CF₃Br—H₂ Reaction in Shock Waves

YOSHIAKI HIDAKA, TAKUJI NAKAMURA, and HIROYUKI KAWANO

Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790, Japan

TOHRU KOIKE

Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239, Japan

Abstract

 CF_3Br-H_2 mixtures highly diluted with Ar were studied by using a time-resolved IRemission of HBr and a gas-chromatography for reaction products. The temperature range covered was 1000-1600 K and the total pressure behind the reflected shock waves used was 1.2-2.6 atm. CF_3H , C_2F_6 , and C_2F_4 were produced and the yields of these products were determined as a function of temperature. The main product under our experimental conditions was CF_3H . The mechanism and the rate constants of CF_3Br-H_2 reaction at high temperatures were discussed. The experimental data was satisfactorily modeled using a 14reaction mechanism. Reaction (5) played an important role in the formation of CF_3H together with reaction (4).

$$(4) CF_3 + HBr \longrightarrow CF_3H + Br$$

The rate constant expression $k_5 = 2.2 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ gave the best agreement between the calculated and observed results. © 1993 John Wiley & Sons, Inc.

Introduction

 CF_3Br is a known flame inhibiting agent. The main features of the high temperature mechanism for the $CF_3Br-H_2-O_2$ system have been established [1,2], but no previous work on the mechanism of the CF_3Br-H_2 reaction at high temperatures (above 1000 K) has been reported.

In this article we present the results of a shock tube study of the CF_3Br — H_2 system carried out in order to obtain insight into the values of the rate-constants of the reactions involved at high temperatures.

Experimental

The magic-hole-type shock tube employed in this experiment serves functions of both single-pulse and time-resolved spectroscopic methods [3-5]. The apparatus and procedures have been described in detail previously [3-5]. Two CaF₂ windows, a barium titanate gauge and a pipe (0.5 mm in inner diameter and 6 cm in length) connecting a valve used for gas collection were located at 1 cm from the end plate. IR-emission from a HBr molecule was observed through the CaF₂ window, an interference

International Journal of Chemical Kinetics, Vol. 25, 983–993 (1993) © 1993 John Wiley & Sons, Inc. CCC 0538-8066/93/120983-11

filter ($\lambda_{max} = 3.70 \ \mu$ m, half-width = 0.18 μ m) and two 0.8 mm slits with Fujitsu IV-200C4 InSb detector. The reacted gases were analyzed on a gaschromatograph (Shimazu GC-3BT1) with a thermal-conductivity detector, as described previously, [3–5]. The gas-chromatographic analysis of the reacted gas was done for carbon-containing compounds. An effective heating time was determined using the same method as that described previously [3,4]. The reaction was assumed to be frozen perfectly at the effective heating time, which was defined as the time between the arrival point of the reflected shock front and 80% point of the reflected shock-front pressure.

The reaction mixtures used were A (1% CF₃Br, 4% H₂, 95% Ar), B (2% CF₃Br, 2% H₂, 96% Ar), and C (4% CF₃Br, 1% H₂, 95% Ar). The initial pressure used was 50 torr. The Ar (Teisan Co.) and H₂ (Chuunenfaingasu Co.), specified to be 99.99% and 99.99% pure, respectively, were obtained from commercial cylinders and used without further purification. The CF₃Br (Daikin Kogyo Co.), specified to be 99.6% pure, was purified by trap-to-trap distillation before use.

Data interpretation was carried out by computer simulation in essentially the same manner as described previously [3,4]. Thermochemical properties were computed from polynomial fits to JANAF data [6]. All references to temperature herein refer to the full relaxation, no-reaction shock front value.

