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THE REACTION OF GASEOUS BROMINE PENTAFLUORIDE WITH URANIUM COMPOUNDS—I*

THE KINETICS OF THE REACTIONS WITH UF_4 AND UO_2F_2

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Abstract—The kinetics of the gas–solid reactions between BrF_5 and UF_4 and UO_2F_2 have been studied in the temperature range 175–300°C and in the BrF_5 partial pressure range of 130–370 torr. Both of these reactions produce UF_6 as the main product, and in the case of the UF_4–BrF_5 reaction the intermediate uranium fluorides (U_2F_9, U_4F_{17}, and UF_5) as minor products. Analysis of the reaction products of the UF_4–BrF_5 reaction showed elemental bromine to be the other gaseous product of that reaction. The data were correlated using the diminishing sphere model which describes the gas–solid reaction occurring at a continuously diminishing spherical interface. Values of the activation energy of 16·9 and 8·3 kcal/mole and of the order of the pressures dependence of 0·38 and 0·71 were calculated for the reactions with UF_4 and UO_2F_2, respectively. The following equations were derived to represent the temperature and BrF_5 partial pressure dependence of these two reactions.

$$UF_4\text{–}BrF_5\text{: } \log k' = 0{\cdot}38 \log P_{BrF_5}(\text{torr}) - 3690/T(^\circ K) + 4{\cdot}286$$

$$UO_2F_2\text{–}BrF_5\text{: } \log k' = 0{\cdot}71 \log P_{BrF_5}(\text{torr}) - 1810/T(^\circ K)$$

INTRODUCTION

A study is being made of the gas–solid reactions between BrF_5 and various uranium compounds. Previously reported studies of reactions of uranium compounds with interhalogen compounds have included, reactions of ClF_3 with UF_4,(1–4) UO_2F_2,(5,6) and various uranium oxides,(7) and recently the reaction between BrF_3 and U_3O_8.(8) In the present work, the temperature and pressure dependence of the reaction between BrF_5 and either UF_4 or UO_2F_2 has been determined over the temperature range 175–300°C and the partial pressure range of 130–370 torr.

EXPERIMENTAL

Materials

The UF_4 contained 75·6% uranium and 23·8% fluorine (theor. 75·8% U, 24·2% F) as shown by analysis and had an average particle size of 84 μ. The surface area as measured by the BET using nitrogen was 0·30 m^2/g. The UO_2F_2 contained the theoretical quantity of uranium (77·3%) as shown by analysis and had an average particle size of 55 μ. The surface area, measured by the BET method using nitrogen, was 12·2 m^2/g. Bromine pentafluoride was used as obtained from a commercial

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(1) V. Y. Labaton, *J. inorg. nucl. Chem.* **10**, 86 (1959).

(2) W. Davis, Jr. and R. L. Jarry, USAEC Report K-849, Dec. 8 (1953).

(3) H. Ngyuen-Nghi, *C.r. hebd. Séanc. Acad. Sci., Paris* **256**, 3465 (1953).

(4) N. S. Nikolaev and Yu. D. Shishkov, *Dokl. Akad. Nauk. SSSR* **143**, 130 (1962).

(5) J. F. Ellis and C. W. Forrest, *J. inorg. nucl. Chem.* **16**, 150 (1960); See also, J. J. Barghusen, *Reactor Fuel Process* **7**, 247 (1964); *ibid.* **8**, 26 (1965).

(6) R. C. Shrewsberry and E. L. Williamson, USAEC Report KY-L-362, Part I (1964).

(7) R. L. Jarry and W. Davis, Jr., USAEC Report K-847, Dec. 21 (1951).

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

source (The Matheson Co., East Rutherford, New Jersey) and was stated to be of a purity of at least 98%. A check of the vapor pressure at 0° and at room temperature did not show evidence of volatile contaminants. An i.r. scan of the BrF_5 vapour was also made. The very strong peak at 664 cm^{-1} and the weak peak at 580 cm^{-1} which had been reported by STEIN,(9) were observed. Peaks at 1192 and 1226 cm^{-1} were also found but not in the strength reported by STEIN. Further inspection of the i.r. scan did not show the very strong peak at 613 cm^{-1} for BrF_3 reported by CLAASSEN *et al.*(10) The nitrogen used as a diluent was obtained from vaporized liquid nitrogen and was passed through a bed of Linde Type 4A Molecular Sieves to remove water.

