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Complex Compounds of Uranium Hexafluoride with Sodium Fluoride and Potassium Fluoride[1,2]

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The reaction of UF_6 with NaF goes to completion rapidly if the NaF is suspended in an inert solvent, C_7F_{16}. Two compounds are formed, $NaUF_7$ and Na_2UF_8. Single crystals of Na_2UF_8 have been obtained. The Na_2UF_8 phase is body-centered tetragonal with $a = 5.27$ Å. and $c = 11.20$ Å. A model based on this symmetry and cell size leads to an eightfold coordination of fluorine atoms around each uranium atom, with all U–F distances equivalent. The preparation of the analogous compounds KUF_7 and K_2UF_8 is also described.

Introduction

In 1946 Martin and Albers[3] reported the formation of stable complexes between uranium hexafluoride and a number of inorganic fluorides. Further work,[4–7] primarily with the sodium fluoride complex, indicated its composition to be Na_3UF_9. Exchange studies using F^{18}, however, pointed to the formula Na_2UF_8.[8] Recently, Katz has prepared pure Na_2UF_8 by means of a gas–solid reaction.[9] Exchange studies with several other fluorides including KF gave no evidence for complex formation. Nikolaev and Sukhoverkhov[10] reported the preparation of complexes of the type MUF_7 (M = Cs, NH_4) by combining the reactants dissolved in chlorine trifluoride. They proposed a tentative scheme whereby ClF_3 acted as an ionizing solvent in which intermediate species of the type $(ClF_2)_n$-UF_{6+n} were formed which combined with the simple fluorides to form the isolated complexes. Volavsek,[11] however, also prepared NH_4UF_7 by treating UF_6 with a suspension of NH_4F in tetrachloroethane. In this case, an ionic reaction mechanism appears unlikely.

We report here studies which confirm the formula obtained by F^{18} exchange work, Na_2UF_8. In addition, we have prepared the new compound $NaUF_7$, as well as the analogous complexes K_2UF_8 and KUF_7.

Experimental Section

Materials.—Reagent grade sodium fluoride powder (J. T. Baker Co.) of greater than 99% purity was used. Potassium fluoride was obtained by decomposing reagent grade potassium bifluoride (J. T. Baker Co.) at 500°. The powders had a particle size range of 3–15 μ. The materials were loaded into the reactor (the KF in a drybox) and outgassed at 350° under vacuum. A tank of pure UF_6 was obtained from Oak Ridge. It was additionally purified by repeated sublimations under reduced pressure as described previously.[12] The inert solvent, *n*-perfluoroheptane, C_7F_{16}, was obtained from Carbide and Carbon Chemicals Co. This was dried over P_2O_5 for 24 hr. with intermittent heating to 100°. The C_7F_{16} was pretreated with UF_6. The mixture was then contacted with NaF to remove the UF_6, and after several distillations the C_7F_{16} was transferred to a thoroughly outgassed glass storage vessel.

Procedure.—Reactions were carried out in 10-ml. glass erlenmayer flasks connected *via* housekeeper seals to brass Hoke valves. The glass reactors contained glass enclosed magnetic stirring bars. Reaction flasks and storage containers were attached to a metal manifold described elsewhere.[12] The weighed glass reactor was loaded with about 0.20 g. of NaF or KF and heated at 350° overnight under high vacuum and weighed. About 5 ml. of C_7F_{16} was distilled onto the NaF or KF. With an ice bath surrounding the reactor, the suspension was magnetically stirred, and about 2.5 g. of UF_6 was distilled into the reaction vessel. The valve was closed, and the reaction was allowed to proceed under various conditions. The unreacted UF_6 and the C_7F_{16} were then distilled off under reduced pressure until constant weight was obtained. The extent of conversion of the alkali fluoride to UF_6 complex was determined from the increase in weight of the starting materials. Occasionally the reactor was opened in a drybox, and a small amount of the

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

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product was removed for X-ray analysis. The C_7F_{16}–UF_6 mixture was distilled back into the vessel, and the reaction continued.

Chemical Analysis.—Analytical determinations for U, F, and Na were made on three separate samples of weighed $NaUF_7$. Sodium[13] was determined gravimetrically as $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$. Uranium[14] was analyzed by reduction to U^{4+}, addition of excess Ce^{4+}, and back titration with Fe^{2+}. Fluoride[15] was determined by titration with Th^{4+} using sodium alizarin sulfonate as indicator.

