THE FLUORINATION OF NEPTUNIUM(IV) FLUORIDE AND NEPTUNIUM(IV) OXIDE

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Abstract – Rates of formation of NpF₆ by the reactions at 250-400°C of NpF₄ with fluorine, with BrF₃, and with BrF₅ can be represented by a rate law that assumes the reaction site to be a continuously diminishing spherical interface. The rates of reaction of NpF₄ at 350°C lie in the order fluorine (100 mole%) > BrF₃(6-13 mole%) > BrF₅(33-35 mole%). Correlation of the derived rate constants by the Arrhenius equation yielded activation energies of 20 kcal/mole for the reaction of NpF₄ with fluorine and 26 kcal/mole for the reaction of NpF₄ with BrF₅. The solid residues from the reactions of NpF₄ with either BrF₅ or fluorine contained no species other than NpF₄. The fluorination of NpO₂ by either BrF₅ or fluorine proceeds through the intermediate compound NpF₄. Thus, the fluorination of NpO₂ is analogous to that of PuO₂, which proceeds through the intermediate compound UO₂F₂.

INTRODUCTION

PREVIOUS work[1-3] showed that solid NpF₄ reacts with gaseous fluorine to form NpF₆, a stable compound with volatility[2] similar to that of the other actinide hexafluorides, UF₆ and PuF₆. The present work was undertaken to measure the rate of reaction of NpF₄ with fluorine, to establish whether NpF₄ is fluorinated by BrF₅ and BrF₃, and to measure the rates of these reactions.

Reports of previous work [4, 5] indicate that the reaction of PuO_2 with fluorine proceeds through the intermediate formation of PuF_4 , which subsequently reacts with fluorine to form PuF_6 . In contrast, the reaction of UO_2 with fluorine [5, 6] proceeds with the intermediate formation of UO_2F_2 , which subsequently reacts with fluorine to form UF_6 . The reaction of UO_2 with BrF_5 also proceeds with the intermediate formation of UO_2F_2 [7]. One of the objectives of the work reported here was to identify the intermediate solid species formed in the reactions of NpO_2 with fluorine and with BrF_5 , and thus to determine which of its actinide neighbors neptunium resembles in the fluorination of the tetravalent oxides.

EXPERIMENTAL

Materials

Neptunium tetrafluoride was prepared from $^{237}NpO_2$ obtained from Oak Ridge National Laboratory. Chemical analysis of the NpO₂ showed that it contained 0.13 wt % plutonium and 0.04 wt %

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uranium. Spectrographic analysis of the NpO₂ showed that it contained only minor amounts of other metallic impurities. Three batches of neptunium tetrafluoride for fluorination were each prepared by the reaction at 500°C of NpO₂ with a gaseous mixture of hydrogen fluoride (75 mole%) and oxygen (25 mole%) at a total pressure of about one atmosphere. For each batch, the solid phase was brought to a constant weight corresponding to complete conversion to NpF₄. The first batch of NpF₄ contained 77·2 wt % neptunium and 24·3 wt % fluorine (theor. 75·7 wt % Np, 24·3 wt % F). The surface area of the NpF₄, measured by the BET method using nitrogen, was 0·3 m²/g. The bulk density of the NpF₄ was 3·1 g/cc.

Bromine pentafluoride and BrF_3 were obtained from a commercial supplier. The BrF_3 as received contained some BrF_5 as an impurity that was removed by freezing part of the BrF_3 sample and discarding the gas phase. Infra-red spectra of gas samples taken before and after purification showed this procedure to be effective in purifying small (1-5 g) samples. The BrF_5 as received contained bromine as an impurity. The bromine was removed by treatment with fluorine.

Fluorine, obtained from a commercial source, was passed through a bed of sodium fluoride pellets at 100°C to remove HF impurity. The gaseous nitrogen used as a diluent for interhalogen vapors was obtained by vaporization of liquid nitrogen.