Apparatus

A thermobalance was used for the experiments with UF_4 and a horizontal boat reactor was used for the experiments with UO_2F_2. It was not possible to utilize the thermobalance for the UO_2F_2 experiments due to the large temperature rise and concurrent very rapid rate of reaction in the initial stages of the reaction. This effect was considered to result from the high surface area of the UO_2F_2. In the boat reactor this initial temperature rise was damped out by the greater mass of the reactor (see section below describing this reactor) and the effect of an initially high rate would be minimized by the greater size of the UO_2F_2 sample (2 g for the boat reactor vs. 0·3 g for the thermobalance). Descriptions of the two reaction systems follows.

Sartorious thermobalance. This apparatus was previously described by JOHNSON and FISCHER.(11) Briefly, the thermobalance consists of a vertical tubular reactor $1\frac{1}{2}$ in. dia. and 20 in. long and a Sartorious Rapid 200 analytical balance equipped with an optical-electronic weight sensing system and a remote recording output. The sample pan was positioned at about the midpoint of the heated portion of the tubular reactor. A chromel–alumel thermocouple in a nickel sheath placed about $\frac{1}{8}$ in. below the sample pan sensed the reaction temperature.

The top of the reactor was maintained at a pressure slightly less than the inlet pressure of the reactor by pumping on the outlet line. A nitrogen bleed stream was brought into a chimney attached to the top of the reactor tube just above the outlet line to prevent any reactive gas from escaping from the open top of the reactor. The reagent gases and the products were drawn off through the outlet line and passed through a trap containing soda-lime. Soda-lime at 100°C was found to be a satisfactory reactant for disposing of BrF_5 and UF_6 since all components of the mixture react to form nonvolatile solids.

Boat reactor. This apparatus consisted of a horizontal tubular reactor, a gas metering manifold and a general purpose manifold to which a system of cold traps and vacuum services were attached. The manifolds were constructed of nickel tubing and fittings. The valves were Hoke 413 Series Monel with nickel diaphragms. The tubular reactor was constructed from a 1-ft length of nominal 2-in. schedule 40 nickel pipe flanged at one end. A nickel boat, 4 in. long, $1\frac{3}{8}$ in. wide, and $\frac{3}{16}$ in. deep, contained the solid reactant. A hemicylindrical nickel bar, with a cross section half that of the reactor, was placed in the reactor to act as a support for the nickel reaction boat and to distribute heat evenly to the bottom of the boat. The temperature of the boat was sensed by a chromel–alumel thermocouple placed in a well within the bar at the midpoint of the boat and approx. $\frac{1}{16}$ in. from the top surface of the bar.

Procedure

The BrF_5 was metered through a rotameter constructed of Kel-F (a polymer of chlorotrifluoroethylene, flow meter manufactured by Brooks Instrument Div. Emerson Electric, Hatfield, Pa.), and the nitrogen used to dilute the BrF_5 was metered by a glass rotameter. The BrF_5 source was maintained at about 50°, resulting in a pressure at the rotameter of about 1000 torr. According to the liquid-vapour equilibria data of LONG,(12) at 50°C and a pressure of $\sim$1000 torr, the vapour phase in equilibrium with a liquid phase containing as much as 15 mole% BrF_3 would contain 99 mole % BrF_5. All of the connecting lines and the BrF_5 rotameter were maintained at a temperature of 70°C.

The quantity of solid reactant used, 300 mg for the thermobalance and about 2 g for the boat reactor, was chosen so that the reaction time at the higher temperatures would not be too short to

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(9) L. STEIN, *J. Am. chem. Soc.* **81**, 1273 (1959).

(10) H. H. CAASSEN *et al.*, *J. chem. Phys.* **28**, 285 (1958).

(11) C. E. JOHNSON and J. FISCHER, *J. phys. Chem.* **65**, 1849 (1961).

