Fluorination in Molten Lithium Fluoride-Sodium Fluoride-Potassium Fluoride Eutectic: Synthesis of Platinum Hexafluoride

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Introduction

The use of molten salts as reaction media has been reviewed recently by Sundermeyer.[2] The fluorination of uranium(IV) in fluoride melts with elemental fluorine to form the volatile uranium hexafluoride has been developed into a process useful in nuclear technology.[3] It became of interest to us to extend this approach to the formation of more reactive and less stable volatile fluorides. It was decided to attempt the preparation of platinum hexafluoride[4] since it is believed[5] to be one of the least stable of the known hexafluorides. In addition, the present method for the preparation of PtF_6 involves ignition of platinum in a fluorine atmosphere,[4,6] a reaction which appears to be more difficult to develop into a continuous process than the fluorination in molten fluorides. It was clear from previous work[4] that rapid quenching of the products will be required in order to prevent the dissociation of PtF_6 into fluorine and a lower platinum fluoride.

Experimental Section

Equipment. In the molten fluoride reactor, shown schematically in Figure 1, the products are collected on the liquid nitrogen cooled surface directly above the melt. The reactor was constructed out of nickel. The eutectic and the material to be fluorinated were added through the one-inch pipe connecting the reactor to the trap. Fluorine was introduced through one of two 1/4" inlet tubes (the other tube served as a spare in case of plugging by the salt), about 2" below the surface of the melt. Inlet and outlet pressures were monitored using ACCO Helicoid 30-0-30 gauges. The reactor was wound with an eighteen-gauge nichrome wire heating element, using alumina cement for insulation. The temperature was measured with a chromel-alumel thermocouple, inserted in a 1/4" thermocouple well that extended below the liquid level in the reactor.
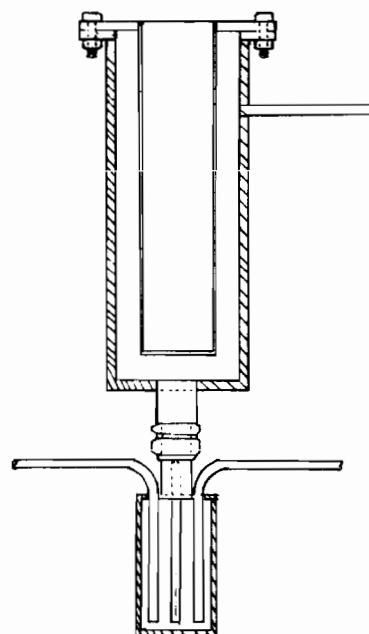

Figure 1. Molten fluoride reactor.

The reactor was joined to a vacuum system consisting of two nickel traps, an activated alumina trap for fluorine disposal, a Wallace and Tiernan Model FA 145 gauge and several connections to infrared cells or storage vessels. Prior to each run, the system was passivated with fluorine at 500°C by passing fluorine through the system at the pressure of 800 torr.

Materials. K_2PtCl_4, K_2PtCl_6 and $Pt(CN)_2$ were obtained from Alfa Inorganics, Inc. and used without further purification. LiF—NaF—KF eutectic (46.5–11.5–42.0 mole %) was obtained from the Reactor Chemistry Division, Oak Ridge National Laboratory. Fluorine, obtained from General Chemical Division, Allied Chemical Corporation, was passed through an activated sodium fluoride trap to remove hydrogen fluoride.

Analysis. The infrared spectra were obtained in a 10 cm cell equipped with silver chloride windows; Beckman IR-5A and Perkin-Elmer 337 infrared spectrometers were used.

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The solid in the first trap (see below) was decomposed with water (water was added to the sample at −196°C; the mixture was then warmed to room temperature), and reduced with hydrazine. Platinum was determined as the metal. Chloride ion was determined by anodic chronopotentiometry using a silver electrode. Fluoride was determined potentiometrically with an Orion fluoride ion electrode. The above methods were checked with standard samples.

Fluorination of K_2PtCl_4 and K_2PtCl_6. The nickel reactor was charged with 100 grams (2.4 moles) of LiF–NaF–KF, heated to 500°, and fluorinated at this temperature with a gas stream containing 50% fluorine and 50% helium to remove any residual impurities tained through the melt to prevent plugging. the reactor was charged with 0.250 grams (0.60 mmoles) of K_2PtCl_4 in the dry box, attached to the vacuum system, and checked for leaks. While the reactor was being heated to the desired temperature, it was constantly purged with helium at 720 torr pressure. At 460°, the helium was gradually displaced by a 50-50 mixture of fluorine and helium and the pressure was reduced to 150 torr at the inlet and 50 torr at the outlet. The flow rate, calculated from the pressure drop in the calibrated mixing and storage cylinder, was maintained between 75 to 100 cc/min. (STP). After one hour, the fluorine mixture was replaced by helium and the reactor was allowed to cool. The products were separated by low temperature distillation. The first trap, kept at −78°C during distillation, was found to contain a deep red gas and a yellow solid. The infrared spectrum of the gas is in agreement with the spectrum reported for PtF_6[7] (although the spectra of ClF_3,[8] ClF_5,[9] and PtF_6 have a certain similarity, PtF_6 may be distinguished from the two chlorine fluorides by the lack of absorption in the 730-800 cm^{-1} region). The chemical analysis of the yellow solid results in the empirical formula $PtClF_8$ (Calcd. for $PtClF_8$: Pt, 51.0; Cl, 9.27; F,

39.7. Found: Pt, 51.2; Cl, 8.8; F, 37.0). The compound is probably $ClF_2^+PtF_6^-$, reported previously.[6,10] The yield of PtF_6 was poor; no chemical analyses of PtF_6 were obtained. The second trap, kept at −196°C during distillation, contained predominantly ClF_3 and some ClF_5; the two fluorides were separated by gas chromatography (using a perfluorokerosene-Fluoropak 80 column) and identified by their infrared spectra.

In the experiments in which separation of products was not attempted, ClF_5 and $ClF_2^+PtF_6^-$ were formed. The pyrolysis of the solid ClF_2PtF_6 at 350°C resulted in the formation of the volatile ClF_3, F_2 (identified by its vapor pressure at −196°C and its reaction with mercury) and solid PtF_4; in agreement with previous resulted in the same products.

Fluorination of $Pt(CN)_2$. The same procedure as used for the chloroplatinates was employed. The more volatile products identified by their infrared spectra were nitrogen trifluoride[11] and carbon tetrafluoride.[12] The product collected at −78°C was again PtF_6.

Discussion

Apparently fluorination in the molten fluoride solvent results in the highest oxidation state of platinum known. The yield can probably be increased by decreasing the distance between the molten salt and the cold trap.

The oxidation of ClF_3 to ClF_5 by PtF_6 in experiments in which separation of products was not attempted, provides additional evidence[10] that platinum hexafluoride is a better oxidizing agent than chlorine trifluoride. The procedure employed in this work may be extended to the synthesis of other volatile fluorides. The use of melts with a lower liquidus temperature is presently being investigated.

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