Results and Discussion

The product distributions with mixtures A (1% CF₃Br, 4% H₂, 95% Ar), B (2% CF₃Br, 2% H₂, 96% Ar), and C (4% CF₃Br, 1% H₂, 95% Ar) are summarized in Table I. Under our experimental conditions, CF₃Br, CF₃H, C₂F₆, and C₂F₄ were detected by the gas-chromatograph, but fluorinated C₁- and C₂-hydrocarbons, other than CF₃Br, CF₃H, C₂F₆, and C₂F₄, were not detected. The increase of the $[H_2]_0/[CF_3Br]_0$ ratio brought about an increased rate of CF₃Br consumption, where $[H_2]_0$ and $[CF_3Br]_0$ are the initial concentrations of H₂ and CF₃Br, respectively. The ratio of $[CF_3H]/[CF_3Br]_0$ in mixture A at a given temperature was the largest. In every mixture, the yield of CF₃H was always larger than those of C₂F₆ and C₂F₄. The ratio of $[C_2F_4]/[CF_3Br]_0$ was always smaller than that of $[C_2F_6]/[CF_3Br]_0$.

IR-emission profiles were observed for mixtures A, B, and C. A typical profile is shown in Figure 1. A relationship between the HBr concentration and the temperature was determined by using the same method mentioned in a previous report [5]. These relationships at 100 μ s, 200 μ s, and 400 μ s with mixtures A, B, and C are shown in Table II. At a given temperature below 1300 K, the HBr concentration for mixture A is comparable to those for mixtures B and C, but at a given temperature above 1300 K, the HBr concentration for mixtures B and C.

At first, a combination of two published mechanisms [5,7] was tried: one was a pyrolysis mechanism of CF_3Br over the temperature range 1100-1600 K at pressure 1.5-2.6 atm [5], the other was a pyrolysis mechanism of CF_3H over the temperature range of 1150-1570 K at pressure 1.5-2.6 atm [7]. The CF_3H concentration calculated was definitely

Т	[CF ₃ Br] ₀	[CF ₃ Br]/[CF ₃ Br] ₀	[CF ₃ H]/[CF ₃ Br] ₀	[C2F6]/[[CF3Br]0	[C ₂ F ₄]/[[CF ₃ Br] ₀	Effective
K	$[H_2]_0$	obs	obs	obs	obs	Heating time (ms)
1032		99.5	0.3	0	0	2.52
1052		99.7	0.6	0	0	2.43
1080		94.4	5.5	0	0	2.47
1145		83.6	16.5	1.5	0	2.30
1165	1/4	74.2	15.1	1.1	0	2.18
1199		55.1	44.2	3.4	0	2.17
1234		40.1	48.2	3.6	0.5	2.24
1236		45.3	45.2	3.8	0.4	2.12
1239		51.1	45.4	3.5	0.2	2.18
1279		9.1	68.2	4.9	2.1	2.10
1140		93.7	3.2	0	0	2.17
1162		93.4	5.5	1.8	0	2.04
1241		79.0	16.1	3.5	0	1.82
1276	4/1	67.0	23.0	7.0	0	1.84
1338		57.2	25.0	9.9	0.3	1.73
1456		40.2	18.5	15.9	1.5	1.48
1162		87.4	8.7	1.7	0	2.48
1242		56.8	28.0	4.0	0	2.38
1250		47.8	35.7	5.3	0	2.35
1307	2/2	25.9	50.3	7.1	1.7	2.17
1347		16.9	53.1	8.2	3.0	2.06
1428		7.1	43.4	8.7	7.5	1.98
1437		7.2	41.2	8.6	7.9	1.88



Figure 1. Comparison of the observed [HBr] with the calculated one. \bigcirc : observed with mixture A at 1500 K; _____: calculated with the mechanism and the rate constant expressions shown in Table I; _____: calculated by using Table I in which the rate constant expression $k_3 = 4.4 \times 10^{14} \exp(-9.46 \operatorname{kcal/RT}) \operatorname{cm}^3 \operatorname{mol}^{-1} \operatorname{s}^{-1}$ for reaction (3) was changed to $k_3 = 2.2 \times 10^{14} \exp(-9.46 \operatorname{kcal/RT}) \operatorname{cm}^3 \operatorname{mol}^{-1} \operatorname{s}^{-1}$; and _____: calculated by using Table I in which the rate constant expression $k_5 = 2.2 \times 10^{13} \exp(-12 \operatorname{kcal/RT}) \operatorname{cm}^3 \operatorname{mol}^{-1} \operatorname{s}^{-1}$ for reaction (5) was changed to $k_5 = 1.1 \times 10^{13} \exp(-12 \operatorname{kcal/RT}) \operatorname{cm}^3 \operatorname{mol}^{-1} \operatorname{s}^{-1}$.

