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Inorganic Chemistry

Communications

Chemical Synthesis of Elemental Fluorine

Sir:

The chemical synthesis[1] of elemental fluorine has been pursued for at least 173 years[2] by many notable chemists, including Davy,[2] Fremy,[3] Moissan,[4] and Ruff.[5] All their attempts have failed, and the only known practical synthesis of F_2 is Moissan's electrochemical process, which was discovered exactly 100 years ago.[6]

Although in principle the thermal decomposition of any fluoride is bound to yield fluorine, the required reaction temperatures and conditions are so extreme that rapid reaction of the evolved fluorine with the hot reactor walls preempts the isolation of significant amounts of fluorine. Thus, even in the well-publicized case of K_3PbF_7,[7,8] only trace amounts of fluorine were isolated.[5,9]

These failures, combined with the fact that fluorine is the most electronegative element and generally exhibits the highest single bond energies in its combinations with other elements,[10] have led to the widely accepted[11-15] belief that it is impossible to generate fluorine by purely chemical means.

The purpose of this communication is to report the first purely chemical synthesis of elemental fluorine in significant yield and concentration. This synthesis is based on the fact that thermodynamically unstable high-oxidation-state transition-metal fluorides can be stabilized by anion formation. Thus, unstable NiF_4, CuF_4, or MnF_4 can be stabilized in the form of their corresponding MF_6^{2-} anions. Furthermore, it is well-known that a weaker Lewis acid, such as MF_4, can be displaced from its salts by a stronger Lewis acid, such as SbF_5.

$$K_2MF_6 + 2SbF_5 \rightarrow 2KSbF_6 + [MF_4] \qquad (1)$$

If the liberated MF_4 is thermodynamically unstable, it will spontaneously decompose to a lower fluoride, such as MF_3 or MF_2, with simultaneous evolution of elemental fluorine.

$$[MF_4] \rightarrow MF_3 + {}^1/{}_2F_2 \qquad (2)$$

Since a reversal of (2) is thermodynamically not favored, fluorine can be generated even at relatively high pressures.

Consequently, the chemical generation of elemental fluorine might be accomplished by a very simple displacement reaction, provided a suitable complex fluoro anion is selected which can be prepared without the use of elemental fluorine and is derived from a thermodynamically unstable parent molecule. The salt selected for this study was K_2MnF_6. It has been known[16] since 1899 and is best prepared from aqueous HF solution.[17]

$$2KMnO_4 + 2KF + 10HF + 3H_2O_2 \xrightarrow{50\%\ \mathrm{aq\ HF}} 2K_2MnF_6\downarrow + 8H_2O + 3O_2 \qquad (3)$$

The literature yield of 30% was increased to 73% and can probably be improved further by refining the washing procedure (use of acetone instead of HF).[18] The other starting material, SbF_5, can be prepared[19] in high yield from $SbCl_5$ and HF.

$$SbCl_5 + 5HF \rightarrow SbF_5 + 5HCl \qquad (4)$$

Since both starting materials, K_2MnF_6 and SbF_5, can be readily prepared without the use of F_2 from HF solutions, the reaction

$$K_2MnF_6 + 2SbF_5 \rightarrow 2KSbF_6 + MnF_3 + {}^1/{}_2F_2 \qquad (5)$$

represents a truly chemical synthesis of elemental fluorine.

The displacement reaction between K_2MnF_6 and SbF_5 was carried out in a passivated Teflon–stainless-steel reactor at 150 °C for 1 h. The gas, volatile at −196 °C, was measured by *PVT* and shown by its reaction with mercury and its characteristic odor to be fluorine. The yield of fluorine based on (5) was found to be reproducible and in excess of 40% but most likely can be improved upon significantly by refinement of the experimental conditions. Fluorine pressures of more than 1 atm were generated in this manner.