Results

Preliminary studies of the reaction of NaF with gaseous UF_6 in nickel cans at 100° showed that two compounds were present. One of these was stable at room temperature but evolved UF_6 at 100° to form a second compound, which gave off UF_6 rapidly only at 300°. It became apparent that the heat of the reaction caused the finely divided NaF and/or the $NaF \cdot UF_6$ complex to sinter, resulting in slow and incomplete reaction. Although cycling by alternate formation and decomposition of the compounds enhanced the reactivity of the sodium fluoride, it was impossible to attain $NaF:UF_6$ ratios below 1.5.

Subsequent experiments were conducted by treating UF_6 with NaF suspended in the inert liquid, C_7F_{16}. Typical results are shown in Table I. The reaction rate is strongly temperature dependent. It is seen that in the presence of excess UF_6 the reaction goes to completion at 100° to form white $NaUF_7$. The dissociation pressure of $NaUF_7$ is about 35 mm. at 100°. Upon heating $NaUF_7$ at this temperature *in vacuo*, UF_6 is given off rapidly and yellow Na_2UF_8 is formed according to the reaction

$$2NaUF_7 \longrightarrow Na_2UF_8 + UF_6 \qquad (1)$$

At 300° the decomposition proceeds further according to the reaction

$$Na_2UF_8 \longrightarrow 2NaF + UF_6 \qquad (2)$$

The results of a chemical analysis of $NaUF_7$ (preparation 2, Table I) are: Na, 6.4; U, 58.5; F, 34.2%. These results are in fair agreement with the formula $NaUF_7$ (Calcd.: Na, 5.8; U, 60.4, F, 33.8%). The values for Na and F are high, indicating the presence of unreacted NaF below the limits of detection by X-ray powder photographs.

Results of analogous experiments with KF are given in Table II. The compounds KUF_7 and K_2UF_8 are formed. At 100° *in vacuo*

$$2KUF_7 \longrightarrow K_2UF_8 + UF_6 \qquad (3)$$

No attempts were made to remove UF_6 from K_2UF_8 at higher temperatures.

X-Ray powder photographs were obtained which correlated with the above results. Only two distinct phases were observed corresponding to $NaF:UF_6$ ratios of 2 and 1. For ratios between these values, mixtures of the two phases were found. When the ratio of $NaF:UF_6$ was greater than 2, the X-ray patterns corresponded to Na_2UF_8 and unreacted NaF.

TABLE I

REACTION OF UF_6 AND NaF IN n-C_7F_{16}

	Temp., °C.	Time, hr.	Moles of NaF/mole of UF_6
0.1995 g. of NaF, 2.25 g. of UF_6, 5 ml. of C_7F_{16}			
	25	1[a]	4.92
	90	5.5[a]	1.60
	100	4[a]	1.32
	25	53[a]	1.16[b]
	100	18	1.01
	100	5	1.06[b]
0.1964 g. of NaF, 2.5 g. of UF_6, 4.2 ml. of C_7H_{16}			
	25	21	2.27
	92	20	1.03[b]
Pump off UF_6	100	2	1.94
Pump off UF_6	100	4	1.95[b]
Add excess UF_6	25	41	1.03[b]

[a] Inadequate stirring. [b] X-Ray sample taken.

TABLE II

REACTION OF KF AND UF_6 IN C_7F_{16}

	Temp., °C.	Time, hr.	Moles of KF/mole of UF_6
0.1574 g. of KF, 2 g. of UF_6, 5 ml. of C_7F_{16}			
	25	17	2.00[a]
	100	4	0.99[a]
0.0914 g. of KF, 1.5 g. of UF_6, 5 ml. of C_7F_{16}			
	100	4	...
	25	17	1.68
	100	3	1.10
Pump off UF_6	100	1	2.03
Add excess UF_6	25	16	1.05[a]

[a] X-Ray sample taken.

In the KF system X-ray powder photographs show correlations similar to those observed in the NaF–UF_6 systems.

X-Ray Studies

Single crystals of Na_2UF_8 suitable for X-ray diffraction studies were produced by sintering at 400° under high UF_6 pressures. Only limited X-ray data could be obtained because of the hygroscopic nature of the material. However, based upon the observed cell size and symmetry, as well as upon known U–F distances for U^{6+}, a model for the structure has been made using a space group chosen arbitrarily.

Single crystal data show that the cell is body-centered tetragonal, with $a = 5.27$ Å. and $c = 11.20$ Å. The uranium atoms dominate the intensities, and the symmetry is based therefore on the uranium positions. The volume of the cell corresponds to two formula weights, and this leads to a calculated X-ray density of 4.68 g. cm.$^{-3}$. If space group I4/mmm is chosen, atoms can be placed in the following positions: $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2) +$ 2 U in 0, 0, 0, 4 Na in $0, {}^1/_2, {}^1/_4; {}^1/_2, 0, {}^1/_4$, 16 F in $x, x, z; \bar{x}, \bar{x}, z; \bar{x}, x, z; x, \bar{x}, z; x, x, \bar{z}; \bar{x}, \bar{x}, \bar{z}; \bar{x}, x, \bar{z}; x, \bar{x}, \bar{z}$, with $x = 0.25$ and $z = 0.119$.