smaller than the observed one. To solve this problem, reaction (5), $CF_3 + H_2 \rightarrow CF_3H + H$ with $k_5 = 5.01 \times 10^{11} \exp(-9.3 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [14], was introduced. Reaction (6), $CF_3 + H \rightarrow CF_2 + HF \quad k_6 = 5.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [20], was also included to account for the observed C_2F_4 formation at higher temperatures. However, though this mechanism and the rate constant expressions could roughly interpret our observed results, these could not interpret well our observed results.

To account for the data of the CF_3Br-H_2 reaction, computer modeling was performed. Through trial and error, we endeavored to find a mechanism and the corresponding rate constant expressions that were able to predict our results.

Though the main product CF_3H is formed by reactions (4), (5), and (8) under our experimental conditions, it was found that these reactions (4) and (5) were the more important. The yield of CF_3H is also strongly dependent upon the values of the rate constants of reactions (1), (3), (4), (5), and (7), as shown in Table III. The yield of HBr is strongly dependent upon the values of the rate constants of reactions (1), (3), (5), (7), and (11). Therefore, we discuss the influence of the rate constants k_1 , k_3 , k_4 , k_5 , k_7 , and k_{11} upon $[CF_3H]$ and [HBr], and then determine a final mechanism and the rate constant expressions which can account for both our present results and reported results [5], as mentioned below. The final mechanism and the rate constant expressions determined are shown in Table IV.

In a previous article [5] we evaluated $k_1 = 8.80 \times 10^{17} \exp(-60 \text{ kcal}/RT)$ cm³ mol⁻¹ s⁻¹ for reaction (1) assuming reaction CF₃ + CF₃ + M = C₂F₆ + M with $k_7 = 8.0 \times 10^{15}$ cm⁶ mol⁻² s⁻¹. However, Glanzer et al. [8] showed that the rate constant at ~1300 K and ~2 atm ([Ar] ~ 1.7 $\times 10^{-5}$ mol/cc)

T/K	$\frac{[CF_{3}Br]_{0}}{[H_{2}]_{0}}_{\%/\%}$	$100 \ \mu s$ [HBr]/10 ⁻⁷ mol cc ⁻¹ obs	$200 \ \mu s$ [HBr]/10 ⁻⁷ mol cc ⁻¹ obs	$\begin{array}{c} 400 \ \mu \text{s} \\ [\text{HBr}]/10^{-7} \ \text{mol cc}^{-1} \\ \text{obs} \end{array}$
1276		0.20	0.31	0.54
1322		0.21	0.41	0.75
1410	1/4	0.62	1.11	1.39
1500		1.10	1.29	1.59
1531		1.32	1.51	1.68
1641		1.49	1.65	1.69
1224		0.08	0.14	0.26
1272		0.25	0.38	0.68
1341	4/1	0.50	0.92	1.52
1447		1.22	1.80	1.78
1544		1.85	1.51	1.20
1243		0.03	0.18	0.32
1256		0.14	0.28	0.47
1310		0.22	0.58	1.12
1379	2/2	0.58	1.13	1.80
1457		1.10	1.81	2.46
1507		1.72	2.31	2.70
1561		2.25	2.62	2.50

TABLE II. HBr concentration at each time.

