and related species under certain conditions.

The prolonged reaction between CF$_3$SO$_3$H and AgF$_2$ at room temperature leads to paramagnetic brown (CF$_3$SO$_3$)$_2$Ag(II) (first reported in 1979[24]).

$$2 \text{ CF}_3\text{SO}_3\text{H}_{(l)} + \text{AgF}_{2(s)} \rightarrow 2 \text{ HF}_{(g)} + (\text{CF}_3\text{SO}_3)_2\text{Ag} \quad (23)$$
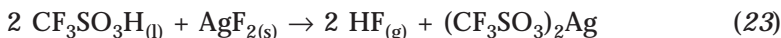
The solution becomes dense and oily, which corresponds to parallel redox reaction

$$2 \text{ CF}_3\text{SO}_3\text{H}_{(l)} + \text{AgF}_{2(s)} \rightarrow \text{CF}_3\text{SO}_3{}^{\bullet}{}_{(g)} + 2 \text{ HF}_{(g)} + \text{CF}_3\text{SO}_3\text{Ag}_{(\text{HSO}_3\text{CF}_3)}. \quad (24)$$

CF$_3$SO$_3{}^{\bullet}{}_{(g)}$ is in equilibrium with its dimer in the gas phase, while CF$_3$SO$_3$Ag can be recovered from the acid. If the reaction (*23*) is conducted at low

temperature (limited by the acid's melting point of –40 °C), high purity $(CF_3SO_3)_2Ag(II)$ can be obtained. Reaction (*24*) gains in importance as the temperature is increased, and at 170 °C (which is close to the boiling temperature of triflic acid) only $CF_3SO_3Ag$ can be recovered.

Higher sulfonic acids are oxidized with even greater ease, liquid $n\text{-}C_4F_9SO_3H$ is converted into $n\text{-}C_4F_9SO_3Ag$ within a day (only a small amount of Ag(II) compound could be recovered), while solid $n\text{-}C_8F_{17}SO_3H$ reacts similarly with $AgF_2$ upon melting at 90 °C.

Given the substantial inertness of $HSO_3F$ to oxidation with $AgF_2$ [13], the ranking of susceptibility of sulfonic acids towards oxidation is as follows

$$FSO_3H < CF_3SO_3H < n\text{-}C_4F_9SO_3H < n\text{-}C_8F_{17}SO_3H . \tag{25}$$

## 8. Amides and Imides of Carboxylic and Sulfonic Acids

Trifluoroacetamide, $CF_3CONH_2$, and the imide of the triflic acid, $(CF_3SO_2)_2NH$, react slowly with $AgF_2$ upon melting (at 65 and ca. 50 °C, respectively), yielding AgF and unidentified organic products (formation of the N–F bond is likely).

## 9. Potassium Salts of Carboxylic and Sulfonic Acids of Their Imides and of Alcoholates

The propensity of carboxylic and sulfonic acids to oxidation is at least in part driven by the substantial thermodynamic stability of gaseous HF. It is, therefore, of interest whether the potassium salts of these acids react similarly in the presence of $AgF_2$.

It turns out that $CF_3COOK$ reacts explosively with $AgF_2$ yielding large amounts of gaseous products and a small amount of yellowish-black solid residue. Reactions similar to (*21*) and (*22*) are anticipated.

In turn, $CF_3SO_3K$ and $n\text{-}C_8F_{17}SO_3K$ are quite inert to $AgF_2$, even during prolonged heating at temperatures as high as 200 °C. This renders them similar to $KSO_3F$ [13], but contrasts with the behaviour of the corresponding acids. Such behaviour confirms a general rule that oxidizing properties are reduced in the basic environment and suggests that one might even attempt synthesis of $MAgF_2L$, $M_2AgF_2L_2$, $MAgL_3$, and $M_2AgL_4$ salts, where M is alkali metal and L anion of a sulfonic acid. These hypothetical pseudo-

ternary salts should be more thermally stable than the corresponding pseudobinary AgL$_2$ compounds[25].

Having studied potassium salts of the acids, we have turned to salts of rather acidic triflic imide and, less so, perfluorinated *tert*-butyl alcohol. (CF$_3$SO$_2$)$_2$NK does not react with AgF$_2$ to an appreciable extent, but when its melting temperature of 187 °C is reached, a non-quantitative redox reaction occurs in which AgF$_2$ is reduced to a nonstoichiometric dark yellow AgF. The small conversion is, however, remarkable. The (CF$_3$SO$_2$)$_2$N$^-$ anion must be viewed as one of the imides least susceptible to oxidation, and there is a good prospect for the synthesis of novel Ag(II)(CF$_3$SO$_2$)$_2$N$^-$ compounds. The undesired redox reaction

$$(CF_3SO_3)_2NK_{(l)} + 2\ AgF_{2(s)} \rightarrow (CF_3SO_3)_2NF_{(?)} + KF_{(s)} + 2\ AgF_{(s)} \qquad (26)$$

could possibly be avoided at low temperatures.

(CF$_3$)$_3$COK is inert to AgF$_2$ at ambient temperature but when it sublimes at ca. 150–170 °C, a light-brown-yellowish mixture results, which contains some amount of AgF. It must be said that the (CF$_3$)$_3$CO$^-$ anion is remarkably resistant to fluorination compared to other alcoholates.

