# THE REACTION OF GASEOUS BROMINE PENTAFLUORIDE WITH URANIUM COMPOUNDS-II THE KINETICS OF THE REACTION WITH U<sub>3</sub>O<sub>8</sub>, UO<sub>2</sub> AND UO<sub>3</sub>[1]\*

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(First received 24 May 1967; in revised form 30 June 1967)

Abstract – The kinetics of the reaction of  $BrF_5$  with  $U_3O_8$ ,  $UO_2$ , and  $UO_3$  have been determined. The following equations represent the combined temperature and pressure dependence of the reactions

 $\begin{aligned} & U_{3}O_{8}; \log k' = 0.90 \log P - 2000/T - 0.220 \\ & UO_{2}; \log k' = 0.84 \log P - 1630/T - 0.270 \\ & UO_{3}; \log k' = 1.05 \log P - 1680/T - 0.767. \end{aligned}$ 

Activation energies of 9.2, 7.5 and 7.7 kcal/mole were calc. for reactions of  $U_3O_8$ ,  $UO_2$  and  $UO_3$ , respectively. Bromine was the other volatile product of the reaction along with UF<sub>6</sub> and oxygen. These reactions proceed through the formation of  $UO_2F_2$  as an intermediate. The presence of UF<sub>4</sub> in the reaction of  $U_3O_8$  and BrF<sub>5</sub> was probably due to the interaction of the product UF<sub>6</sub> with  $U_3O_8$ .

# INTRODUCTION

THE KINETICS of the reaction of  $BrF_5$  with the uranium oxides  $U_3O_8$ ,  $UO_2$  and  $UO_3$  have been determined and are reported in this paper. The kinetics of the reactions of  $BrF_5$  with  $UF_4$  and  $UO_2F_2$  and a review of prior work on the reaction of interhalogen compounds with various uranium oxides was presented in a previous paper[1].

#### Materials

#### EXPERIMENTAL

The specifications for the uranium compounds used in this work are listed in Table 1. The  $U_3O_8$  was obtained from the Mallinckrodt Chemical Co.,; the ANL-UO<sub>2</sub> was prepared by the steam-hydrogen reduction of UF<sub>6</sub>; the Numec-UO<sub>2</sub> was prepared by crushing and grinding pellets produced by

	Analytical results					
Compound	Found (%)		Theor (%)		A vergge norticle	Surface area
	U	0	U	0	size (µ)	(m²/g)
U <sub>3</sub> O <sub>8</sub>	84.7	15.2	84.8	15.2	10	0.23
ANL-UO2	88.3	12.0	88.2	11.9	81	0.46
Numec-UO <sub>2</sub>	88.1	12.0	<b>88</b> ·2	11.9	81	0.04
$UO_3$	82.7	16.7	83-2	16.8	81	0.67

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\*Work performed under the auspices of the U.S. Atomic Energy Commission, under Contract No. W-31-109-eng-38.

1. Part I of this series, J. inorg. nucl. Chem. 29, 1591 (1967).

Numec (Nuclear Material and Equipment Corp., Apollo, Pa.) and the  $UO_3$  was prepared by the thermal decomposition of  $UO_4 4H_2O$ . The BrF<sub>5</sub> was characterized in a previous paper[1]. The nitrogen used in mixtures with the BrF<sub>5</sub> was obtained from vaporized liquid nitrogen and was passed through Linde Type 4A Molecular Sieves to remove any water picked up in the distribution piping.

### Apparatus and procedure

The thermobalance and the procedure used in these experiments were described in the previous paper of this series[1].

#### Results

The data were treated using the "diminishing sphere" model developed by Anderson[2]. In this kinetic model, the reaction rate is related to the changing surface area available for reaction as a function of the reduction in diameter of the solid particles with reaction time. The final equation developed is:

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

in which F is the fraction of the solid reacted, k' is a rate constant and t is the reaction time. The rate constant k' is related to the true rate constant k, by the expression  $k' = k/r_0\rho$ , in which  $r_0$  is the initial particle radius and  $\rho$  is the bulk density of the solid.

Data for the temperature and pressure dependence of the rates of reaction with  $U_3O_8$  are shown in the plots of Fig. 1. The data for the temperature dependence of the reaction rates with the two types of



Fig. 1. Temperature dependence of rate constants for the reaction of BrF<sub>5</sub> with  $U_3O_8$ BrF<sub>5</sub> Partial pressure:  $\Delta - 89$  torr,  $\Phi - 108$  torr, x - 189 torr,  $\bigcirc -241$  torr,  $\oslash -369$  torr.

