Journal of Alloys and Compounds 269 (1998) 63–66

Reactions of dioxygen difluoride with neptunium oxides and fluorides

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Received 4 October 1997; received in revised form 16 December 1997

Abstract

Neptunium dioxide and tetrafluoride are converted in essentially quantitative yield to volatile neptunium hexafluoride by dioxygen difluoride (O_2F_2), both in gas–solid reactions at ambient temperatures and in liquid anhydrous hydrogen fluoride at −78°C. Neptunium dioxydifluoride was identified by Raman spectroscopy as a dominant reaction intermediate in the neptunium dioxide reaction. Direct reaction of NpF_4 with liquid O_2F_2 resulted in violent decomposition of O_2F_2 with little or no conversion to NpF_6. These reaction temperatures contrast markedly with the elevated temperatures (above 200°C) required for NpF_6 generation using elemental fluorine or halogen fluorides.

Keywords: Neptunium tetrafluoride; Neptunium dioxide; Dioxygen difluoride; Neptunium hexafluoride

1. Introduction

Neptunium hexafluoride is a powerful oxidizer and one of the few known neptunium compounds with an appreciable vapor pressure (ca. 100 torr) at ambient temperature [1]. The high vapor pressure of NpF_6 makes it attractive for neptunium separations and compound synthesis. Normally, NpF_6 preparation requires the use of elemental fluorine or halogen fluorides at temperatures above 200°C, as in reactions 1–3 [1–5].

$$NpO_2 + 3F_2 \rightarrow NpF_6 + O_2 \tag{1}$$

$$NpF_4 + ClF_3 \rightarrow NpF_6 + ClF \tag{2}$$

$$2NpO_2 + 3BrF_5 \rightarrow 2NpF_6 + 2O_2 + 3BrF \tag{3}$$

In high temperature fluorination of NpO_2, only NpF_4 has been reported as an intermediate [2,3]. No intermediates have been reported in high temperature fluorination of NpF_4.

Krypton difluoride has been used to prepare NpF_6 at room temperature or below from NpO_2 and NpF_4 [6–10]. The intermediates NpO_2F, $NpOF_3$, NpO_2F_2 and $NpOF_4$ were inferred from the reaction of KrF_2 with NpO_2 in anhydrous HF. Neptunium pentafluoride was inferred as a product from the corresponding reaction with NpF_4 [6–8]. The intermediates $NpOF_3$ and NpO_2F_2 also have been suggested from the reaction of HF gas with Np_2O_5 and $NpO_3 \cdot H_2O$, respectively [11].

However, conclusive identification has not been reported for any of these neptunium oxyfluoride compounds.

Dioxygen difluoride is a volatile (b.p. −63°C), HF-compatible compound which is one of the most powerful oxidative fluorinating agents known [12–26]. The reactivity of O_2F_2 is equivalent to that of molecular fluorine at temperatures hundreds of degrees higher. Despite its extreme reactivity and short half-life (seconds) at ambient temperature, effective methods for preparing and using large quantities of O_2F_2 have been developed, and the utility of O_2F_2 in low temperature preparation of UF_6 and PuF_6 is well established [14–26].

In this paper we describe the application of O_2F_2 to the conversion of NpO_2 and NpF_4 to NpF_6 at room temperature and below, both in gas–solid reactions and in re-

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0925-8388/98/$19.00
PII S0925-8388(98)00005-X

actions in liquid anhydrous hydrogen fluoride. Oxyfluoride intermediates in the neptunium dioxide reactions were inferred by Raman spectroscopy.

2. Experimental

Caution! Because O_2F_2 is thermally unstable and is one of the most powerful oxidative fluorinating agents known, it can initiate extremely violent reactions accompanied by explosive pressure rises. Appropriate precautions are essential when handling this compound. Neptunium hexafluoride also is a potent fluorinating agent and must be handled accordingly. Due to radiological hazards, neptunium compounds must be handled in containment facilities designed for work with transuranium elements.

2.1. Materials

Dioxygen difluoride was prepared as previously described [14–21]. Anhydrous hydrogen fluoride was purified by fractional distillation. Neptunium tetrafluoride was obtained from an aqueous HF precipitation process and neptunium dioxide was prepared by thermal decomposition of neptunium (IV) oxalate below 800°C. Based on our prior experience with these preparations, purity in excess of 99% was estimated. Neptunium pentafluoride was kindly provided by Dr. John G. Malm and was prepared as described in Ref. [27]. Uranium pentafluoride was prepared as described by Halstead et al. [28].