In summary, the purely chemical generation of elemental fluorine can be achieved in high yield and concentration by a very simple displacement reaction between starting materials that can

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(1) In the context of this communication, the term "chemical synthesis of elemental fluorine" implies the generation of F_2 by purely chemical means and excludes either techniques such as electrolysis, photolysis, discharge, etc. or the use of elemental fluorine for the synthesis of any of the starting materials. The regeneration of fluorine from materials prepared from fluorine obviously is just a method for chemically storing but not for chemically generating fluorine.

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be prepared in high yields from HF solutions and have been known for 80 years or longer. As in the cases of noble gas[20] or $NF_4{}^+$[21] chemistry, the successful chemical synthesis of elemental fluorine demonstrates that one should never cease to critically challenge accepted dogmas.

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Electrochemical Generation of Iron(IV)-Oxo Porphyrins and Iron(IV)-Oxo Porphyrin π Cation Radicals

Sir:

With weakly basic ligands, such as chloride or perchlorate, the first electrochemical 1e oxidation of an iron(III)porphyrin is porphyrin-centered, resulting in the formation of an iron(III)-porphyrin π cation radical.[1] We were the first to show[2,3] that when the ligands are the strongly basic oxy anions, HO^- and CH_3O^-, the first electrochemical 1e oxidation is iron-centered, providing an iron(IV) porphyrin. In our investigations (dry CH_2Cl_2 solvent), potentials were determined by cyclic voltammetry, coulometry was determined by controlled-potential oxidation at the potentials corresponding to the CV peak positions, and the nature of the products was established by low-temperature spectroelectrochemistry and comparison of the spectra to those of known porphyrin species. In addition, the identification of electrochemically generated iron(IV) porphyrin species was verified by chemical conversion to known species at the same oxidation level. To obviate μ-oxo dimer formation all investigations employed (*meso*-tetrakis(2,6-disubstituted phenyl)porphinato)iron(III) hydroxide and methoxide salts. In this manner, we showed that (tetrakis(2,4,6-trimethylphenyl)porphinato)iron(III) hydroxide ((TMP)Fe^{III}OH) on 1e oxidation (+1.01 V)[4] provides an iron(IV) porphyrin ((TMP)Fe^{IV}O),[5] and the second 1e oxidation (+1.13 V) gives an iron(IV) porphyrin π-cation radical (($^{\bullet+}$TMP)Fe^{IV}O).

In a recent communication in this journal, Groves and Gilbert reexamined the electrochemistry of (TMP)Fe^{III}OH in wet CH_2Cl_2 saturated with Na_2CO_3.[6] Their results substantiated our original discovery that the first and third oxidation peaks observed with (TMP)Fe^{III}OH are for the formation of (TMP)Fe^{IV}O and ($^{2+}$TMP)Fe^{IV}O, respectively, but disputed the value of our second oxidation potential for the formation of ($^{\bullet+}$TMP)Fe^{IV}O. The two 1e oxidation potentials that they report are +1.01 and +1.40 V. They attributed our results to the presence of chloride ion impurity and to the absence of Na_2CO_3 and water. We show here that chloride ion is not present in our system; we provide additional data in support of our assignment of potentials for 1e oxidation of iron(IV) porphyrins to the corresponding iron(IV) porphyrin π cation radicals; and we show that the potential (+1.01 V)[6] assigned by Groves and Gilbert for the 1e oxidation of (TMP)Fe^{III}OH to (TMP)Fe^{IV}O is in actuality due to two 1e oxidations.