Apparatus

A Cary Model 14 spectrophotometer was used to measure spectra in the visible and near-infrared regions, and a Beckman IR-4 spectrophotometer was used to measure spectra in the infrared region. Cylindrical nickel cells[8] with quartz or silver chloride windows were used to contain the gases for spectral measurements. To contain alpha-active ²³⁷Np, the equipment was housed in a glovebox[9].

The equipment used to contain neptunium fluorides was constructed of nickel and Monel parts joined by Teflon gaskets. The fluorination reactions were performed in a horizontal tube reactor connected to a vacuum manifold. A nickel thermocouple well extended through one flange and housed a calibrated thermocouple to measure the temperature of a hemicylindrical nickel bar on which a nickel boat containing the solid neptunium compound rested during fluorination reactions.

The flow rate of the fluorine was measured by a thermal flowmeter[10]. The flow rate of BrF_5 was measured by a rotometer manufactured from Kel-F (Brooks Instrument Division of Emerson Electric Co., Hatfield, Pa.). The BrF_5 container was maintained at about 50°C, resulting in a pressure at the rotometer of about 1000 mm Hg. All of the connecting lines and the BrF_5 rotometer were maintained at 70°C. Bromine trifluoride was supplied in a similar manner; the temperatures of the container and lines were 100°C and 120°C, respectively. The flow rate of BrF_3 was measured by collecting and weighing all condensible materials from the reactor effluent, and correcting for the weights of reaction products. The flow rate of nitrogen was measured with a glass rotometer.

Procedure

Fluorination rates were measured by determining weight losses of solid NpF₄ during exposure to a gaseous stream of fluorinating agent for a measured time period. A sample of NpF₄ (1-3 g) was weighed into a nickel boat. The boat was placed in the reactor at room temperature, and a stream of nitrogen gas was passed through the reactor while the furnace temperature was raised to the reaction temperature. The flow of fluorinating agent was then started, and the reaction was allowed to continue for a measured time period. The reaction was stopped either by purging the reactor with nitrogen gas or by evacuating the reactor. After the reactor had cooled, the boat was removed from the reactor and weighed to determine the loss of NpF₄. A test, in which only gaseous nitrogen was passed over NpF₄, indicated that any weight-loss error by mechanical removal of dust was negligible.

The fluorination mechanism of NpO₂ was studied by exposing samples of powdered NpO₂ in the tube reactor to a flowing stream of either pure, gaseous fluorine at 310°C or a gaseous mixture of BrF_5 and nitrogen at 350°C. The reaction was stopped in each case after the major portion of the solid had undergone a color change, but before no more than a minor fraction of the total neptunium had been converted to NpF₆ and removed by sublimation.

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RESULTS AND DISCUSSION

Chemical species involved in the fluorination of NpF₄

Weight-loss determinations indicated that neptunium was volatilized when fluorine, BrF_5 , or BrF_3 was contacted with powdered NpF_4 at 200-500°C. Results obtained in previous work[1-3] showed that the reaction of fluorine with NpF_4 proceeds with the formation of NpF_6 only. The present work demonstrated that the end products of reaction of BrF_5 with NpF_4 are NpF_6 , identified by its absorption spectrum in the infrared region[11], and bromine, identified by its absorption spectrum in the visible region. The reaction of BrF_3 with NpF_4 in the present work produced bromine and a gaseous neptunium compound, assumed to be NpF_6 since it is the only neptunium fluoride species known to be volatile at the temperatures of the experiment.

Analyses of the solid residues were performed to determine whether the same solid species persisted throughout an experiment. The results of the analyses were examined especially for evidence of neptunium fluoride species analogous to the intermediate fluorides of uranium, U_4F_{17} , U_2F_9 , and UF_5 . No evidence for the existence of such compounds of neptunium has ever been presented. Labaton and Johnson[12] found that intermediate fluorides of uranium were produced in the reaction of fluorine with UF_4 . Jarry and Steindler[13] found that intermediate fluorides of BrF_5 with UF_4 .