2.2. Reaction procedures

Reactions on the 200–1000 mg scale typically were carried out in $\frac{3}{4}''$ Kel–F tubes (35 ml) which were attached to vacuum systems through monel metal flare fittings. Gas reactants and products were handled in nickel or monel metal high vacuum systems fitted with Bourdon or capacitance manometer gauges.

For gas–solid reactions, a dynamic pressure of about 10 torr of O_2F_2 was maintained in the Kel–F reactor by control of the temperature of a bulk O_2F_2 supply container while evacuating the reactor. After treatment was terminated, the system was pumped out. Solid residuals were removed from the reaction vessels in an inert atmosphere glovebox and weighed to determine the actinide fraction volatilized.

For reactions in liquid HF, approximately 5 ml of HF was condensed at liquid nitrogen temperature into a Kel–F reactor containing a weighed amount of neptunium substrate. An excess of O_2F_2 was condensed on the frozen mixture at liquid nitrogen temperature. The temperature then was raised to and maintained at −78°C using a Dewar packed with dry ice. At the termination of the treatment, the Dewar was removed and volatiles were pumped away. Solid residues were removed from the reaction vessels in an inert atmosphere glovebox and weighed to determine the actinide fraction volatilized.

2.3. Raman spectra

Raman spectra were obtained on samples sealed in fused silica capillaries. Secondary fused silica sleeves surrounded the capillaries to prevent incidental capillary breakage and subsequent dispersal of contamination. A Spex model 1403 spectrometer equipped with Kr and Ar ion lasers (647.1, 514.5, and 488.0 nm exciting lines) was used. Because of concern for laser damage to samples, low incident power (typically <10 millwatts) and averaging of multiple scans were used.

3. Results and discussion

The gas–solid reaction of NpF_4 with O_2F_2 at ambient temperature proceeded smoothly with >95% conversion to NpF_6 after 45 min (Reaction 4). The corresponding reaction with NpO_2 also proceeded smoothly with >95% conversion to NpF_6 after 30 min (Reaction 5).

$$NpF_4(s) + xO_2F_2(g) \rightarrow NpF_6(g) + xO_2(g) + (x-1)F_2(g) \tag{4}$$

ambient temperature, 45 min, >95% yield;

$$NpO_2(s) + xO_2F_2(g) \rightarrow NpF_6(g) + (x+1)O_2(g) + (x-3)F_2(g) \tag{5}$$

ambient temperature, 30 min, >95% yield.

In liquid anhydrous HF at −78°C, O_2F_2 fluorination reactions proceeded more slowly, but eventually essentially complete conversion to NpF_6 was observed. With NpF_4, >95% conversion was found after 2 h of reaction and 75% conversion of NpO_2 was noted after 3 h.

Reactions in which neptunium(IV) substrates were treated directly by condensing O_2F_2 on to the solid and allowing the solid mixture to warm to −78°C (above the melting point of O_2F_2) were investigated. With this procedure, the reaction typically became uncontrollable with vigorous sparking, audible noise, and vigorous gas evolution. In these instances, total O_2F_2 decomposition was observed from disappearance of its characteristic red color. No detectable NpF_6 was produced, based on lack of conversion of the substrates and failure to cryotrap any volatile NpF_6.

In some experiments, the fluorination reactions were arrested before complete conversion to NpF_6 occurred. The intermediate solids remaining after warming and evacuating the system were examined by Raman spectroscopy. Fig. 1 illustrates the Raman spectra of solids recovered from the arrested reactions of NpO_2. Raman spectra for arrested reactions of NpF_4 gave no indication of inter-

