JOURNAL OF FLUOREINE CHEMISTRY

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PII:	S0022-1139(19)30428-2
DOI:	https://doi.org/10.1016/j.jfluchem.2019.109436
Reference:	FLUOR 109436
To appear in:	Journal of Fluorine Chemistry
Received Date:	19 September 2019
Revised Date:	25 November 2019
Accepted Date:	27 November 2019

Please cite this article as: Niu Y, Sun L, Hu C, Zhou J, Dou Q, Li Q, Study on the Fluorination Reaction of Uranium Tetrafluoride by Nitrogen Trifluoride, *Journal of Fluorine Chemistry* (2019), doi: https://doi.org/10.1016/j.jfluchem.2019.109436

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Study on the Fluorination Reaction of Uranium Tetrafluoride by

Nitrogen Trifluoride

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Graphical abstract



Highlights

- The fluorination of UF₄ induced by NF₃ at different temperatures was investigated using in line Fourier transform infrared (FTIR) spectroscopy.
- The fluorination between NF₃ and UF₄ occurred only when the temperature was above 723 K, and the temperature had a significant effect on the average reaction rate and the utilization rate of NF₃.
- ▶ With the temperature increased from 723 K to 873 K, the average fluorination rate increased from 1.97 to 3.45 gU•h⁻¹ and the utilization of NF₃ increased from 10.5% to 22.5%.
- ►The calculated rate constant of the fluorination between NF₃ and UF₄ increased from 1.6×10⁻² to 3.1×10⁻² min⁻¹ in the range of 723 K to 873 K, and the activation energy of the reaction was 22.56 kJ/mol.

Abstract

The fluorination of UF₄ by NF₃ at different temperatures was investigated using in-line Fourier transform infrared (FTIR) spectroscopy. The results indicated that the fluorination between NF₃ and UF₄ occurred only when the temperature was above 723 K, and the temperature had a significant effect on the average reaction rate and the utilization rate of NF₃. The in-line FTIR spectrum analysis and thermodynamic calculation indicated that UF₄ was converted to UF₆ with the following reaction mechanism: $2/3NF_3(g) + UF_4(s) = UF_6(g) + 1/3N_2(g)$. The conversion rate of UF₄ to UF₆ increased from 1.53 to 2.68 gU•h⁻¹ and the utilization rate of NF₃ increased from 10.5% to 22.5% when the reaction temperature increased from 723 K to 873 K. The calculated rate constant increased from 1.6×10^{-2} to 3.1×10^{-2} min⁻¹ in the range of 723 K to 873 K, and the activation energy of the reaction was 22.56 kJ/mol.

Keywords

NF₃, UF₄, Fluorination, In-line FTIR, Kinetics

1. Introduction

The fluoride volatility process (FVP) is an invaluable technique that can efficiently recover uranium from uranium-containing material by converting the uranium compounds (such as uranium oxide and uranium tetrafluoride) to volatile $UF_6^{[1,2]}$. This technique has been widely used in the uranium conversion process for nuclear fuel production and is considered as a promising pyroprocessing technique to recover uranium from spent nuclear fuel (SNF)^[3,4,5]. The United States initially developed the FVP to treat SNF, especially to treat spent molten salt fuel from the aircraft reactor experiment (ARE) and the molten-salt reactor experiment (MSRE) during the 1960s and 1970s^[2,6].

Although the uranium conversion industry has decades of production and operation experience, along with a relatively high technical maturity with the FVP as a pyroprocessing technique, it still faces some technical problems, such as the corrosion of equipment materials caused by the strong, aggressive fluorine gas. It was reported that the service life of a flame furnace in the uranium conversion industry is less than $1\sim2 a^{[7]}$. Oak Ridge National Laboratory (ORNL) reported that the corrosion rate of Hastelloy N alloy in a fluoride molten salt environment was less than 0.03 mm/a; however, it greatly accelerated to 20 mm/a in the fluorination of SNF from MSRE^[8,9]. In addition, the strong oxidation of fluorine gas can result in the formation of volatile fission products (such as Mo, Nb and Ru), which enter the gas phase as impurities without exception^[10]. To remove the volatile fission products from the UF₆ product, an adsorption-desorption process with multistage NaF adsorption columns have been commonly used in the FVP^[11]. Due to the similar volatilities of UF₆ and some fission product fluorides, such as MoF₆, the final effect of the adsorption-desorption process is not as satisfactory ^[12,13].