was in its unimolecular falloff range, and obtained the value $k_7 = 5 \times$ 10^{12} cm³ mol⁻¹ s⁻¹; the high-pressure rate constant k_7 reported was $1.9 \times$ 10^{13} cm³ mol⁻¹ s⁻¹. In our present work the quantities of products produced in the simulations were very sensitive to the value of the recombination rate constant, k_7 . Furthermore, reaction (7) had a large influence on the evaluation of the rate constant of reaction (1). So, we tried to reevaluate the k_1 value using reported rate constants of reaction (7) as follows. We first used the Glanzer et al.'s value $k_7 = 5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8] for our simulation because our experimental pressure used was about 2 atm: the high-pressure rate constant k_7 reported was 1.9×10^{13} cm³ mol⁻¹ s⁻¹. When the value $k_7 = 5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was used for a simulation of pyrolysis using a mixture (4% CF₃Br, 96% Ar) shown in Figure 1 of ref. [5], to predict well the pyrolysis data it was necessary to use $k_1 =$ $1.37 \times 10^{16} \exp(-60 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction (1): this k_1 was one fourth of that shown in Table IV. When these values, $k_1 = 1.37 \times 10^{16} \exp(-60 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_7 = 5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, were also applied for a simulation of mixture C, CF₃Br, and HCl concentrations calculated were much larger and smaller, respectively, than the observed ones. These discrepancies, simulated to observed results, were removed only when the rate constant values reported for reaction (5) [2,13,14] were increased by a factor of about 10 to 150: this reaction is very sensitive to CF_3Br consumption and HBr production as may be seen in Table III. However, the changes of values for reaction (5) of this order are not acceptable. Thus, when Glanzer et al.'s value $k_7 = 5 \times 10^{12} \text{ cm}^3$ $mol^{-1} s^{-1}$ [8] was used for a prediction of both the CF₃Br pyrolysis and CF_3Br-H_2 data, we had to use the unacceptable value for the rate constant

$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	2F ₆	C_2F_6	C_2F_6	H C_2F_6	CF ₃ H C ₂ F ₆	CF ₃ H C ₂ F ₆	CF ₃ H C ₂ F ₆	3r CF ₃ H C ₂ F ₆	CF ₃ Br CF ₃ H C ₂ F ₆
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$100 \ \mu s$		sπ ($1000 \ \mu s$	us 1000 μs	100 μs 1000 μs	us 100 μs 1000 μs	1000 μs 100 μs 1000 μs	<u>ts 1000 μs 100 μs 100 μs</u>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	×0.2 ×5		×£	×0.2 ×5	×5 ×0.2 ×5	×0.2 ×5 ×0.2 ×5	×5 ×0.2 ×5 ×0.2 ×5	×0.2 ×5 ×0.2 ×5 ×0.2 ×5	×5 ×0.2 ×5 ×0.2 ×5 ×0.2 ×5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.75 1.21	0.06		0.29	0.61 0.29	0.88 0.61 0.29	-0.07 0.88 0.61 0.29	-0.12 - 0.07 0.88 0.61 0.29	0.04 - 0.12 - 0.07 0.88 0.61 0.29
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.04 0.06	0.01		0.02	0.03 0.02	0.02 0.03 0.02	-0.00 0.02 0.03 0.02	-0.01 - 0.00 0.02 0.03 0.02	0.00 - 0.01 - 0.00 0.02 0.03 0.02
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.14 0.04	0.03		0.10	0.02 0.10	0.06 0.02 0.10	-0.02 0.06 0.02 0.10	-0.05 -0.02 0.06 0.02 0.10	0.00 - 0.05 - 0.02 0.06 0.02 0.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-0.01 - 0.06	0.15		0.11	0.03 0.11	0.01 0.03 0.11	-0.03 0.01 0.03 0.11	-0.01 - 0.03 0.01 0.03 0.11	0.00 -0.01 -0.03 0.01 0.03 0.11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-0.04 - 0.26	0.15		0.39	0.82 0.39	0.95 0.82 0.39	-0.03 0.95 0.82 0.39	-0.07 -0.03 0.95 0.82 0.39	-0.03 - 0.07 - 0.03 0.95 0.82 0.39
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-0.02 - 0.07	-0.04		-0.01 -	-0.03 -0.01 -	-0.01 -0.03 -0.01 -	0.02 -0.01 -0.03 -0.01 -	0.00 0.02 -0.01 -0.03 -0.01 -	0.00 0.00 0.02 -0.01 -0.03 -0.01 -
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.86 0.58	-0.22		- 60.0-	-0.18 -0.09 -	-0.06 -0.18 -0.09 -	0.02 - 0.06 - 0.18 - 0.09 -	-0.01 0.02 -0.06 -0.18 -0.09 $-$	0.00 - 0.01 0.02 - 0.06 - 0.18 - 0.09 -
0 0.00 -0.01 -0.03 0.12 0.46 0.85 1. 0 0.00 0.00 0.00 0.06 0.46 0.82 0. 9 0.17 0.13 0.06 0.46 0.44 0.21 0. 0 0.00 0.00 0.00 0.00 0.00 0.00 0. 0 0.00 0.00 0.00 0.00 0.00 0.00 0. 0 0.00	0.00 0.00	0.00		0.00	0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00
0 0.00 0.00 0.00 0.05 0.46 0.43 0.62 0. 9 0.17 0.13 0.06 0.46 0.44 0.21 0. 0 0.00	0.00 0.00	-0.08		-0.02	0.00 - 0.02	0.00 0.00 -0.02	0.01 0.00 0.00 -0.02	0.00 0.01 0.00 0.00 -0.02	0.00 0.00 0.01 0.00 0.00 -0.02
9 0.17 0.13 0.06 0.46 0.44 0.21 0. 0 0.00 0.00 0.00 0.00 0.00 0.00 0. 0 0.00 0.00 0.00 0.00 0.00 0.00 0.	0.00 0.00	0.00		0.00	0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00 0.00
0 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0	0.19 0.17	0.02		0.04	0.10 0.04	0.09 0.10 0.04	-0.02 0.09 0.10 0.04	-0.03 - 0.02 0.09 0.10 0.04	0.01 - 0.03 - 0.02 0.09 0.10 0.04
0 0.00 0.00 0.02 0.00 0.00 0.00 0.00 0.	0.00 0.00	0.00		0.00	0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00 0.00
	0.00 0.00	0.01		0.00	0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00 0.00
0 0.00 0.00 0.00 v.vv v.vv v.vv	0.00 0.00	0.00		0.00	0.00 0.00	0.00 0.00 0.00	0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00	0.00 0.00 0.00 0.00 0.00 0.00

