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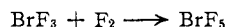
## The Reaction of Bromine Trifluoride and Fluorine to Form Bromine Pentafluoride

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The kinetics of the gas phase reaction of bromine trifluoride and fluorine to form bromine pentafluoride have been studied from 68 to 121° in a nickel reactor and with the initial pressures varying from 30 to 300 mm. The reaction is bimolecular, homogeneous and has an activation energy of 16.4 kcal. The observed frequency factor  $2.6 \times 10^{11}$  cc mole<sup>-1</sup> sec.<sup>-1</sup>, corresponds to a probability factor of  $10^{-3}$ , thus indicating that only a part of the bimolecular collisions of sufficient energy to cause reaction actually results in the formation of bromine pentafluoride.

Conditions under which the bromine fluorides are formed have been fairly well defined; however, there have been no published investigations from a kinetic viewpoint. Bromine monofluoride has been reported to exist only in equilibrium with bromine and bromine trifluoride.<sup>1</sup> Bromine trifluoride is formed from bromine and fluorine at temperatures below 50°. Above this temperature bromine pentafluoride is formed in appreciable amounts<sup>3</sup> and at 200° the reaction is rapid.<sup>4</sup> A partial, but unpublished, study of the gas phase reaction<sup>5</sup> has been made at the Argonne National



Laboratory by Jack Fischer who found that the reaction goes to completion at an easily measurable rate at 75 to 115°.

## Experimental

The reaction was studied in an all-metal system constructed of nickel and Monel metal. The nickel reactor had an internal diameter of 11.1 cm. and the total volume was 1.23 l. The three types of valves which were used, Hoke No. 1103, No. M483M and 410 series, had to be replaced periodically due to corrosion by bromine trifluoride. A Booth-Cromer pressure transmitter<sup>6</sup> was used to measure the pressure. In this instrument a thin nickel diaphragm prevented the corrosive vapors from reaching mercury in the manometer. Pressures were measured to within about 0.3 mm.

**Materials.**—Commercial grade fluorine containing somewhat over 98% F<sub>2</sub> by volume, as determined by reaction with mercury, was used in this study. Commercial grade bromine trifluoride was refined by simple distillation. A middle cut having a melting point of 8.55° was chosen for use. Pure bromine trifluoride melts at 8.77°. Using Oliver and Grisard's value for the cryoscopic constant,<sup>7</sup> the impurity was calculated to be somewhat less than 0.40 mole %.

**Procedure.**—The desired pressure of bromine trifluoride was admitted to the evacuated reactor from a nickel vessel. (Although molecular weights slightly greater than the ideal value, 136.9, for bromine trifluoride were observed, no correction was made on the observed pressure of bromine trifluoride.) A measured volume of fluorine then was added rather slowly to the reactor (total time about one minute) and the gases were allowed to mix spontaneously. Reaction was followed by observing the change of pressure of the gas as time passed.

(1) J. Fischer, J. Bingle and R. C. Vogel, *THIS JOURNAL*, **78**, 902 (1956); R. K. Steunenber, R. C. Vogel and J. Fischer, *ibid.*, **79**, 1320 (1957).

(2) J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 191.

(3) I. Sheft, H. H. Hyman and J. J. Katz, *Anal. Chem.*, **25**, 1877 (1953).

(4) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 49 (1931).

(5) J. Fischer, Argonne National Laboratory, Lemont, Illinois, private communication.

(6) S. Cromer, "The Electronic Pressure Transmitter and Self-balancing Relay," (MDDC-803), Atomic Energy Commission, declassified March 20, 1947.

(7) G. D. Oliver and J. W. Grisard, *THIS JOURNAL*, **74**, 2705 (1952).

## Results and Discussion

It may be seen from the data in column 4 of Table I that the reaction between bromine trifluoride and fluorine went to completion. At temperatures above 125° the reaction was too rapid to be followed by the method used in this work. A temperature rise of approximately 0.6° usually occurred on mixing the reactants. In one run the rapid admission of the fluorine to the reactor caused the reaction to take place instantaneously, with the temperature rising several degrees.

