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Comparison of the Fluorinations of Uranium Dioxide by Bromine Trifluoride and **Elemental Fluorine**

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Uranium dioxide powder was fluorinated by gaseous BrF3 and F2, separately, in order to compare the characteristics of the two fluorinating agents. The BrF₃-UO₂ reaction proceeds under lower temperatures and a lower concentration of the reacting gas than the F_2 -UO₂ reaction. The temperature dependence of its rate is very small; the apparent activation energy is only 1.6 kcal/mol. In the F₂-UO₂ reaction, the production of UF_6 was not observed below 390°. The rate of this reaction increases remarkably with an increase in temperature; the apparent activation energy for this reaction is 26.0 kcal/mol. In both of these reactions, UO₂F₂ is formed as an intermediate, and the further uptake of fluorine in the solid is not observed in either case. The solution from the residue of BrF₃-UO₂ reaction contains trace amounts of bromine, which possibly arises by hydrolysis of the BrF₃ chemisorbed on the solid. Oxygen fluorides were not detected in the F2-UO2 reaction. The diffusion rate of the reacting gas onto the solid surfaces influences the rates of both reactions. The results indicate that the physical adsorption of BrF_3 functions as the precursor to its chemisorption, and that the adsorption of fluorine is activated and dissociative.

Introduction

Bromine trifluoride (mp 8.8°, bp 127.6°) is readily prepared by direct combination of bromine and fluorine, and has been used as a liquid fluorinating agent or a solvent by many other workers.¹⁻⁴ Extensive data on its physical and chemical properties are available.¹⁻⁴

Recently, gaseous BrF_3 has been used in the author's laboratory for the fluorination of nuclear fuels and fission products. In the series of studies,^{5,6} the author has noticed that gaseous BrF3 has higher reactivity with such inorganic materials as uranium compounds than F2. For example, gaseous BrF₃ fluorinates UF₄ even at 55°,⁵ whereas Labaton and Johnson have reported that the fluorination of UF₄ by F_2 does not proceed below 220°.⁷ The reason for this has not been made clear yet. Moreover, details of their reactivities are not obtained from the literature available, because the experimental data are not sufficient or each worker used specimens with different histories of preparation.

The purpose of the present study is to obtain information on the reactivities of $\mathrm{Br}F_3$ and $\mathrm{F}_2.$ Uranium dioxide powder was fluorinated by gaseous BrF3 and F2, separately, and the reaction rates and processes were studied. On the basis of the results, the difference in reactivity between the two fluorinating agents is discussed.



Figure 1. Examples of the weight change vs. time curve in the BrF_3-UO_2 and the F_2-UO_2 reaction: initial weight of UO_2 100 mg; temperature 208° for the BrF_3-UO_2 and 450° for the F_2-UO_2 reaction; BrF_3 partial pressure 15 mm; F_2 partial pressure 152 mm; helium was used as the carrier or diluent gas, the linear gas velocity being 1 cm/sec.

Experimental Section

Materials. Commercial-grade bromine trifluoride, from the Matheson Co., was purified by distillation as reported previously.⁸ Fluorine, from Daikin Kogyo Co., was used after passage through a sodium fluoride column to eliminate hydrogen fluoride. Uranium dioxide powder with a purity greater than 99.9% was supplied by Mitsubishi Kinzoku Kogyo Co. Prior to the experiment the material was treated with pure hydrogen at 1050° for 10 hr; the surface area, determined by means of krypton adsorption, was 2.2 m²/g. Argon, nitrogen, and helium, used as a diluent for F₂ and as a carrier gas for BrF₃, were of purities greater than 99.99%.

Thermogravimetric Study. The weight change of the solid phase was obtained with a thermobalance, details of which were described in a previous paper.⁵ All valves and tubes in the apparatus in contact with the reacting gases and the reaction products are made of Monel, nickel, or Teflon; they were kept at 40° to prevent condensation of BrF_3 and UF_6 . Leaks from the apparatus were checked with a helium leak detector; they were less than 10^{-9} atom cm^3/sec . UO₂ (100 mg) was placed in a sample pan suspended in the reaction tube. After having been evacuated, the reaction tube was filled to atmospheric pressure with an inert gas, and the sample was then heated to a specified temperature. A chromel-alumel thermocouple in a Monel sheath 0.3 cm below the sample pan sensed the reaction temperature. Subsequently, the inert gas containing BrF_3 or F_2 of a given partial pressure was passed through the reaction tube at a constant flow rate. The linear gas velocity was kept at 1 cm/sec, because the rates of both reactions were constant in the linear velocity range 0.9-2.4 cm/sec.^{9,10} The partial pressure of fluorine was controlled by using a flowmeter with nickel filaments,¹¹ and that of $\mathrm{Br}F_3$ was varied by saturating the inert gases with BrF₃ vapor at different temperatures.⁵ The weight

change of the solid phase with time was recorded continuously on a recording potentiometer.

