the pressure dependence and activation energy of the reaction unchanged, suggesting that the same process was rate-determining. However, from Fig. 1(a) and Equation (1) one obtains $K_1 = 2 \cdot 2 \times 10^{-5}$ sec⁻¹ at 200°C, while from Fig. 2(a) and Equation (3) $K'_1 = 2 \cdot 3 \times 10^{-3}$ sec⁻¹ at 200°C, i.e. 5 atomic per cent barium dissolved in the sodium caused a hundredfold increase in the reaction rate. Since the addition of barium is expected to alter the electronic nature of the metal, then the fact that the reaction rate is markedly increased supports the assumption that the rate-determining step involves electrons from the metal surface.

A possible explanation for the rate increase is that the addition of barium to sodium modifies the electron energy distribution in such a way as to increase the number of electrons with sufficient energy to bring about the dissociation of the H—H bond. This is consistent with the suggestion[8] that electrons in barium have some *d*-band character, since this would imply a higher electron level density at the Fermi surface than for an *s*-band alone. The high catalytic activity of barium has been explained on this basis [9].

Similar concepts have been used by Addison *et al.*[10] to explain the nature of nitrogen reactions with solutions of barium in sodium; although detailed kinetic studies have not yet been reported, it is interesting to note that initial rates of nitrogen absorption increased rapidly with increasing barium concentration.

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The reaction of gaseous bromine trifluoride with U_3O_8

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RECENTLY, Iwasaki and Sakurai[1] published a study of the reaction of gaseous BrF_3 with U_3O_8 . Their study covered the temperature range 50-300°C and the BrF_3 partial pressure range 7-23 torr. H. These workers reported a minimum in the value of the reaction rate constant at a temperature of about 230°C and a BrF_3 partial pressure of 10 torr. H. They attributed this decrease in the UF_6 production to the formation of UO_2F_2 , either as an intermediate product or as the result of the reaction of the volatile product UF_6 with U_3O_8 . This paper presents the results of a study of the kinetics of the reaction of gaseous BrF_3 with U_3O_8 in the temperature range 100-400°C and the BrF_3 partial pressure range 18-44 torr. During the course of this work, an attempt was made to verify the minimum in the reaction rate reported by the Japanese workers.

EXPERIMENTAL

Materials

The U_3O_8 used was from the same batch as that used in a previously reported study of the BrF₅- U_3O_8 reaction[2]. It contained 84.7% U and 15.2% O (theoretical 84.8% U and 15.2% O) and had a surface area of 0.23 m²/g and an average particle size of 10 μ .

The BrF_3 used was material which had been purified by distillation. Trace quantities of BrF_5 present were reacted to form BrF_3 by adding bromine and heating the liquid to 80–100°C. This treatment was repeated until the i.r. absorption spectrum of the product showed the BrF_5 peak at 664 cm⁻¹ to be negligible compared with the BrF_3 peak at 703 cm⁻¹. The unreacted bromine was

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Notes

subsequently removed by vacuum transfer. Nitrogen, used as carrier gas for BrF_3 , was obtained by vaporizing liquid nitrogen.

Apparatus and procedure

The thermobalance and the procedure used in these experiments were described in a previous paper[3]. Bromine trifluoride was supplied to the thermobalance by transpiration, using nitrogen as the carrier gas. The quantity of BrF_3 used in a series of experiments was determined from weight change of the BrF_3 source vessel, and thus the partial pressure of BrF_3 in the feed gas could be accurately calculated.

RESULTS AND DISCUSSION

The data were treated using the diminishing sphere model, as outlined in a previous paper[3]. This model relates the reaction rate to the changing surface area available, which is a function of the reduction in diameter of the solid particles with reaction time. The equation used is:

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

which relates the rate constant k' (min^{-1}) to the fraction of solid reacted F in time t (min).

Reaction rate data obtained at a BrF_3 partial pressure of 18 torr. and a gas phase linear velocity of 0.46 cm/sec are shown as an Arrhenius plot in Fig. 1. Also shown on Fig. 1 are plots of interpolated data at 18 torr. from the work of Iwasaki and Sakurai[1] and extrapolated data at 18 torr. for the $BrF_5-U_3O_8$ reaction from the work of Jarry and Steindler[2]. The solid line drawn through the data points, which represents the fit of the integrated form of the Arrhenius equation to the data, resulted in the following equation for the temperature dependence of the rate constant:

$$\log \mathbf{k}' = 1.950 - 152.3/T(^{\circ}\mathrm{K}). \tag{2}$$

An activation energy of 0.7 kcal/mole derived from these data compares favorably with the value of 0.9 kcal/mole reported by the Japanese workers[1].

The effect of BrF_3 partial pressure on the reaction rate constant was investigated at partial pressures of 18, 35, and 44 torr., and the data obtained are listed in Table 1. A value of 1.3 was derived

able 1. Effect of BrF_3 partial press to the rate constant, k', for the Brl U_3O_8 reaction		
Temp. (°C)	P _{BrF3} (torr.)	$k' \times 10^{3}$ (min ⁻¹)
174	18	3.93
175	18	3-95
1 76	18	5.01
176	18	4.93
174	35	11.4
174	35	9.3
174	44	12.7
174	44	15.5
179	44	17-1

from these data for n, the pressure dependence coefficient in the Arrhenius equation. Combining this value of n with Equation (2) resulted in the following equation which represents the combined tem-

$$\log k' = 1.35 \log P(\text{torr.}) - 3.640 - 152.3/T(^{\circ}\text{K}).$$
(3)

Iwasaki and Sakurai[1] reported a sharp drop in the value of the rate constant at about 230°C

3. R. L. Jarry and M. J. Steindler, J. inorg. nucl. Chem. 29, 1591 (1967).

perature and pressure dependence of the rate constant:



Fig. 1. Temperature dependence of the rate constant for the $BrF_3-U_3O_8$ reaction $(P_{BrF_3} = 18 \text{ torr.}).$

at a BrF₃ partial pressure of 10 torr, H: The value of the rate constant dropped from 0.016 to about 0.009 min⁻¹, but increased again to the previous higher value above 230°C. In the present study an attempt to reproduce this minimum in the rate constant was not successful. X-ray diffraction analyses of reaction residues from experiments carried out over the entire temperature range failed to show the presence of UO_2F_2 . While UO_2F_2 may be formed as an intermediate product, its formation is apparently not rate controlling in this reaction. Scatter in the experimental values of the rate constant could conceivably have masked this effect, but the random nature of the scatter of the data in this temperature region suggests that this was not the case. It is, therefore, concluded that the kinetics of the BrF₃-U₃O₈ reaction do not show a discontinuity in the relation of the rate constant and the reciprocal absolute temperature.

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