Although plutonium fluoride species analogous to the intermediate fluorides of uranium have never been isolated, several investigators have presented evidence of their existence. Mandleberg *et al.* [14] interpreted the results of chemical analysis and X-ray powder diffraction analyses as proof of the existence of Pu_4F_{17} in solid residues of the reaction of PuF_4 with fluorine. Others[15, 16] have attributed a break in the temperature dependence of the rate of reaction of PuF_4 with fluorine to a change of the solid phase from PuF_4 to an intermediate fluoride. On the other hand, no evidence for the formation of intermediate fluorides of plutonium in residues of the reaction of PuF_4 with fluorine was observed by Steindler *et al.* [4, 17] or by Vandenbussche[5].

In the present work, at various stages of the reaction NpF₄ with fluorine, small samples of the solid residues were removed for X-ray powder diffraction analyses. The results indicated the presence of no species other than NpF₄. The capability of X-ray powder diffraction analysis to distinguish between NpF₄ and the possible intermediate compound Np₄F₁₇ is limited, however, by the expected similarity of the two structures. The X-ray pattern of U₄F₁₇ is described as that of a distorted UF₄ lattice[18]. The evidence presented[14] for the exis-

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tence of Pu_4F_{17} is based partly on minor lines in X-ray powder diffraction photographs of a solid with a lattice similar to the distorted UF₄ lattice.

Solid residues of the reaction of NpF₄ with BrF_5 were also removed for chemical analyses for neptunium and fluoride and for X-ray powder diffraction analyses. The X-ray powder diffraction patterns showed only lines that could be attributed to NpF₄. The results of chemical analyses of the solid residues showed that the atom ratio, F/Np, found in the solid was 4, with no discernible dependence on reaction temperature or the fraction of NpF₄ reacted.

Correlation of observed results

The observed weight-loss data have been correlated by the rate law originally derived by Anderson[19], with the assumption that the reaction takes place at a continuously diminishing spherical interface. This rate law has the form,

$$(1-F)^{1/3} = 1 - k't, \tag{1}$$

in which F is the fraction of the solid reacted in reaction time, t, and k' is a reaction rate constant. The rate constant k' is related to the true rate constant, k, by the expression,

$$\mathbf{k}' = \frac{\mathbf{k}}{r_0 \rho},\tag{2}$$

where r_0 is the initial particle radius and ρ is the bulk density of the solid.

Derivation of activation energies

The rate constants k' derived from the expreimental data and Equation (1) for the reactions of NpF₄ with fluorine and with BrF₅ have been correlated by the Arrhenius equation $k' = Ae^{-E}a^{/RT}$. The temperature dependence of the rate constants is illustrated graphically in Fig. 1. The apparent activation energies, E_a , obtained by least-squares analysis of the data, are 20 kcal/mole for the reaction of NpF₄ with fluorine and 26 kcal/mole for the reaction of NpF₄ with BrF₅.

Comparison of reaction rates and activation energies

Table 1 shows a comparison of the activation energies for the fluorination of NpF_4 , determined in the present work, with activation energies for the fluorination of UF_4 and PuF_4 determined by other authors.

Exact comparison of rate constants k' is fitting only for reactions involving samples of the same batch of solid. The rate constants k' at 350°C for reactions with samples of the same batch of NpF₄ were 0.0013 min⁻¹ for BrF₅ (33–35 mole% in nitrogen) and 0.0051 min⁻¹ for BrF₃ (6–13 mole% in nitrogen). Rate constants k' for fluorination of the tetrafluorides of uranium, neptunium, and plutonium are summarized in Table 2. Although the values cannot be precisely compared without information on r_0 and ρ (Equation (2)), some conclusions are made in terms of inequalities: (1) The rates of reaction of NpF₄ with the fluorinating agents lie in the order fluorine (100 mole%) > BrF₃(6–13 mole%) > BrF₅(33–

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Fig. 1. Temperature dependence of rate constants for the fluorination of NpF₄.

35 mole%). (2) The rates of reaction of the actinide tetrafluorides with pure fluorine lie in the order $UF_4 > NpF_4 > PuF_4$. (3) The rate of reaction of BrF_5 with UF_4 is greater than the rate of reaction of BrF_5 with NpF_4 .