TABLE I  
SUMMARY OF RUNS

<i>t</i> , °C.	Initial pressures, mm. F <sub>2</sub>	BrF <sub>3</sub>	Final pressure, mm.	<i>k</i> × 10 <sup>5</sup> , mm. <sup>-1</sup> min. <sup>-1</sup>
68.0	265.7	42.3	"	2.67
68.0	29.0	74.8	"	2.54
68.8	80.9	70.5	"	2.50
69.9	130.9	75.0	"	2.74
81.2	190.5	57.2	192.2	6.38
81.8	74.9	123.2	"	5.68
82.0	26.5	118.7	"	5.32
97.0	109.1	100.3	"	16.5 <sup>b</sup>
97.2	241.6	90.2	241.9	16.0 <sup>b</sup>
97.4	316.8	44.6	315.0	19.1 <sup>b</sup>
97.8	80.7	101.5	"	17.4
98.0	263.8	40.2	262.4	15.6
98.1	35.9	38.8	"	15.6
98.2	157.5	81.9	"	16.7
108.0	113.2	79.6	"	30.5
108.4	190.6	123.4	189.4	29.4
108.6	118.6	95.7	116.8	33.9
120.3	47.1	248.0	248.2	52.2
120.5	53.8	87.3	89.1	62.6
120.8	251.3	59.6	249.4	63.1

<sup>a</sup> These runs were not followed to completion. <sup>b</sup> The surface area of the reactor was increased 5.5 times.

The rate of formation of bromine pentafluoride was found to be first order with respect to bromine trifluoride and first order with respect to fluorine, as shown in equation 1.

$$\frac{d(P_{\text{BrF}_5})}{dt} = k(P_{\text{BrF}_3})(P_{\text{F}_2}) \quad (1)$$

The integrated expression is

$$t = \frac{2.303}{k(P'_{\text{BrF}_3} - P'_{\text{F}_2})} \log \frac{P'_{\text{F}_2}}{P'_{\text{BrF}_3}} + \frac{2.303}{k(P'_{\text{BrF}_3} - P'_{\text{F}_2})} \log \frac{P_T - P'_{\text{F}_2}}{P_T - P'_{\text{BrF}_3}} \quad (2)$$

where  $P'_{\text{BrF}_3}$  and  $P'_{\text{F}_2}$  are initial pressures of the reactants,  $P_T$  is the total observed pressure at time

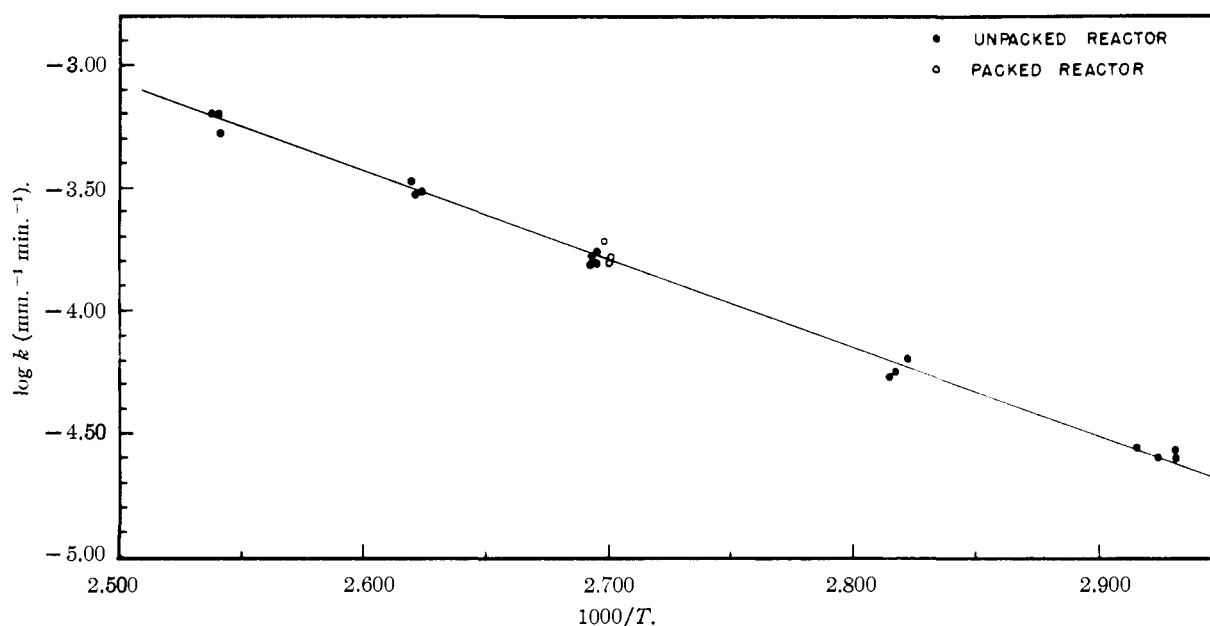


Fig. 1.—Dependence of rate constant  $k$  upon temperature.