The following observations establish the absence of all chloride ion. In our experiments pure (TMP)Fe^{III}OH was used and the solvent and electrolyte system was devoid of chloride ion. Reactions were carried out at −71 °C where CH_2Cl_2 solvent does not undergo oxidation. In Figure 1 there is shown repetitive visible spectral scans of the first two sequential 1e oxidations of (TMP)Fe^{III}OH (conditions, positions of isosbestic points, peak heights, etc. provided in the caption). That the spectral changes of parts A and B of Figure 1 are associated with 1e oxidations follows from their generation by controlled-potential coulometry. From the isosbestic points there is seen to be no competitive change of ligand nor accumulation of intermediate. Inspection of Figure 1A reveals the absence of the spectral characteristics (absorbance at 380 and 510 nm) of (TMP)Fe^{III}Cl. Indeed, spectroelectrochemistry at −71 °C with (TMP)Fe^{III}Cl shows that 1e oxidation at 1.18 V is accompanied by a decrease in the Soret absorbance at 420 nm and an increase in absorbance at 398 nm with an isosbestic point at 528 nm. Additional evidence for the absence of chloride ion in our experiments is shown by the observation that the presence of trace concentrations (10^{-5}–10^{-4} M) of $[(n\text{-}C_4H_9)_4N^+][Cl^-]$ in a solution of (TMP)Fe^{III}OH results in a CV where the first oxidation is no longer reversible. Such is not the case with the CV's we have reported.[2,3] It is known[7] that the reduction of iron(III) porphyrin to iron(II) porphyrin is strongly influenced by the axial ligand. Employing (TMP)Fe^{III}OH, we find that the 1e-reduction potential is at −1.05 V while the potential for 1e reduction of (TMP)Fe^{III}Cl occurs at −0.75 V (dry CH_2Cl_2, 25 °C). The samples of (TMP)Fe^{III}OH employed in the electrochemical and spectroelectrochemical studies showed no evidence of a peak potential at −0.75 V. In our hands the electrochemical oxidations of (TMP)Fe^{III}OH have been found to be both chemically and electrochemically reversible.

Groves and Gilbert (working in a solvent composed of CH_2Cl_2 wet with water and saturated with Na_2CO_3) reported that the oxidation of (TMP)Fe^{IV}O to ($^{\bullet+}$TMP)Fe^{IV}O is irreversible and occurs at a higher potential (+1.40 V) than the potential (+1.14 V) for the (TMP)Fe^{III}Cl to ($^{\bullet+}$TMP)Fe$^{III}(Cl)_2$ oxidation. A CV similar to theirs, with the exception of the absence of the irreversible peak at +1.40 V, is obtained for (TMP)Fe^{III}OH in CH_2Cl_2 that has been wet by being passed through air-equilibrated alumina (Figure 2A). By simple visual observation of the CV, it might appear as though the first oxidation wave (1.01 V) represents a single 1e process, as they assumed. Controlled-potential coulometry (at 1.06 V) at −71 °C showed that there are two electrons ($n = 2.1 \pm 0.2$) associated with this wave. For the low-temperature controlled-potential coulometry, the system was first calibrated by using (TMP)Fe^{III}Cl. The coulometric oxidation was monitored by change of current measurement with time and also by running a CV when n is equal to 1. Therefore, the first oxidation wave must represent two 1e oxidations that are so close in potential that they cannot be distinguished by CV.[8] A possible explanation for

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(4) All potentials given in this paper are vs. a saturated caromel electrode (SCE). The potentials given by Groves and Gilbert are corrected to SCE by using the conversion factor in their paper.

(5) The nature of the oxo ligand is not known. Though the iron(IV)-oxo porphyrin is written as (TMP)Fe^{IV}O, the oxo ligand may be −OH or perhaps a second oxo ligand may be present since it is virtually impossible to free a polar organic solvent of all traces of water. In our previous publications (ref 2 and 3), we used the notation (TMP)Fe^{IV}OH.

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(8) There is no reason that two 1e oxidations so close in potential should resemble a 2e oxidation with CV. Bard and Faulkner (Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 233–235) point out that when the potential difference between two 1e processes is less than 100 mV the individual waves are merged into a broad wave. Also, they show that if the difference is 35.6 mV (theoretical), which occurs when there is no interaction between the redox groups on the substrate, then the observed wave has all the characteristics of a 1e transfer.

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