(12) R. D. LONG, USAEC Report ANL-5405, March (1955).

measure accurately and to provide approx. a one particle deep layer of solid on the reaction pan. The thin layer of solid reactant tended to minimize any effect of the formation of intermediates on the rate of reaction. This quantity of solid reactant was also found to be suitable in work by JOHNSON and FISCHER[(11)] in a thermobalance study of the kinetics of the reaction of SF_4 with UO_3 and UO_2F_2.

The sample of UF_4 or UO_2F_2 was weighed in the sample pan of the thermobalance or the nickel boat of the boat reactor, placed in the reactor and the nitrogen flow started. After the reaction temperature was reached, the BrF_5 flow was started and the reaction continued for 60 min or, at the higher temperatures for shorter time. A temperature rise of about 3°C was noted when the BrF_5 was added to the gas phase in the thermobalance experiments. A similar temperature rise was noted at all reaction temperatures and was presumed to be primarily due to a change in thermal conductivity of the gas stream. It is assumed that the temperature of the sample was that of the gaseous environment. The temperature rise was not observed in the boat reactor experiments. This is not surprising considering the larger mass of sample and reactor and the excellent thermal contact between reaction boat and the metal tubular reactor.

The weight change of the solid reactant was used to determine the fraction of UF_4 or UO_2F_2 converted to UF_6 during any increment of reaction time.

RESULTS AND DISCUSSION

The rate data were treated using the "diminishing sphere" model developed by ANDERSON.[(13)] 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 the 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 radius of the particle and ρ is the bulk density of the solid.

Kinetic data were obtained for the UF_4–BrF_5 reaction in the temperature range 200–275°C and the BrF_5 partial pressure range 138–370 torr, and for the UO_2F_2–BrF_5 reaction in the temperature range 175–300°C and the BrF_5 partial pressure range 130–357 torr. The reaction conditions and the values of the rate constants are listed in Tables 1 and 2 and the effect of temperature on the rate constants is shown in Figs. 1 and 2, for the reaction with UF_4 and UO_2F_2, respectively. Also listed in Tables 1 and 2 are equations representing the least squares solution of the Arrhenius equation for the various sets of data.

Values of the rate constant calculated at selected temperatures were used to derive values of the pressure dependence term n for the equation $k' = Ae^{-E/RT}P^n$. The average values obtained were 0·38 and 0·71 for the UF_4–BrF_5 and UO_2F_2–BrF_5 reactions, respectively. Averaging the constants for the Arrhenius equations (see Tables 1 and 2) and using the average value of the coefficient n, the following equations were derived to represent the simultaneous temperature and pressure dependence of the rate constant for these reactions.

$$UF_4\text{–}BrF_5\text{: } \log k' = 0{\cdot}38 \log P_{BrF_5}(\text{torr}) - 3690/T(°\text{K}) + 4{\cdot}286$$

$$UO_2F_2\text{–}BrF_5\text{: } \log k' = 0{\cdot}71 \log P_{BrF_5}(\text{torr}) - 1810/T(°\text{K}).$$

Values of the apparent activation energy calculated using these equations are 16·9 and 8·3 kcal/mole for the reaction of BrF_5 with UF_4 and UO_2F_2, respectively.

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(13) J. S. ANDERSON, *Bull. Soc. chim. Fr.* **20**, 781 (1953).

TABLE 1.—VALUES OF THE RATE CONSTANTS, k', FOR THE UF_4–BrF_5 REACTION*

Temp. (°C)	Rate constant $k' \times 10^3$ (min^{-1}) Exp.	Calc.	Calc. − Exp. $\Delta k' \times 10^3$(min^{-1})
$P_{BrF_5} = 138$ torr. $\log k' = 5{\cdot}157 - 3720/T$			
200	1·97	1·98	+0·01
225	4·92	4·92	0·00
250	11·3	11·2	−0·10
274	22·7	22·9	+0·20
$P_{BrF_5} = 239$ torr. $\log k' = 5{\cdot}181 - 3690/T$			
200	2·42	2·45	+0·03
210	3·62	3·55	−0·08
230	6·87	7·14	+0·27
240	10·4	9·91	−0·49
262	19·0	19·6	+0·60
274	28·2	27·7	+0·50
$P_{BrF_5} = 370$ torr. $\log k' = 5{\cdot}185 - 3650/T$			
199	2·82	2·84	+0·02
219	5·90	5·85	−0·05
234	10·0	9·69	−0·31
249	15·2	15·6	+0·40
260	22·2	21·8	−0·40

* Linear velocity of gas phase 0·64 cm/sec, UF_4 sample size 300 mg.