Analysis of the Solid Phase. The change in composition of the solid phase with time was examined as follows. After uranium dioxide had been in contact with the reacting gas stream for a given time, the residue was taken out of the reaction tube and added to 25 ml of distilled water. The insoluble residue (UO₂) was removed by filtration, and then the amounts of fluorine, bromine, and UO_2^{2+} in the solution were determined. The alizarin complexone (ALC) photometric method was used for determination of the fluorine.¹² The UO_2^{2+} content was determined by measuring its absorbance at 425 nm. The presence of trace amounts of bromine was observed by potentiometry,¹³ after the solution had been treated with sodium sulfite for reduction of BrO⁻ and BrO₃⁻ into Br⁻.⁸

Analysis of the Gas Phase. The gas phase was analyzed by infrared spectroscopy, in order to see whether or not oxygen fluorides are produced in the F_2 -UO₂ reaction. Uranium dioxide was treated with F_2 at various temperatures between 300 and 500°, and, before completion of the reaction, the gas in the reaction tube was quenched rapidly to -78° in order to prevent the thermal decomposition of oxygen fluorides.¹⁴ The UF₆ produced was thus caught in the cold trap and the remainder was introduced into an absorption cell. A Shimadzu Model IR-27B spectrophotometer was used. The cell with silver chloride windows was made of Monel.

Results and Discussion

Changes in Weight and Composition of the Solid Phase. In order to compare characteristics of the two reactions, "weight change vs. time" curves are shown in Figure 1 for the runs in which the two reactions give similar rates. In both of the reactions, the weight of the solid phase increases slightly in the initial stage of reaction, and then decreases with time. Although both of the reactions shown in Figure 1 terminated 25 min after the start, it should be noted that the reaction temperature was 450° for the F₂- UO_2 and 208° for the BrF₃- UO_2 reaction, and the partial pressure of the reacting gas was 152 mm in the former and only 15 mm in the latter reaction. The BrF₃- UO_2 reaction thus proceeds under milder experimental conditions than the F₂- UO_2 reaction.

For the F_2 -UO₂ reaction, it is known that UO₂ F_2 is produced as an intermediate.¹⁰ The change in composition of the solid phase with time was examined to obtain information on the mechanism of reaction. Table I shows the results for the runs which were carried out under the same experimental conditions as in Figure 1. The mole ratio $[F^-]/[UO_2^{2+}]$ is nearly 2 for both the reactions, except that in the initial stage. This fact indicates that UO_2F_2 is an intermediate also in the BrF_3 -UO₂ reaction, and the further uptake of fluorine in the solid phase, corresponding to the formation of such intermediates as UOF₄, does not take place in either of the reactions. UO₂ may be fluorinated to UF₆ through the following two steps in both the reactions

The weight increase in the initial stage of reaction is ascribable to step 1 (see Figure 1).

Idrissi, et al., reported that $(UO_2)_4F$, $(UO_2)_3F$, and $(UO_2)_xF_y$, with $x = y \le 2$, were formed in the F_2 - UO_2 reaction, preceding to the formation of UO_2F_2 .¹⁵ The low

BrF_3 -UO $_2$ reaction						F_2 -UO ₂ reaction				
Time elapsed, min	Reaction residue, mg	$\mathrm{UO}_{2^{2^{+}}},\mathrm{mg}$	F ⁻ , mg	Mole ratio, [F ⁻]/ [UO ₂ ²⁺]	Br -, μg	Time elapsed, min	Reaction residue, mg	UO2 ²⁺ , mg	F ⁻ , mg	Mole ratio, [F ⁻]/ [UO _{2²⁺]}
4	101.6	53.3	7.1	1.89	42	2	104.5	82.3	10.8	1.86
8	80.4	35.1	5.1	2.06	28	6	82.5	67.5	9.3	1.96
10	67.7	31.7	4.6	2.06	42	11	58,9	50.0	7.0	1.99
13	48.1	18.2	2.7	2.11	28	14	43.5	36.5	5.1	1.99
19	21.7	9.8	1.4	2.03	32	19	20.2	17.7	2.6	2.09