Compared with traditional fluorinating agents (F_2 , ClF_3 and BrF_3), NF_3 has the advantage of temperature sensitivity in addition to low chemical toxicity, which makes it possible to recover uranium with high purity through a temperature-dependent selective reaction. In recent years, Randall D. Scheele and Bruce McNamara of the Pacific Northwest National Laboratory (PNNL)^[14,15,16,17] carried out a feasibility study on the reaction between NF_3 and different

uranium-containing compounds using thermogravimetric and differential thermal analysis (TG-DTA). The results indicated the reaction of uranium or uranium-containing compounds with NF₃ gave UF₆ when the temperature was in the range of 373 K to 773 K, and the heating rate had a significant influence on the volatilization of UF₆ from uranium-containing compounds.

In this paper, the reaction of NF₃ and UF₄ was studied systematically on a homemade FVP research device. The relative concentration curve of formed UF₆, average fluorination rate, UF₄ conversion rate and NF₃ utilization rate in the fluorination process were obtained by using an in-line monitoring technique with Fourier transform infrared spectroscopy (FTIR)^[18,19]. To validate the sensitivity of fluorination to the temperature, the reaction rate constant and activation energy were calculated according to the experimental data.

2. Experimental

2.1 Reagents and materials

UF₄ ((99.9%, depleted uranium, the abundance of ²³⁵U is less than 0.3%, the surface area is about 0.45 m²/g) was supplied by China National Nuclear Corporation. NF₃-Ar mixed gas (20:80 by volume, written as NF₃/Ar, purity of NF₃ > 99.99%, N_xO_y<10 ppm, O₂+Ar < 5 ppm, CF₄ < 40 ppm and HF < 1ppm, respectively in the volume concentration) was purchased from Tianjin Vista Technology Development Co., Ltd.

2.2 The fluorination of UF₄ by NF₃ at different temperatures

The experiments were conducted in the equipment illustrated in Fig. 1. The equipment mainly includes a fluorinator, an in-line FTIR, a NaF trap (673 K), NaF adsorbers (373 K) and an off-gas treatment system. Except for the off-gas treatment system, all other parts of the equipment were placed in an argon-covered glove box (oxygen content <1 ppm). The construction material of fluorinator and the gas pipelines is Hastelloy C-276. In order to prevent the condensation and deposition of formed UF₆ product, F_2 was used to passivate the fluorinator (including the Ni-crucible) and all the pipelines before experiments. The passivation procedure is shown in the Table 1. All the pipelines the formed UF₆ passing through were heated

to 373 K before introduction of NF₃.



Fig. 1. The flow diagram of the experiment setup

Table 1 The passivation procedure of the fluorination system

Duration / h	Temperature rise	F ₂ flow rate	Purpose
0.5	298K	0.2 L/min	Remove the air in equipment and pipelines
2	298K-373K	0.1 L/min	Dehydration and pre-fluorination
2	373K-623K	0.1 L/min	Slow formation of passivation film
4.5	623K	0.1 L/min	Key formation stage of passivation film
Natur	ral cooling	0.1 L/min	Maintain the integrity of the film

The fluorination process was as follows: (1) approximately 6.4×10^{-3} mol of UF₄ powder was placed in a nickel crucible located in the fluorinator; (2) after the fluorinator was heated to the specified temperature, the NF₃/Ar gas was introduced with a flow rate of 0.2 L/min, which was controlled and measured by a thermal mass flowmeter (5850 EM, Brooks, USA) with a NF₃/Ar range of 0.05-1 SLM(Standard Liter per Minute, uncertainty: \pm 1% full scale); (3) the outlet gas from the fluorinator passed through the NaF trap at 673 K, which intercepted salt mist and absorbed volatile corrosion products; (4) the gas from NaF trap went through NaF adsorbers at 373 K, where UF₆ was absorbed; and (5) the off-gas was discharged through the activated alumina absorption tank, buffer tank and KOH-KI absorption tank successively.