TABLE 2.—VALUES OF THE RATE CONSTANTS, k', FOR THE UO_2F_2–BrF_5 REACTION*

Temp. (°C)	$k' \times 10^3$ (min^{-1}) Exp.	Calc.	Calc. − Exp. $\Delta k' \times 10^3$ (min^{-1})
$P_{BrF_5} = 131$ torr. $\log k' = 1{\cdot}561 - 1850/T$			
200	4·30	4·57	+0·27
225	7·42	7·17	−0·25
250	11·6	10·8	+0·2
275	15·9	15·6	−0·3
300	20·5	21·9	+1·4
$P_{BrF_5} = 198$ torr. $\log k' = 1{\cdot}484 - 1740/T$			
175	4·04	3·99	−0·05
200	5·97	6·41	+0·44
225	10·5	9·80	−0·70
250	13·1	14·4	+1·3
275	21·2	20·4	−1·2
300	27·6	28·1	+0·5
$P_{BrF_5} = 359$ torr. $\log k' = 1{\cdot}848 - 1830/T$			
212	10·4	11·7	+1·3
225	16·9	14·7	−2·2
250	21·9	22·0	+0·1
275	32·0	31·8	−0·2
300	43·2	44·5	−1·3

* Linear velocity of gas phase 1·28 cm/sec, UO_2F_2 sample size 2 g.

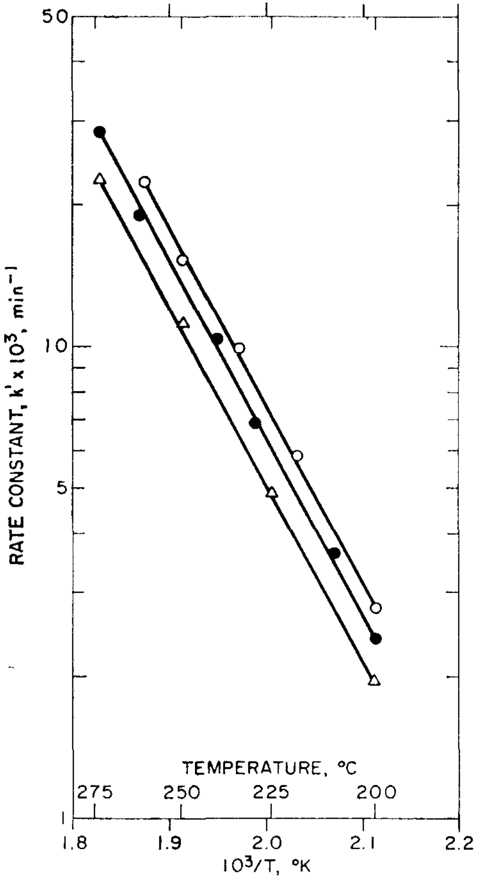

FIG. 1.—Temperature dependence of rate constants for the UF_4–BrF_5 reaction. BrF_5 partial pressure: △–138 torr, ●–239 torr, ○–370 torr.