TABLE I: Results of the Analysis of the Solutions Prepared from the Reaction Residues^a

^a Experimental conditions of the fluorination were as follows: initial amount of UO₂ was 102 ± 1 mg, temperature was 208° for the BrF₃–UO₂ and 450° for the F₂–UO₂ reaction, BrF₃ partial pressure was 15 mm, F₂ partial pressure was 152 mm, and the carrier or diluent gas was helium, the linear gas velocity being 1 cm/sec.



Figure 2. Changes of the mole fractions of UO₂, UO₂F₂, and UF₆ during the reactions.

values of the mole ratio $[F^-]/[UO_2^{2+}]$ in the initial stages of both the reactions, *i.e.*, 1.89 and 1.86, may be due to these intermediates.

The solution from the residue of BrF_3-UO_2 reaction contains trace amounts of bromine; the mole ratio $[Br^-]/[UO_2^{2+}]$ is in the range of 10^{-3} to 10^{-2} . The bromine in the solution is possibly produced by hydrolysis of the BrF_3 chemisorbed on the reaction residue.⁸

From Table I and Figure 1, the changes in amounts of UO_2 , UO_2F_2 , and UF_6 can be obtained; Figure 2 shows the results. The ordinates in the figure are the mole fractions of UO_2 , UO_2F_2 , and UF_6 , and the abscissas the reaction time, which is the same as that in Figure 1. Elemental fluorine converts most of the UO_2 into UO_2F_2 in the first 2 min; therefore, in the F_2 - UO_2 reaction the apparent weight loss of the solid phase can be regarded as the loss of UO_2F_2 due to step 2. On the other hand, in the BrF₃- UO_2 reaction, the solid phase consists of nearly equal amounts of UO_2 and UO_2F_2 throughout the reaction, and, therefore, the apparent weight loss of the solid phase is 6%, or less, smaller than the loss of UO_2F_2 due to step 2. This difference may be due to the step 1 in the



Figure 3. Temperature dependence of the rates of the two reactions and the F(T) curve for $E = 2.0 \times 10^{-13}$ erg: initial weight of UO₂ 100 mg; BrF₃ partial pressure 15 mm; F₂ partial pressure 152 mm; the carrier or diluent gas was helium, the linear gas velocity was 1 cm/sec. The dotted line shows a theoretical temperature function for the rate of BrF₃-UO₂ reaction, details of which are described later.

 F_2 -UO₂ reaction being highly exothermic; a rapid increase in the reaction temperature takes place in the beginning of this reaction, as shown later (see Figure 4).¹⁰

Rates of the Reactions. In many cases of gas-solid reactions in which the products are entirely gaseous, the diminishing sphere model has been used to treat the rates.^{7,10,16} The final equation derived from this model is $(1 - F)^{1/3} = 1 - k't$, where F is the fraction of the solid reacted, t the reaction time, and k' a rate constant. The slope of the straight line in a graph of the value of $(1 - F)^{1/3} vs$. time gives the rate constant.

However, in the present case, the plot of $(1 - F)^{1/3}$ vs. time did not give a straight line for either of the reactions and that of (1 - F) vs. time was linear, except its initial and final portions, for both the reactions. This fact indicates that the thickness of the solid phase decreases with time at a constant rate, as the present author and other workers reported already for the BrF₃-UF₄ and the SF₄-UO₃ reaction, respectively.^{5,16} Therefore, in the present study, the slope of the straight line approximating the middle portion of the weight change vs. time curve was used as a reaction rate K in g/min.