### 10. Quinones

Tetracyanoethylene (TCNE, [=C(CN)$_2$]$_2$) and perfluorinated quinones such as *para*-benzoquinone (*p*-C$_6$F$_4$O$_2$ also called fluoranil) and tetracyanoquinodimethane (*p*-C$_6$F$_4$[=C(CN)$_2$], i.e. F$_4$-TCNQ) rank among the most powerful organic oxidizing agents known. They are capable of two subsequent one-electron reductions, must be handled in anhydrous conditions, and they form colored charge-transfer salts with organic electron donors and ionic salts with alkali metals.

*p*-C$_6$F$_4$O$_2$ proves to be inert to AgF$_2$ even at its sublimation temperature (180 °C); a very small AgF$_2$/AgF conversion was observed. On the other hand, *p*-C$_6$F$_4$[=C(CN)$_2$] cannot be sublimed (*T*$_S$ = 285 °C) in the presence of AgF$_2$; a redox reaction takes place at ca. 190 °C leading to AgF and a black unidentified product. TCNE behaves in a similar fashion, yielding AgF and a black glassy product only at 200 °C. Additional analyses are now being conducted in our laboratory to identify the glassy organic products of these reactions.

In conclusion, three classical organic electron acceptors, TCNE, $F_4$-TCNQ and $p$-$C_6F_4O_2$, prove to be remarkably resistant to the action of $AgF_2$; they are fluorinated only at temperatures as high as 180–200 °C.

## 11. Other Compounds

$C_6F_5NO_2$ and $n$-$C_8F_{17}SO_2F$ are inert to $AgF_2$; these chemicals can be distilled over $AgF_2$ (b.p. at ca. 155–160 °C) without decomposition. They might be utilized as, for example, mulling agents, while measuring the IR and/or UV-VIS spectra of various Ag(II)-containing samples.

$C_6F_5NCS$ reacts very slowly with $AgF_2$ at room temperature, but much faster upon heating to 100–115 °C, forming a black solid residue, which is not very sensitive to atmospheric moisture or oxygen (Fig. 5). This feature suggests that the product does not contain divalent silver. Indeed, elemental analysis (S content) and XRD (Fig. 5) confirms that the product is essentially pure monoclinic $Ag_2S$.
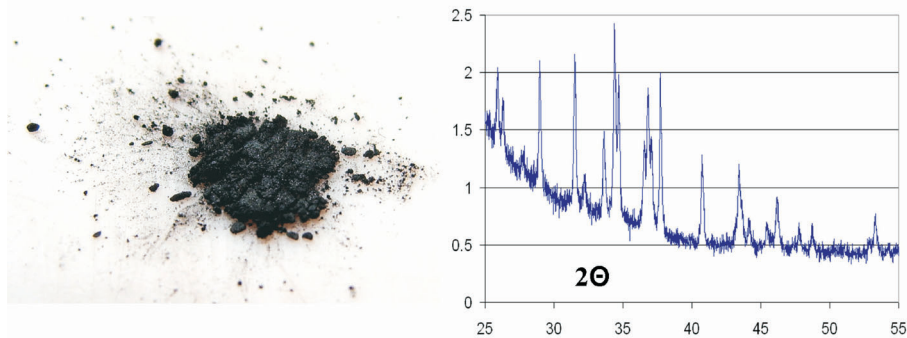


FIG. 5
Black product of the reaction between $AgF_2$ and $C_6F_5NCS$ (left) and its XRDP (right)

### CONCLUSIONS

The divalent state is in many ways an unusual oxidation state for silver (see ref.[1], where properties and structures of higher silver fluorides have been reviewed). In this work we have scrutinized reactions of $AgF_2$, the binary representative of Ag(II) compounds, and 46 distinct organic chemicals; 8 of these reagents are capable of reducing $AgF_2$ at ambient temperature, 15 do so at elevated temperature (usually at their melting or boiling point), and the remaining 23 are inert to $AgF_2$ under the experimental conditions.

Carbon–element (C–E) bonds and lone pairs on the E atom are thermodynamically resistant to the action of AgF$_2$ for the most electronegative elements E coming from Period 2 (E = N, O, and obviously F). Compounds with heavier Period 3 atoms (P and S), react vigorously with AgF$_2$, while the remarkable inertness of Cl is of purely kinetic nature; the behaviour of heavier Group 15 and 16 elements is likely to be similar to that of P and S. Br from Period 4 is an intermediate case, with some reactions taking place and some not, while I is extremely reactive in all connections to C.

Interestingly, none of the perfluorinated Lewis bases, which are redox-inert to AgF$_2$, form coordination compounds with it. New approaches are needed to generate AgF$_2$-based inorganic/organic hybrid materials of varying dimensionality, similar to those formed by uranium and thorium fluorides.

**NOTE ADDED IN PROOF**

While this paper was in proof we have confirmed that CCl$_2$F–CClF$_2$ liquid is inert to AgF$_2$ at ambient temperature (similarly to many other chlorinated saturated hydrocarbons) whereas yellow chloranile reacts with AgF$_2$ only at its melting temperature (260 °C) leading to AgF and unidentified organic products.

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17. It cannot be excluded that the Cl/F ligand exchange may take place to a slight degree, since we have observed that $AgF_2$ which had been kept under $CCl_4$ and then dried was much more prone to photochemical decomposition than the parent $AgF_2$.

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