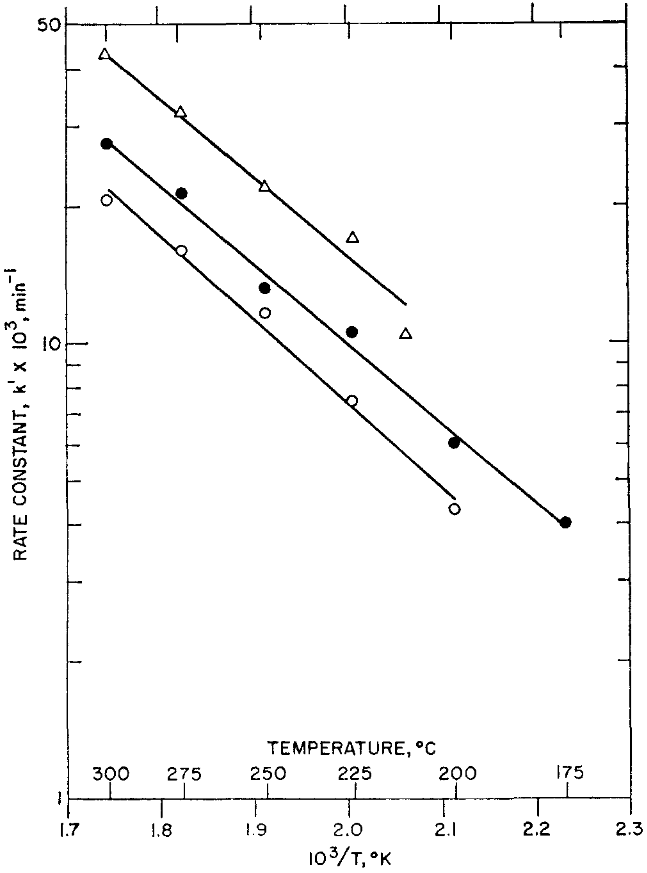

FIG. 2.—Temperature dependence of the rate constants for the UO_2F_2–BrF_5 reaction. BrF_5 partial pressure: ○–1·30 torr. ●–197 torr, △–357 torr.

The effect of the linear velocity of the gas phase (BrF_5–N_2) upon the rate constant was investigated in experiments performed at 250°C and a BrF_5 partial pressure of 197 torr for the reaction with UO_2F_2, and at 235°C and a BrF_5 partial pressure of 243 torr for the reaction with UF_4. Table 3 lists the results obtained in the linear velocity ranges of 0·46–1·28 and 0·86–2·92 cm/sec for the reactions with UF_4 and UO_2F_2, respectively. For both of these reactions an increase in the linear velocity of the gas phase resulted in a decrease in rate constant. The change in rate constant for a threefold change in the linear velocity was only about 10 per cent.

TABLE 3.—EFFECT OF LINEAR VELOCITY OF GAS PHASE ON RATE CONSTANT (Reaction conditions: UF_4: Temp. 235°; P_{BrF_5}(torr) 243. UO_2F_2: Temp. 250°; P_{BrF_5}(torr) 197)

Linear velocity gas phase (cm/sec)	Rate constant k' ($min^{-1} \times 10^3$)
UF_4–BrF_5 reaction	
0·46	6·62
0·64	6·33
1·28	5·80
UO_2F_2–BrF_5 reaction	
0·86	13·5
1·28	13·1
2·92	12·2

The overall reaction between UO_2F_2 and BrF_5 is considered to proceed as shown in the following equation:

$$5\,UO_2F_2 + 4\,BrF_5 = 5\,UF_6 + 2Br_2 + 5\,O_2 \qquad (1)$$

The reaction between UF_4 and BrF_5 is complicated by the formation of intermediate fluorides, U_2F_9, U_4F_{17}, UF_5, either as the result of the direct reaction or by the interaction of UF_6 with UF_4. The possible reactions that can be expected, using UF_5 as the example of the intermediate fluoride, are as follows:

$$5UF_4 + 2BrF_5 \rightarrow 5UF_6 + Br_2 \qquad (2)$$

$$5UF_4 + BrF_5 \rightarrow 5UF_5 + 1/2Br_2 \qquad (3)$$

$$UF_4 + UF_6 \rightarrow 2UF_5 \qquad (4)$$

$$5UF_5 + BrF_5 \rightarrow 5UF_6 + 1/2B_2 \qquad (5)$$

Although the colour of the reaction residues, either brown, or black, indicated the presence of the intermediate compounds, no evidence of an induction period in the weight change of the samples was observed. Evidently the reaction to form volatile UF_6 does not require formation of significant quantities of the intermediate fluorides. Hence, the reaction is believed to proceed by direct conversion of UF_4 to UF_6. Prior work by LABATON and JOHNSON(14) demonstrated that the UF_4–F_2 reaction did not proceed through a step involving the formation of intermediate fluorides, but rather proceeded by the direct fluorination of UF_4 to UF_6. These workers also showed that the rate of fluorination of the intermediate fluorides was lower by a factor of 2 to 4 than the rate of fluorination of UF_4. It is assumed that these relative rates are valid for the fluorination reaction with BrF_5 as well.