The behavior of NpF₄ with BrF_3 and with BrF_5 parallels the fluorination behavior of UF₄; Jarry and Steindler[13] found that the rate of reaction of BrF_3 with UF₄ is greater than the rate of reaction of BrF_5 with UF₄.

The relationship between the rates of reaction of NpF₄ with BrF_3 and with BrF_5 can be used to construct an inference about the rate-determining step in the reaction of BrF_5 with NpF₄. Since the reduction of BrF_5 involves breaking several bonds per molecule, it is assumed that the reaction of BrF_5 with NpF₄ occurs in a series of steps, each involving the reduction of a successively lower bromine fluoride. The only bromine fluoride species sufficiently stable to be ob-

	\mathbf{E}_{a}	\mathbf{E}_{a}
	Reaction with	Reaction with
	BrF₅*	pure fluorine
Compound	(kcal/mole)	(kcal/mole)
UF₄	16.9†	18.1-18.7‡
NpF ₄	26	20
PuF₄	no reaction§	15·5‡ (200–460°C)
-	·	10·4 (170–500°C)
		9.97-10.36§ (200-370°C)
		8·70-8·83§ (>370°C)

Table 1. Activation energies for reaction of actinide tetrafluorides with gaseous fluorinating agents

*33-35 mole% in nitrogen. †Jarry and Steindler, Ref. [7]. ‡Vandenbussche, Ref. [5]. §Jarry and Stockbar, in USAEC Rep. No. ANL-7125, pp. 66-73. May 1966. "Steindler and Steidl, Ref. [17]. §Gendre, Ref. [15].

Table 2.	Comparison o	of rate cons	stants for	r reactio	on of	solid	tetraf	luoride	es wi	th
	ga	seous fluor	rinating a	igents at	t 350°	°C				

	Rate constants, k'				
- Tetrafluoride	Reaction with pure fluorine (min ⁻¹)	Reaction with BrF ₃ * (min ⁻¹)	Reaction with BrF ₅ † (min ⁻¹)		
UF ₄	0.05-0.13‡	Data unavailable	0·19§		
NpF₄	0.014-0.023	0.0051	0.0013		
PuF₄	0·0062‡ 0·0032"	No reaction	No reaction		

*6-13 mole% BrF₃ in nitrogen.

†33-35 mole% BrF₅ in nitrogen.

[‡]Vandenbussche, Ref [5].

§Jarry and Steindler, Ref [7].

Interpolation of data presented by Steindler and Steidl, Ref. [17].

served under the experimental conditions are BrF_5 , BrF_3 , and possibly BrF. The rate of reaction of NpF_4 with BrF_3 has been shown to be greater than the rate of reaction of NpF_4 with BrF_5 . Therefore, if the mechanism of the reaction of NpF_4 with BrF_5 involves at least two successive steps,

$$NpF_4 + BrF_5 \rightarrow NpF_6 + BrF_3$$
 (3)

$$3NpF_4 + 2BrF_3 \rightarrow 3NpF_6 + Br_2 \tag{4}$$

the first step, Equation (3) must be rate-determining.

Intermediates formed in the fluorination of NpO_2

The solids resulting from partial fluorination of NpO₂ by either fluorine or BrF_5 were similar in appearance. In each case, a small amount of dark-brown underlayer, resembling the initial NpO₂, remained, but the major portion had been converted to a green solid. In each case both layers were sampled and identified by X-ray powder diffraction techniques; the green layer was NpF₄ containing a trace of NpO₂, and the brown layer was NpO₂ containing a trace of NpF₄. X-ray diffraction analysis showed no evidence of a compound with a pattern analogous to that of UO₂F₂[20]. Since NpO₂F₂ and UO₂F₂ would be expected to have the same structure and similar unit cell dimensions[21] it is concluded that NpO₂F₂ was not present in the solid reaction residues. Thus the mechanism of fluorination of Np(IV) oxide involves the intermediate formation of NpF₄ and is analogous to the fluorination of Pu(IV) oxide, but differs from the fluorination of U(IV) oxide.

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