Effect of Temperature on the Reaction Rate. Temperature dependence of the reaction rate was examined by keeping both partial pressure of the reacting gas and linear gas velocity constant. The temperature was varied between 40 and 500°; the partial pressure was 152 nm for F_2 and only 15 mm for BrF₃. Figure 3 shows the results. The BrF₃-UO₂ reaction proceeds even at 40°, producing UF₆; the rate increases only slightly with temperature. In the F₂-UO₂ reaction, the weight decrease due to the production of UF₆ was not observed up to 390°, though the sorption of fluorine was confirmed even at 300° through a pressure study. The rate of this reaction increases remarkably with increasing temperature, and beyond 480° it exceeds that of the BrF₃-UO₂ reaction. The Arrhenius plot for F₂-UO₂ reaction is linear, and gives the apparent activation energy of 26.0 kcal/mol. The least-squares method was used in the Arrhenius plot for BrF₃-UO₂ reaction, in order to determine the straight line approximating the plot; the apparent activation energy thus obtained was only 1.6 kcal/mol.

Influence of the Inert Gases on the Reaction Rate. When a gas-solid reaction is diffusion controlled, its rate is proportional to $V^{0.5}$, where V is the linear gas velocity.¹⁷ However, the present author reported previously⁹ that the BrF₃-UF₄ reaction was still diffusion controlled even in the range where the linear gas velocity little influenced the reaction rate (this phenomenon could be explained as the influence of a sample pan). Therefore, in the present study, the carrier or diluent of the reacting gas was changed in order to see the influence of the diffusion of the reacting gas on the reaction rate.

When the carrier gas was changed from helium to argon or nitrogen, the rate of BrF_3 -UO₂ reaction decreased by nearly a half. This is attributed to the decrease in diffusion rate of BrF_3 in the relatively stagnant gas film between the solid phase and the main gas stream.⁹

In the F_2 -UO₂ reaction, a similar decrease in reaction rate was also observed at 450° by changing the diluent of F_2 . However, at higher temperatures, e.g., 475°, the reaction proceeds more rapidly in argon than in helium in the initial stage. Figure 4 shows the changes in weight and in reaction temperature during the runs at 475°. The reaction temperature increases rapidly in the beginning of the F_2 -UO₂ reaction, and argon keeps this high temperature for a considerably longer time than helium; the production of UF_6 is accelerated remarkably with argon during this interval. The reaction in argon then slows down as the temperature returns to the original line (475°) , and becomes slower than that in helium in the final stage. This phenomenon is ascribed to the lower thermal conductivity of argon and the great temperature dependence of the rate of F_2 -UO₂ reaction.

Thus, the diffusion rate of the reacting gas onto the solid surfaces influences the reaction rate in both the cases.

Study of the Reaction Products. The question has been raised whether oxygen difluoride is produced or not as a product in the fluorination of uranium oxides by F_{2} .¹⁸ However, infrared spectra of the gas phase did not show any peaks corresponding to oxygen fluorides.

Difference in Mechanism between the Two Reactions. The BrF₃-UO₂ reaction proceeds under lower temperatures and a lower concentration of the reacting gas than the F₂-UO₂ reaction, and application of heat only slightly increases its rate. This reaction does not involve any activated steps. In addition, the author reported previously¹⁹ that gaseous BrF₃ was adsorbed by ionic crystals such as sodium fluoride in the same partial pressure region as in the present experiment, *i.e.*, $P/P_s \leq 0.02$, where P_s denotes the saturated vapor pressure of BrF₃. These findings indicate that BrF₃ molecules are attracted to UO₂ surfaces by the electrostatic force between the dipole of BrF₃ molecules ($\mu = 1.0$ D²) and the surface ions. Since UO₂ crystal is a semiconductor,¹⁸ the fluorine atoms of the



Figure 4. Changes in weight and temperature during F_2 -UO₂ reactions at, 475° in different diluents: diluent of F_2 helium or argon; initial weight of UO₂ 100 mg; F_2 partial pressure 152 mm; linear gas velocity 1 cm/sec.

 BrF_3 molecules adsorbed form acceptor bonds with uranium ions on the surfaces by trapping surface electrons of the semiconductor.^{20,21} This process may correspond to the case that the potential energy curve for chemisorption crosses that for physical adsorption while the van der Waals force is still attractive, and no activation energy is required for the chemisorption.²¹