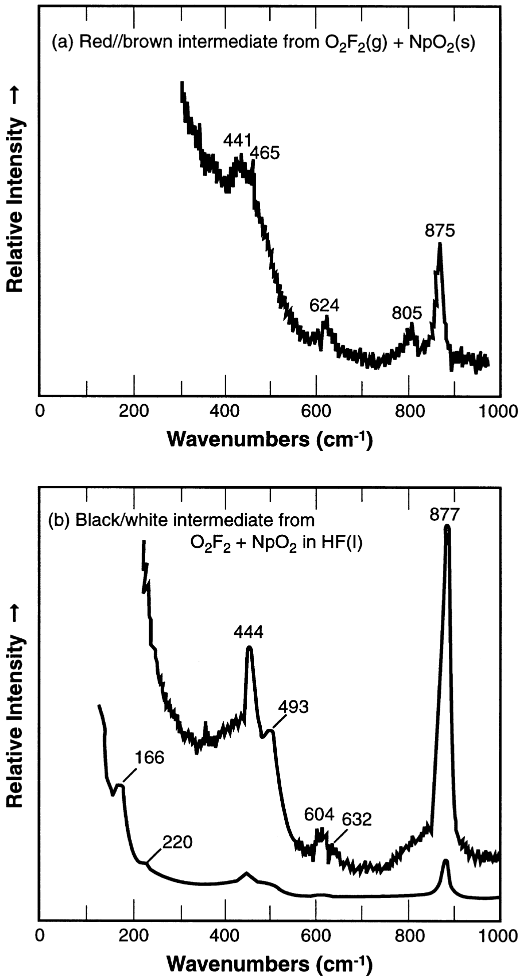

Fig. 1. Raman spectra of the intermediate solids from the arrested reactions of neptunium dioxide with (a) gaseous O_2F_2 at ambient temperature and (b) O_2F_2 in liquid anhydrous hydrogen fluoride at −78°C.

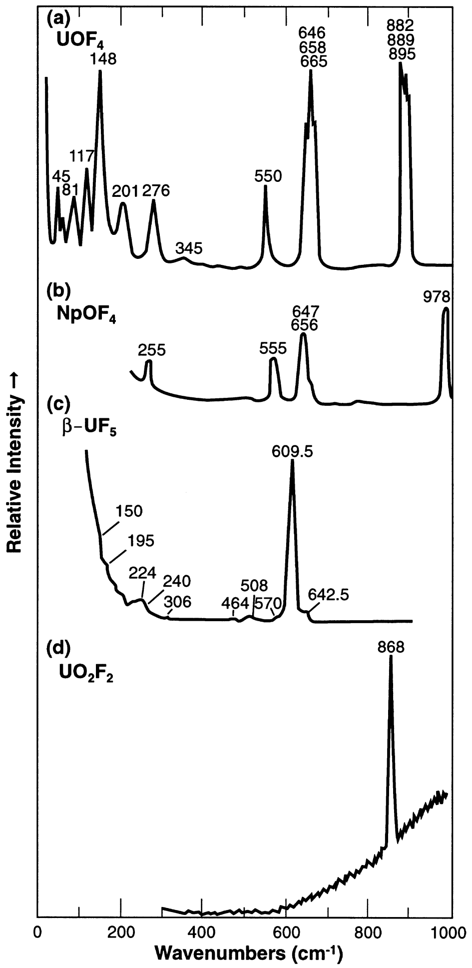

Fig. 2. Vibrational spectra of reference actinide fluorides and oxyfluorides. The UOF_4 spectrum is from Ref. [29] and the $NpOF_4$ spectrum is from Ref. [6–8]. The UF_5 and UO_2F_2 spectra were determined in the present work.

mediates. For comparison, Fig. 2 presents reference spectra for UO_2F_2, UOF_4, beta–UF_5, and $NpOF_4$.

The solid recovered from the arrested ambient temperature reaction of gaseous O_2F_2 with NpO_2 had a red/brown appearance. By comparison of the product's Raman spectrum (Fig. 1a) with the spectrum of UO_2F_2 (Fig. 2d), which has a single strong peak at 868 cm^{-1} attributable to the UO_2^{2+} symmetric stretching mode, the strong band at 875 cm^{-1} is assigned to the NpO_2^{2+} moiety. Thus, NpO_2F_2 is presumed to be a dominant intermediate species.

The lack of strong bands near 650 cm^{-1} precludes $NpOF_4$ as a major component, by comparison with the Raman spectra previously reported for well characterized UOF_4 and less certainly identified $NpOF_4$ (Fig. 2) [6–8,29]. The weaker band observed near 624 cm^{-1} is consistent with the spectrum of UF_5 (Fig. 2c) and that previously reported for NpF_5, suggesting the presence of some pentafluoride intermediate. The broad Raman features near 450 cm^{-1} are tentatively attributed to Np–O stretching modes of unreacted NpO_2 and to Np–F stretching modes from other intermediates, possibly Np(V) oxyfluorides such as NpO_2F which have been suggested previously for the reaction of KrF_2 with NpO_2 [6–8].