TABLE III. Sensitivity spectra pS [20] at 100 μs and 1000 μs at 1300 K for mixture c.

988

The $\times 0.2$ denote the result of multiplying the indicated rate constants by 1/5, while the $\times 5$ denote the result of multiplying by 5. The numbers show the reaction numbering.

No.	Reaction	A	n	E	References
(1)	$\mathbf{CF_3Br} + \mathbf{M} = \mathbf{CF_3} + \mathbf{Br} + \mathbf{M}$	5.50×10^{16}	0.0	60000	See text
(2)	$CF_3 + Br_2 = CF_3Br + Br$	$1.48 imes10^{12}$	0.0	693	[16]
(3)	$CF_3Br + H = CF_3 + HBr$	$4.40 imes 10^{14}$	0.0	9460	See text
(4)	$CF_3 + HBr = CF_3H + Br$	$2.63 imes10^{11}$	0.0	2557	[16]
(5)	$\mathbf{CF_3} + \mathbf{H_2} = \mathbf{CF_3H} + \mathbf{H}$	$2.20 imes10^{13}$	0.0	12000	This work
(6)	$CF_3 + H = CF_2 + HF$	$1.40 imes 10^{13}$	0.0	0	See text
(7)	$\mathbf{CF}_3 + \mathbf{CF}_3 = \mathbf{C}_2\mathbf{F}_6$	6.00×10^{11}	0.0	0	See text
(8)	$\mathbf{CF}_3 + \mathbf{H} + \mathbf{M} = \mathbf{CF}_3\mathbf{H} + \mathbf{M}$	$5.00 imes 10^{13}$	0.0	4000	[2]
(9)	$\mathbf{CF_3H} + \mathbf{M} = \mathbf{CF_2} + \mathbf{HF} + \mathbf{M}$	$1.30 imes 10^{16}$	0.0	58400	[7]
(10)	$C_2F_4 + M = CF_2 + CF_2 + M$	$7.80 imes10^{15}$	0.5	55690	b
(11)	$Br + H_2 = HBr + H$	$1.70 imes10^{14}$	0.0	19150	[15]
(12)	$Br_2 + H = HBr + Br$	$2.28 imes 10^{11}$	0.0	4370	[15]
(13)	$\mathbf{Br} + \mathbf{Br} + \mathbf{M} = \mathbf{Br}_2 + \mathbf{M}$	1.48×10^{14}	0.0	-200	[15]
(14)	Br + H + M = HBr + M	$1.91 imes 10^{21}$	-1.87	0	[15]

TABLE IV. Elementary reactions and rate constant expression.^a

^a Rate constants in the form, $AT^n \exp(-E/RT)$, in cm, mol, cal, and K units.