The fluorination process was monitored by in-line Fourier transform infrared

(FTIR) spectroscopy (Perkin-Elmer Frontier; ZnSe as a reference: 4200-400 cm⁻¹; resolution: 4 cm⁻¹; scanning frequency: 32 cm⁻¹; optical path length: 10 cm⁻¹), and the beginning and end of the reaction were determined by monitoring the characteristic absorption peak of UF₆ at 625 cm⁻¹ in the FTIR spectra. The uranium concentration left in the fluorinator after fluorination was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, NexION 300D, PerkinElmer). The chemical composition of the residue left in the fluorinator after fluorination at different temperatures was characterized by standard powder X-ray diffraction with CuK α radiation (XRD, PANalytical X'Pert Pro MPD X-ray polycrystalline diffractometer, DY3614, Netherlands, the diffraction patterns were obtained over a 2 θ range of 10-90° with a scanning step size of 0.01°). All sample preparation was carried out in the argon-covered glove box. The X'Pert High-Score database and software were used for pattern matching.

The average fluorination reaction rate (v) was calculated according to formula (1). NF₃ gas was regarded as the ideal gas, and its utilization rate was calculated according to formula (2):

$$\overline{v} = \frac{m_0 - m}{t} \tag{1}$$

$$\eta\% = \frac{2}{3} \cdot \frac{n_U}{n_{NF_3}} = \frac{2}{3} \cdot \frac{\frac{m_0 - m}{238}}{\frac{PV_{NF_3}}{RT}} (V_{NF_3} = C \cdot v \cdot t)$$
(2)

Where m_0 (g) is the initial mass of the U from the UF₄ raw material, m (g) is the uranium mass at the end of reaction, and t (h) is the total time of fluorination, 2/3 is theoretical ratio of chemical reaction, 298 is the atomic weight of U, P (Pa) is atmospheric pressure, V_{NF3} (m³) is the volume of NF₃, C (%) is the volume fraction, v (L/min) is the velocity of mixed gas flow, T (K) is the actual experimental temperature and R is the constant(R=8.314 J· mol⁻¹· K⁻¹).

3、Results and discussion

3.1 Fluorination process

The gas from outlet of fluorinator during the fluorination process of UF_4 by NF_3 at 673, 723, 773, 823 and 873 K was monitored by in-line FTIR spectroscopy. No UF₆ was detected when the temperature was 673 K, which is consistent with the results from Bruce McNamara^[16] et. al. The conversion of UF_4 to UF_6 occurred in the range of 723 K to 873 K. Fig. 2 shows the FTIR spectra of outlet gas from the fluorinator, as shown in Fig. 2.a (the spectrum of outlet gas from the fluorinator at 823 K), characteristic peaks of NF₃ (905 cm⁻¹, 1032 cm⁻¹, 1136 cm⁻¹, 1523 cm⁻¹, 1809 cm⁻¹ and 1929 cm⁻¹), HF, CO₂, CF₄ (1283 cm⁻¹), UF₆ (625 cm⁻¹) and MoF₆ (741 cm⁻¹) are evident. The CF₄ came from the reaction of NF₃ with the graphite sealing ring which was used to seal the fluorinator. The MoF₆ was a corrosion product resulting from the reaction between NF₃ and the structure material Inconel. To identify the source of other gases in the gas phase, the typical FTIR spectra of NF₃ gas from the outlet of the empty fluorinator at room temperature and 773 K were obtained. As shown in Fig. 2.b, there only exists characteristic peaks of NF_3 ^[21,22] in the FTIR spectrum at room temperature. When temperature increased to 773 K, except the characteristic peaks of NF₃, characteristic peaks attributed to HF and CO₂ appeared, as shown in Fig. 2.c. It was speculated that HF came from hydrolysis of NF₃ at high temperature During the whole fluorination process at different experimental temperatures, no characteristic absorption peaks of N_xO_y or other nitrogenous compounds were found in the spectra of gas samples. According to the above results, we proposed that UF₄ reacted with NF₃ through the following reaction:

$$2/3NF_3(g) + UF_4(s) = UF_6(g) + 1/3N_2(g)$$
(3)

To demonstrate the feasibility of this reaction on the basis of thermodynamics, the corresponding standard Gibbs free energy changes (ΔG^{θ}) and standard enthalpy changes (ΔH^{θ}) at various temperatures were calculated using HSC Chemistry 6.0 software ^[20]. The calculated ΔH^{θ} and ΔG^{θ} in the range of 373 K to 1073 K(shown in Fig. 3) for formula (3) revealed that this reaction is exothermic, with absolute values increasing with temperature, which indicates that this reaction can process spontaneously in theory. However, whether a chemical reaction can occur in the actual experimental process also needs to be analyzed in combination with the

kinetics of the reaction. Based on the results described above, although the thermodynamic calculation showed that the fluorination for UF_4 by NF_3 could take place at 373 K, the temperature of fluorination in the actual experiment needed to be raised to 723 K. Therefore, the kinetics of NF_3 fluorination with UF_4 were analyzed in this paper, and the effect of temperature on fluorination was studied.