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(14) V. Y. LABATON and K. D. JOHNSON, *J. inorg. nucl. Chem.* **10**, 74 (1959).

The equations listed above show bromine as the reaction product resulting from the BrF_5. The instability of the bromine oxides at temperatures above 0°(15) makes their presence highly improbable. Bromine was indicated by the deep red color of the condensed reaction products of the UF_4–BrF_3 reaction and was quantitatively assayed by conversion of the bromine to BrF_3 using fluorine titration method of SHEFT and co-workers.(16) Fluorine titrations of the condensed products from several experiments showed quantities of Br_2 corresponding to the stoicheiometry of reaction (2) above. Bromine could result from the direct reduction of BrF_5 to Br_2 or from the stepwise reduction to BrF_3 which, in turn, would react further to form Br_2. In either case, the observed kinetics would be those for the UF_4–BrF_5 reaction if the rate of the UF_4–BrF_3 reaction was higher than that for the UF_4–BrF_5 reaction. Since no data are available in the literature for the reaction between UF_4 and BrF_3, boat reactor experiments were performed to obtain rate date at 200°C for the two reactions. For the UF_4–BrF_5 reaction at a BrF_5 partial pressure of 198 torr the rate constant was 0·00235 min^{-1}, while for the UF_4–BrF_3 reaction at a BrF_3 partial pressure of 105 torr the rate constant was 0·0145 min^{-1}. These data show clearly that the reaction with BrF_3 is significantly higher and, therefore, the kinetics measured represent the reaction with BrF_5.

No titrations were performed for the UO_2F_2–BrF_5 reaction. It is reasonable to assume that bromine is the reaction product in this reaction as well.(17) The value of the activation energy, 16·9 kcal/mole, found for the UF_4–BrF_5 reaction is in the range of values reported for the UF_4–F_2 reaction,(14,18) 14–20 kcal/mole, rather than the 2–6 kcal/mole range reported for the UF_4–ClF_3(1–3) reaction. The order of the UF_4–BrF_5 reaction was found to be fractional with respect to BrF_5 pressure, while the orders of both the UF_4–F_2(14) and UF_4–ClF_3(1) reactions were found to be first order with respect to the partial pressure of the fluorination agents. Finally, the temperature dependence of the rate of the UF_4–BrF_5 reaction did not show a minimum as was observed for the UF_4–ClF_3 reaction,(1) and which was ascribed to the formation of the intermediate fluorides and a consequent reduction in volatilization of UF_6.

Previous studies of fluorinations of UO_2F_2 include the reaction with ClF_3(5,6) with fluorine,(18,19) and with SF_4.(11) Activation energies of 8·9, 19·5 and 32 kcal/mole were calculated for the ClF_3,(6) F_2(19) and SF_4(11) reactions, respectively. The dependence of the rate constant on partial pressure of the fluorinating gas was found to be first order for the UO_2F_2–ClF_3 reaction(6) and proportional to the 1·5 power for the UO_2F_2–SF_4 reaction.(11) The present investigation of the UO_2F_2–BrF_5 reaction showed an activation energy, 8·3 kcal/mole, and an order of pressure dependence, 0·71, similar to those found for the UO_2F_2–ClF_3 reaction rather than those found for the UO_2F_2–SF_4 reaction.

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(15) M. SCHMEISSER and K. BRANDLE, Oxides and Oxyfluorides of the Halogens, in *Advances in Inorganic and Radiochemistry*, Vol. 5, p. 70. Academic Press, New York (1963).

(16) I. SHEFT, H. H. HYMAN and J. J. KATZ, *Analyt. Chem.* **25**, 1877 (1953).

(17) Recent work in this laboratory on the U_3O_8–BrF_5 reaction has shown that Br_2 is also the only product of the BrF_5 component in that reaction.

(18) M. J. STEINDLER, USAEC Report ANL-5959, March (1959).

(19) G. VANDENBUSSCHE and T. KEKENDAI, *C.r. hebd. Séanc. Acad. Sci., Paris* **256**, 4657 (1963).