The solid recovered from the arrested reaction of O_2F_2 with NpO_2 in anhydrous HF at −78°C contained both dark and light particles and thus consisted of at least two phases. Fig. 1b illustrates the Raman spectrum of the recovered intermediate. As in the gas-reaction at room temperature, a strong Raman feature appears near 877 cm^{-1} which is attributable to NpO_2F_2 and a broad band is found around 450 cm^{-1} attributable to NpO_2 and neptunium fluoride or oxyfluoride species. Again, the lack of a strong feature near 650 cm^{-1} precludes the major presence of $NpOF_4$. The intermediates for the gas–solid and liquid HF reactions therefore appear to be similar.

As indicated in Fig. 2, the Raman spectrum previously reported for $NpOF_4$ (prepared by reaction of KrF_2 with NpO_2) [6–8], substantially differs from the well characterized spectrum of UOF_4 [28]. From comparisons with vibrational spectra of many other oxyfluoride compounds,

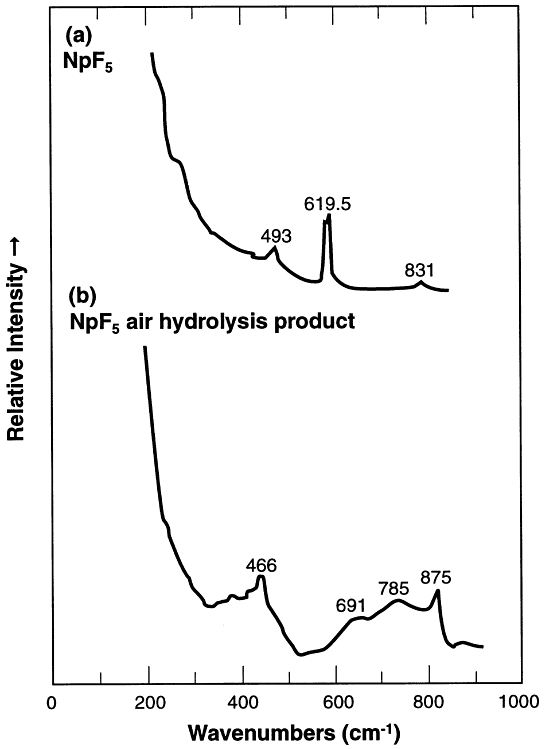

Fig. 3. Raman spectra of NpF_5 and its air hydrolysis product (present work).

it appears that the strong band reported for $NpOF_4$ at 978 cm^{-1} is far too high in energy to be reasonably assigned to this compound. For this reason, the primary spectral comparison in the present paper is with the spectrum reported for UOF_4 rather than with the spectrum reported for $NpOF_4$.

Fig. 3a presents the Raman spectrum of NpF_5 and the product of its hydrolysis in air (25–50% relative humidity) for 24 h at ambient temperature. As observed in the O_2F_2 reactions discussed above, strong features are observed near 875 cm^{-1} assignable to the NpO_2^{2+} moiety and around 450 cm^{-1} assignable to Np–O and Np–F stretching modes, indicative of the presence of neptunyl fluoride. The broad absorption between 600 and 800 cm^{-1} is assigned tentatively to unidentified Np(V) oxyfluorides.

4. Conclusions

Neptunium dioxide and tetrafluoride are converted in essentially quantitative yield to volatile neptunium hexafluoride by dioxygen difluoride (O_2F_2), both in gas–solid reactions at room temperature and in liquid anhydrous hydrogen fluoride at −78°C. Raman spectroscopy was used to indicate that NpO_2F_2 is a dominant reaction intermediate in the neptunium dioxide reactions. Direct reaction of NpF_4 with O_2F_2 resulted in violent decomposition of O_2F_2 with poor conversion to NpF_6. These reaction temperatures contrast markedly with temperatures above 200°C normally required for NpF_6 generation using elemental fluorine or halogen fluorides.

Acknowledgements

This research was supported by the U.S. Department of Energy, Office of Nuclear Materials Production. We gratefully acknowledge many enlightening discussions with Dr. John G. Malm and Dr. Robert A. Penneman.

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