Small temperature dependence of the rate of BrF_3-UO_2 reaction, in Figure 3, may be explained as follows. Of the BrF_3 molecules in the gas phase, only a fraction with total translational energies less than the heat of adsorption, Eerg, will be attracted to UO_2 surfaces by the electrostatic force. On the assumption that the distribution law is applicable to the BrF_3 molecules in the inert gas, the fraction, f(E, T), described above is given as²²

$$f(E,T) = \operatorname{erf}[(E/kT)^{1/2}] - 2/\pi^{1/2}(E/kT)^{1/2} \exp(-E/kT)$$

where k is Boltzmann's constant, T the temperature in $^{\circ}$ K, and erf(x) the error function. The rate of a gas-solid reaction is proportional to $D_{12}(C_{\rm b} - C_{\rm s})$,²³ where D_{12} is the diffusion coefficient in the binary gas system, and $C_{\rm b}$ and $C_{\rm s}$ are the concentration of the reactant in the main gas stream and in the gas phase at the solid surface, respectively. In the present case, $C_{\rm s}$ can be taken as $C_{\rm b}[1 - f(E,T)]$. In theoretical equations,²⁴ D_{12} is related to temperature as $T^{3/2}$. The temperature function of the reaction rate, F(T), is thus expressed as

$$F(T) = T^{3/2} f(E,T)$$

Since f(E,T) decreases with an increase in temperature, F(T) increases slightly or decreases, depending upon the value of E, when temperature is increased. The results of calculation show that the F(T) curves for $E = 1.0 \times 10^{-13}$ $\sim 3.0 \times 10^{-13}$ erg are similar in shape to the temperature-dependence curve for the BrF₃-UO₂ reaction rate shown in Figure 3. The F(T) curve for $E = 2.0 \times 10^{-13}$ erg is shown in Figure 3 by the dotted line; the values of f(E,T) for $E = 2.0 \times 10^{-13}$ erg are 0.94 at 400°K, 0.82 at 600°K, and 0.70 at 800°K.

On the other hand, characteristics of the F2-UO2 reaction are as follows: (i) heating is necessary for its initiation, and (ii) the rate increases remarkably with increasing temperature. Similar characteristics are also observed in other reactions of fluorine: the F_2 -MoO₃ and the F_2 - UF_4 reaction proceed at temperature above 250 and 220° respectively,^{6,7} and the apparent activation energy is 36.8 kcal/mol for the former and in the range 15.5-19.9 kcal/ mol for the latter reaction.

The facts described above indicate that the F_2 -UO₂ reaction involves the activated and dissociative adsorption of fluorine. The heating, necessary for the initiation of this reaction, may be attributed to the energy of stretching the interatomic distance of fluorine molecules so as to match the distances between uranium sites on the surfaces.^{21,25}

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Photochemistry of Rhodium(III) Complexes. Ligand Field Excitation of Hexaamminerhodium(III) and Characteristics of Nonradiative Deactivation Paths¹

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Ligand field excitation of hexaamminerhodium(III), $Rh(NH_3)6^{3+}$, in aqueous solution results in the photoaquation of one coordinated NH₃. The measured quantum yields at 23° are 0.075 mol/einstein for 313nm excitation of the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ transition and 0.07 for 254-nm excitation of the ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ transition, suggesting efficient interconversion of the higher energy state to a common reactive excited state. Under similar conditions, the quantum yield for the perdeuterated complex $Rh(ND_3)e^{3+}$ is about twice as large $(0.14 \text{ in } H_2O, 0.15 \text{ in } D_2O, 313\text{-nm}$ excitation). However, the temperature dependence of the photoaquation quantum yields is measurably greater for the perprotio complex than for the perdeuterio complex. To explain these results, it is proposed that temperature-independent weak coupling and temperaturedependent strong coupling mechanisms are competitive in the nonradiative deactivation of the reactive excited state of $Rh(NH_3)_6^{3+}$.

Introduction

In the past several years, interest^{3,4} in the photoreactivities of d⁶ metal ion complexes has been extended to quantitative studies of the ammine complexes of ruthenium(II)⁵ and rhodium(III).⁶⁻¹⁰ The rhodium(III)-ammine complexes whose photochemistry reported to date have

been halide complexes such as $\mathrm{Rh}(\mathrm{NH}_3)_5\mathrm{X}^{2+}$ or $Rh(en)_2X_2^+$ (X = Cl⁻, Br⁻, or I⁻), for which perturbations of the ligand field involve the stereochemistry of the bis(ethylenediamine) complexes or the identity of the halide ion. In order to consider more subtle differences, we have been examining the photochemistry^{1,11} and lumines-