 $UO_2$  and with  $UO_3$  are shown in the plots of Figs. 2 and 3. Data for the dependence of the rate constants on the BrF<sub>s</sub> partial pressure for the reactions with ANL- $UO_2$  and  $UO_3$  are listed in Table 2. The 2. J. S. Anderson, *Bull. Soc. chim. France* 20, 781 (1953).



Fig. 2. Temperature dependence of rate constants for the reaction of  $BrF_5$  with  $UO_2$  $\bigcirc -ANL-UO_2$ ,  $\bigcirc -Numec-UO_2$ .

Arrhenius equation was fitted by the method of least squares to the various sets of data and the resulting equations are listed in Table 3. The effect of the linear velocity of the gas phase in the range 0.7-1.9 cm/sec on the value of the rate constants was no greater than the normal deviation between replicate points, about 3 per cent. The linear velocity of the gas phase for the majority of the experiments was 0.7 cm/sec.

Using the several equations representing the temperature dependence of the reactions, values of the activation energies were calc. to be 9.2, 7.5, 14 and 7.7 kcal/mole for the reactions of  $U_3O_8$ , ANL- $UO_2$ , Numec- $UO_2$  and  $UO_3$ , respectively. The BrF<sub>5</sub> pressure coefficient *n* of the equation  $k' = Ae^{-E/RT}P^n$  for the reactions of  $U_3O_8$ , ANL- $UO_2$  and  $UO_3$  were found to have the values 0.90, 0.84 and 1.05, respectively. The pressure dependence of the reaction with Numec- $UO_2$  was not determined. The following equations represent the combined temperature and pressure dependence of the rate constants of these reactions:

$$U_{3}O_{8}; \log k' = 0.90 \log P - 2000/T - 0.220.$$
(1)

ANL-UO<sub>2</sub>; 
$$\log k' = 0.84 \log P - 1630/T - 0.270.$$
 (2)

$$UO_3; \log k' = 1.05 \log P - 1680/T - 0.767.$$
 (3)

in which the pressure is in torr, temperature T in °K and k' in min<sup>-1</sup>.

## DISCUSSION

All of these reactions probably proceed through the formation of  $UO_2F_2$  as an intermediate compound. This is indicated by the values of the activation energies which are in the neighbourhood of the 8.3 kcal/mole previously found for the  $BrF_5$ - $UO_2F_2$  reaction[1]. Thermobalance studies of the reaction of fluorine with



Fig. 3. Temperature dependence of rate constants for the reaction of  $BrF_{\rm 5}$  with  $UO_{\rm 3}$ 

Table 2. Dependence of the rate constant, $k'$ , on the partial pressure of $BrF_5$							
	Temp. (°C)	P <sub>BrFs</sub> (torr)	$k'  imes 10^3$ (min <sup>-1</sup> )				
— А.	UO <sub>2</sub> -BrF <sub>5</sub> Reaction						
	242	74	13.8				
	250	74	13.8				
	242	181	23.6				
	250	181	27.2				
	242	369	43.0				
	250	369	60.1				
B.	$UO_3$ -BrF <sub>5</sub> Reaction						
	252	90	12.9				
	253	90	12.9				
	251	189	26.6				
	252	189	31.6				
	251	277	41.8				
	251	277	41.8				

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	log k	$' = A - \frac{1}{T(s)}$	°K)	
	BrF <sub>5</sub> Partial pressure	Cons	stants	
Uranium oxide	(torr)	A	В	E(kcal/mole)
U <sub>3</sub> O <sub>4</sub>	89	1.516	2000	9.2
0 - 0	108	1.892	2130	9.7
	189	1.926	2080	9.5
	241	1.809	1940	8.9
	369	1.813	1860	8.5
				(Ave. 9·2)
$ANL-UO_2$	181	1.493	1630	7.5
Numec-UO <sub>2</sub>	181	3.441	3060	14.0
UO <sub>3</sub>	189	1.636	1680	7.7