Fig. 2. FTIR spectra of outlet gas from the fluorinator: a-spectrum of outlet gas from the fluorinator at 823 K;

b-spectrum of NF₃ from the outlet of the empty fluorinator at room temperature; and c-spectrum of NF₃ from outlet of the empty fluorinator at 773 K.



Fig. 3. The curves of the thermodynamic parameters of formula (3) with increasing

temperature.

3.2 Average fluorination rate and utilization of NF3

From the height change of the peak at 625 cm⁻¹ measured at different reaction times, we could determine when the reaction began and ended. The height of the peak could be regarded as the relative concentration of UF₆ in the outlet of the fluorinator^[23]. The reaction was assumed stop when the relative concentration was lower than the detection limit of the FTIR. Fig.4 shows the curves of the relative concentration of UF₆ in the outlet of the fluorinator with time in the range of 723 K to 873 K. As shown in Fig. 4, the relative concentration of UF₆ in the outlet gas gradually increased and then decreased with reaction time.

As shown in Fig. 4 and Table 2, the maximum concentration increased while the time it took to reach maximum concentration decreased gradually as the temperature increased. The time to convert UF₄ to UF₆ decreased from 62 min at 723 K to 34 min at 873 K. The average reaction rate and the utilization of NF₃ in the reaction according to formulas (1) and (2) were calculated based on the above experimental data and are listed in Table 3. As shown in Table 3, temperature had a significant effect on the average reaction rate and the utilization rate of NF₃. The average reaction rate increased from 1.53 gU•h⁻¹ at 723 K to 2.68 gU•h⁻¹ at 873 K, while the utilization of NF₃ increased from 10.5% to 22.5%.



Fig. 4. Curves of the relative concentration of UF₆ in the outlet of the fluorinator with time in the range of 723 K to 873 K

T	T n		Maximum	Time to reach maximum	
I (V)	n_U	t (min)	concentration of UF ₆	concentration	
(K)	(K) (10^{-3} mol) (r		(a.u.)	(min)	
723	6.6	62	2.4	19	
773	6.4	46	2.8	16	
823	6.7	39	3.2	11	
873	6.4	34	3.8	9	

Table 2 Experimental data of the reaction between NF₃ and UF₄ at different temperatures

Table 3 The average reaction rate and utilization of NF₃ at different temperatures

Т	$n_{U} (10^{-1})$	⁻³ mol)	n_{NF_3}	t	\overline{v}	n% (NF ₂)
(K)	before	after	(10 ⁻² mol)	(min)	$(gU \bullet h^{-1})$	<i>1</i> /0 (1113)
723	6.6	NF	4.2	62	1.53	10.5%
773	6.4	NF	2.9	46	1.98	14.7%
823	6.7	NF	2.3	39	2.46	19.4%
873	6.4	NF	1.9	34	2.68	22.5%

Note: NF-not found.

Corrosion was another issue we concerned during the experiment. We found that no significant corrosion occurred when the reaction temperature was below 773 K and a small amount of black residue was left in the bottom of the crucible when the temperature was higher than 823 K. Fig. 5.a shows the image of the crucible and the XRD pattern of the residue left in the crucible after reacting at 823 K, which shows that the main constituents are NiF₂ and FeF₃. Meanwhile, as shown in Fig. 5.b, a white substance appeared on the inner surface of the fluorinator cover, and the XRD pattern shows that it is NOMoF₆^[24]. NiF₂, FeF₃ are all corrosion products coming from the reaction between the structural materials and NF₃. NOMoF₆ might come from the reaction of NO with MoF₆ (corrosion product), here NO came from NF₃ gas source and the hydrolysis of NF₃ at high temperature. The experimental results show that although NF₃ is a milder fluorinating agent when the temperature is below 823 K,

its reactivity increases significantly when the temperature is above 823 K, which results in a higher reaction rate as well as increased corrosion.



Fig. 5. XRD patterns of corrosion products: a: residue left in the crucible and b: white substance deposited on the inner surface of the fluorinator cover.