$t$  and  $k$  is second-order specific rate constant. A graph in which  $\log k$  is plotted against the reciprocal of the absolute temperature is shown in Fig. 1. The straight line was determined by the method of least squares using the data represented by solid black circles. The equation for this line is

$$\log k (\text{min.}^{-1} \text{min.}^{-1}) = -\frac{3575}{T} + 5.85 \quad (3)$$

From the slope of the line the calculated activation energy is 16.4 kcal. The three open circles in Fig. 1 correspond to runs where the surface area in the reactor was increased 5.5 times by adding nickel screen. The fact that there was no appreciable change in the specific rate constant indicated the homogeneity of the reaction.

The "observed" frequency factor  $Z$  in the Arrhenius equation,  $k = Ze^{-E_a/RT}$ , as calculated from the observed activation energy and the specific rate constant is  $2.6 \times 10^{11}$  cc. mole $^{-1}$  sec. $^{-1}$  at 100°. The value for the "calculated" frequency factor as calculated from collision theory, assuming a molecular diameter for bromine trifluoride of  $5 \times 10^{-8}$  cm., is  $1.6 \times 10^{14}$  cc. mole $^{-1}$  sec. $^{-1}$ . The difference between the "observed" and "calculated" frequency factors corresponds to a  $p$  value, in the modified collision theory expression,  $k = pZe^{-E_a/RT}$ , of  $1.6 \times 10^{-3}$ . This value of the probability term  $p$  indicates that only a part of the collisions of sufficient energy to cause reaction are actually effective in producing bromine pentafluoride. This may result from various causes including: (a) steric effects caused by the unsymmetrical structure of the  $\text{BrF}_3$  molecule, (b) a change in entropy during the reaction.

Fischer and Steunenberg have recently studied the kinetics of the gas phase reaction of iodine pentafluoride and fluorine to form iodine heptafluoride<sup>8</sup> and have found that the reaction is homogeneous and bimolecular. A least squares treat-

ment of their data gives an activation energy of 13.4 kcal. and an observed frequency factor at 100° of  $1.1 \times 10^{11}$  cc. mole $^{-1}$  sec. $^{-1}$ . The  $p$  factor of about  $10^{-3}$  indicated that this reaction is also "slow." The similarity of the reactants for both reactions and of the  $p$  factors suggest that both reactions may be slow for the same reason.

**Surface Effects.**—It was found that the surface condition of the reactor was very important in obtaining a homogeneous reaction. The second-order plots of runs made at first (before the reactor was washed with nitric acid) departed from linearity after the reaction was approximately 60% complete. Cleaning the reactor with dilute nitric acid slowed the reaction rate somewhat and improved the linearity of the plots. In the early runs the rate of reaction was first order with respect to fluorine, but the rate of reaction with respect to bromine trifluoride changed gradually from first-order to zero-order with decreasing fluorine pressure. This suggested the occurrence of a heterogeneous reaction. Four runs made with a silvered screen (having a surface area of 220 sq. in., 2.20 times that of the unpacked reactor) in the cleaned reactor gave second-order plots that were similar to those for the "dirty" nickel surface. Agreement between the specific rate constants as well as the similarity of the second-order plots suggested that the reaction mechanism on the silver surface may have been the same as for the "dirty" nickel surface. The activation energy for the reaction with these two surfaces, as obtained from the slopes of the linear portion of the second-order plots, was practically the same as that for the homogeneous reaction.

**Acknowledgment.**—This work was performed in part under contract with the Office of Naval Research. During a nine month period one of the authors, H. E. K., was supported by a National Science Foundation Fellowship.

(8) J. Fischer and R. K. Steunenberg, *THIS JOURNAL*, **79**, 1876 (1957).