Table 3. Rate equations for the reaction of BrF<sub>5</sub> with uranium oxides

 $U_3O_8$ ,  $UO_3$  and  $UO_2[3,4]$  indicate that these reactions also proceeded through the formation of  $UO_2F_2$  as an intermediate. Uranyl fluoride could also be formed along with  $UF_4$  by the reaction of the product  $UF_6$  with the uranium oxides. G. A. Rampy has reported[5] the following reactions between  $UF_6$  and uranium oxides:

$$U_3O_8 + 2UF_6 \rightarrow 4UO_2F_2 + UF_4 \tag{4}$$

$$UO_2 + UF_6 \rightarrow UO_2F_2 + UF_4 \tag{5}$$

$$2UO_3 + UF_6 \rightarrow 3UO_2F_2. \tag{6}$$

The rapid formation of a layer of  $UO_2F_2$  on the surface of the oxide particles in the reactions with  $U_3O_8$ ,  $UO_2$ , and  $UO_3$  would prevent any reaction between the product  $UF_6$  and the oxide. The sintered nature of the Numec- $UO_2$  particles might result in a lower rate of conversion of the oxide particles to  $UO_2F_2$  by  $BrF_5$ and thus would lead to enhancement of the reaction between  $UF_6$  and  $UO_2$ . The reacting surface would therefore have been an equimolar mixture of  $UO_2F_2$  and  $UF_4$  as indicated by reaction 5 above. For such a mixture, assuming that the activation energies are simply additive, an activation energy of 12.6 kcal/mole can be derived, using the value of 16.9 and 8.3 kcal/mole previously reported[1] for the reaction of  $BrF_5$  with  $UF_4$  and  $UO_2F_2$ , respectively. Reasonable agreement for the additivity of the activation energies was obtained for experiments in which 5 g samples of  $\frac{2}{3}UO_2F_2-\frac{1}{3}UF_4$  mixtures were reacted with  $BrF_5$  in a boat reactor. The calc. activation energy for this mixture is 11.2 kcal/mole, while that obtained from a least squares fit of the Arrhenius equation to the experimental data for the  $\frac{2}{3}UO_2F_2-\frac{1}{3}UF_4$  mixture was 10.0 kcal/mole.

- 4. T. Yahata and M. Iwasaki, J. inorg. nucl. Chem. 26, 1863 (1964).
- 5. G. A. Rampy, U.S. AEC Reports (GAT-L-366, 5 June, 1957 and GAT-265, 5 June, 1959.

<sup>3.</sup> M. Iwasaki, J. inorg. nucl. Chem. 26, 1853 (1964).

The reaction product of the  $BrF_5$  component for the reaction with  $U_3O_8$  was identified as bromine. This was accomplished by titrating the bromine contained in the condensed reaction products with fluorine to convert the bromine to BrF<sub>3</sub>, as described by Sheft et al.[6]. In the previously reported work on the reaction of  $BrF_5$  with UF<sub>4</sub> and UO<sub>2</sub>F<sub>2</sub>[1], bromine was shown by the same method to be the only product of the BrF<sub>5</sub> in the reaction with UF<sub>4</sub>. It is reasonable to assume that bromine is also the reaction product of the  $BrF_5$  in the reactions with  $UO_2$  and  $UO_3$ . These results do not, of course, eliminate the possibility that  $BrF_3$  is formed initially and then reacts further with the oxide to form bromine. The reaction of BrF<sub>3</sub> with U<sub>3</sub>O<sub>8</sub> has been recently reported by Iwasaki and Sakurai [7] and their data show the reaction rates to be considerably greater than those reported in this study for the reaction of BrF<sub>5</sub> with U<sub>3</sub>O<sub>8</sub>. For example, at 200°C and a partial pressure of 18 torr, k' for the reaction with  $BrF_3$  is 0.025 min<sup>-1</sup>, while k' for the reaction with BrF<sub>5</sub> is 0.0006 min<sup>-1</sup>. Therefore, the observed kinetics would be those for the  $BrF_5-U_3O_8$  reaction since the  $BrF_3-U_3O_8$  reaction is much faster. The same conditions are assumed to also hold for the reaction of  $BrF_5$  with UO<sub>2</sub> and UO<sub>3</sub>.

Acknowledgement – The authors wish to express their appreciation to J. J. Stockbar for his excellent assistance in the course of this work.

6. I. Sheft, H. H. Hyman and J. J. Katz, Analyt. Chem. 25, 1877 (1953).

7. M. Iwasaki and T. Sakurai, J. Nucl. Sci. Tech. (Tokyo) 2, 225 (1965).