3.3 Effect of temperature on the kinetics of the reaction

The reaction of UF₄ powder with gaseous fluorinating reagent is a typical gas-solid noncatalytic reaction^[25]. In most reported studies on the kinetics of fluorination of uranium compounds where the products were entirely gaseous, the experimental data were treated by the diminishing sphere model ^[26-32], and the fluorination was assumed proceed through five steps: (1) diffusion of gaseous fluorinating reagent from the gas phase to the surface of UF₄ particles; (2) adsorption of gas molecules on the particle surface; (3) chemical reaction on the surface; (4) desorption of UF₆ from the surface; and (5) diffusion of UF₆ from the particle surface to the gas phase. In general, steps (1) and (5) are diffusion processes. In our experiment, the amount of UF₆ formed was not enough to result in boundary layer resistance and would not limit the diffusion of gas from or to the surface of particles. Steps (2), (3) and (4) are expected to be the rate-determining steps, and all are mainly temperature dependent. Therefore, the following discussion focuses on the effect of temperature on the kinetics of fluorination.

The following formula is a commonly used kinetic formula for a fluorination reaction^[28,29]:

$$(1-\alpha)^{\frac{1}{3}} = 1-kt$$
 (4)

$$\alpha = \frac{\text{mass of reacted UF 4 power}}{\text{mass of initial UF 4 power}}$$
(5)

where α is the conversion of raw material UF₄, %; *t* is the fluorination time, min; and *k* is the reaction rate constant, min⁻¹. The *k* is greatly affected by temperature for a chemical reaction. When the quantity $(1-\alpha)^{1/3}$ is plotted against *t*, the points lie on a straight line according to formula (4); then, the opposite number of the slope is *k*.

Assuming that all the UF₆ gas generated during the experiment was detected by infrared spectroscopy without delay, the numerical value obtained by integrating the curve of Fig. 4 could be regarded as the total amount of generated UF₆ gas, and the ratio of the amount of generated UF₆ gas to the total amount of UF₆ was regarded as the conversion rate (α) of the UF₄ raw material. Fig. 6 shows the curves of the conversion rates with time in the fluorination process. Based on the results of Fig. 6, the curve of $(1-\alpha)^{1/3}$ with respect to fluorination time was obtained (Fig. 7). As shown in Fig. 7, a good linear relationship existed between $(1-\alpha)^{1/3}$ and *t* in the whole fluorination process, which indicated that the kinetic formula based on the diminishing sphere model could better describe the kinetic law of the reaction of NF₃ and UF₄. According to formula (4), the *k* at different temperatures was calculated as listed in Table 4 and increased with the temperature increase. The activation energy (E_a) of the reaction calculated according to the Arrhenius equation was 22.56 kJ·mol⁻¹.



Fig. 6. Conversion rate curves with increasing time





Fig. 7. Plot of $(1-\alpha)^{1/3}$ against time at different temperatures

Fig. 8. Arrhenius plot for the fluorination of UF_4 with NF_3

Table 4 Reaction rate constant and activation energy of the fluorination of NF₃ with UF₄

Temperature	723 K	773 K	823 K	873 K
Reaction rate constant k (min ⁻¹)	1.6×10 ⁻²	2.2×10 ⁻²	2.7×10 ⁻²	3.1×10 ⁻²
activation energy E _a (kJ/mol)		22	2.56	

4、Conclusions

The fluorination process, average fluorination rate, utilization rate of NF_3 and reaction kinetics at different temperatures were studied using a homemade FVP research device, and the reaction process was successfully monitored and analyzed by

in-line FTIR. The results indicated that the temperature had a significant effect on the average reaction rate and the utilization rate of NF₃, and the fluorination between NF₃ and UF₄ occurred only when the temperature was above 723 K. The average fluorination rate increased from 1.97 to 3.45 gU•h⁻¹ and the utilization rate of NF₃ increased from 10.5% to 22.5% when the temperature increased from 723 K to 873 K. The in-line FTIR spectrum analysis and thermodynamic calculation indicated that UF₄ was converted to UF₆ with the following reaction mechanism: $2/3NF_3(g) + UF_4(s) = UF_6(g) + 1/3N_2(g)$. By fitting experimental data based on the diminishing sphere model, the calculated rate constant increased from 1.6×10^{-2} to 3.1×10^{-2} min⁻¹ in the range of 723 K to 873 K, which validated the sensitivity of fluorination to temperature, and the activation energy of the reaction was 22.56 kJ/mol.

Declaration of interests

 $\Box \checkmark$ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Acknowledgments

This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA02030300) and the Young Potential Program of the Shanghai Institute of Applied Physics, Chinese Academy of Sciences (Grant No.Y955081031).

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