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Each uranium atom is surrounded by eight fluorines, with U–F = 2.29 Å. and F–F = 2.63 and 2.67 Å. Each sodium atom is also surrounded by eight fluorines with Na–F = 2.37 Å. and F–F = 2.63 and 2.97 Å. The metal–metal distances are normal. All distances are more or less close to ideal values, based on $R_{U^{6+}} = 0.83$, $R_{Na} = 0.98$ Å., and $R_{F^-} = 1.33$ Å. We hope to obtain additional data in the future in order to check the validity of the model.

For this structure, all U–F distances are equivalent, and all Na–F distances are equivalent. There is therefore no indication of shorter or longer bonds which could lead to the identity of UF_6 or NaF configurations.

Discussion

The preparation of pure Na_2UF_8 substantiates the results of the F^{18}-exchange studies[8] and recent results on solid–gas reactions[9] that the compound originally described as Na_3UF_9 is in fact Na_2UF_8. Earlier erroneous identifications[4–7] were due to the incomplete reaction obtained between gaseous UF_6 and solid NaF. These problems have been overcome however by the use of more finely divided NaF obtained by decomposition of sodium bifluoride.[9] In our experiments these difficulties were obviated by dispersing NaF in an inert liquid, C_7F_{16}. The refluxing of C_7F_{16} carries away the heat of the reaction and retains NaF in a finely divided state. Analogous results were obtained with KF.

In addition, we have obtained two new compounds of the type MUF_7 (M = Na, K) analogous to the previously reported $CsUF_7$[10] and NH_4UF_7.[10,11]

Exchange data with F^{18} did not show evidence of compound formation with KF.[8] Our results do not agree with this. The exchange work was done with readily available reagent grade KF. Our experience with such KF has shown that this material is completely unreactive toward UF_6. Only the very finely divided KF prepared by decomposition of KHF_2 has been found to react with UF_6.

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Nucleophilic Displacement in the Oxidation of Iodide Ion by Dimethyl Sulfoxide[1]

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The rates of oxidation of iodide ion in acidic solution have been studied at 25.00° in various dimethyl sulfoxide–water solvent mixtures: $(CH_3)_2SO + 3I^- + 2H^+ \rightarrow (CH_3)_2S + I_3^- + H_2O$. Second-order hydrogen ion and first-order iodide ion dependence was observed in each solvent employed. The value of the third-order rate constant increases rapidly with decreasing water content. Nucleophilic catalysis by added bromide or chloride occurs, with an observed order of reactivity: chloride > bromide > iodide. The dependence of the relative reactivity of these nucleophiles on the water content of the solvent has been determined. The results indicate halide ions to be very reactive in a dipolar aprotic solvent; the effectiveness of chloride is increased by a factor of 3700 on going from 75.00% to 98.50% dimethyl sulfoxide.

Introduction

Dimethyl sulfoxide (DMSO) has several properties which make it useful as a solvent for inorganic reactions. Important among them are high dielectric constant and ability to dissolve fairly high concentrations of many inorganic solutes.[2] DMSO is a typical dipolar aprotic solvent, which lacks any capacity for hydrogen bonding to solute species. It is reasonable to expect that this marked contrast with solvent water would have an important effect on reaction rates and mechanisms. To learn more about this effect we have studied the rate of reaction of DMSO with iodide ion in acidic DMSO–water solvent mixtures.

$$(CH_3)_2SO + 3I^- + 2H^+ \longrightarrow (CH_3)_2S + I_3^- + H_2O$$

A kinetic analysis of this reaction in DMSO–water solvents has not been reported; however, Landini, *et al.*,[3] have investigated the reduction of sulfoxides by hydriodic acid in acetic acid.

Experimental Section

Solvent.—Crown-Zellerbach commercial grade DMSO was distilled twice at 72° (10 mm.), the center 60% in each distillation being retained for use. A Karl Fischer titration of the freshly distilled DMSO indicated the presence of 0.03% water. Solvent mixtures were prepared on a weight basis by slow addition of redistilled water to a partially frozen sample of DMSO. Both DMSO and water were initially swept with prepurified nitrogen and all subsequent operations were performed under an atmosphere of nitrogen. The solvent mixtures were used immediately after preparation.

For each of the kinetic runs, a stock solution of perchloric acid in DMSO–water was prepared by slow addition of 35% aqueous perchloric acid to the solvent, cooled in an ice bath.

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