^b The reference is ref. [7].

of reaction (5). Hence, we did not adopt Glanzer value $k_7 = 5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Second, we tried to use Selamoglu et al. value [17] for our simulation. They reported a smaller high-pressure rate-constant value of $k_7 = 2.4 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. From this value and $k_7/k_7^{\infty} \approx 1/4$ [8], we assumed $k_7 = 6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $\approx 2 \text{ atm}$ ([Ar] = $1.7 \times 10^{-5} \text{ mol/cc}$) over the temperature range 1100–1500 K because reaction (7) under our experimental conditions might be in its unimolecular falloff range. When this value $k_7 = 6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was used for a prediction of pyrolysis data using mixture of 4% CF₃Br, 96% Ar shown in Figure 1 of ref. [5], to predict well the pyrolysis data it was necessary to assume $k_1 = 5.5 \times 10^{16} \exp(-60 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These values of $k_7 = 6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_1 = 5.5 \times 10^{16} \exp(-60 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction (7), we could not predict well our experimental results, as shown in Figure 2. If we used values higher than $6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction (7), we could not predict both the CF₃Br pyrolysis and CF₃Br—H₂ data well using appropriate values for reaction (5). Hence, we adopted $k_7 = 6 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as shown in Table IV.

When we used the expression $k_3 = 4.4 \times 10^{14} \exp(-9.46 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, this being larger than Baulch et al.'s expression [15] by a factor of about 3 and Westbrook's expression [2] by a factor of about 2, the HBr concentration was predicted well, as shown in Figures 1 and 3. If we used Westbrook's expression $k_3 = 2.20 \times 10^{14} \exp(-9.46 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, the [HBr] calculated for mixtures A were lower than the observed ones, as shown in Figure 1. This tendency was observed in mixtures B and C. Hence, the expression $k_3 = 4.4 \times 10^{14} \exp(-9.46 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was adopted for reaction (3).

Three expressions for the rate constant for reaction (4) are found in previous reports [2,11,16]. Weeks and Whittle's expression [16] is similar to Westbrook's [2]. We adopted Weeks and Whittle's expression, which had



Figure 2. Product distribution with mixture C, 4% CF₃Br, 1% H₂, 95% Ar. [CF₃Br]₀ is the initial concentration of CF₃Br, and C is the concentration of reactant or product at the effective heating time t at temperature T. \triangle : observed [CF₃Br]; \Box : observed [C₂F₆]; \bigcirc : observed [CF₃H]; \bigcirc : observed [C₂F₆]; \bigcirc : observed [CF₃H]; \bigcirc : observed [C₂F₆]; \bigcirc : calculated with the mechanism and the rate constant expressions shown in Table I; -----: calculated by using Table I in which the rate constant expression, $k_7 = 6.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction (7) was changed to $k_7 = 5.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8]; ---: calculated by using Table I in which the rate constant expression $k_5 = 2.2 \times 10^{13} \exp(-12 \text{ kcal/}RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction (5) was changed to $k_5 = 1.1 \times 10^{13} \exp(-12 \text{ kcal/}RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

values smaller than that of Amphlett and Whittle [11] by a factor of about 2. If Amphlett and Whittle's expression, $k_4 = 2.63 \times 10^{11} \exp(-2.63 \text{ kcal}/RT)$ cm³ mol⁻¹ s⁻¹ [11], was used in place of Weeks and Whittle's expression [16], the calculated values of [CF₃H] were larger than the observed ones. This tendency was especially large in mixture *B*. This expression for k_4 could not give satisfactory results for the calculations of these species even if the k_5 value used was smaller than that in Table IV.

The sensitivity spectra pS at 100 and 1000 μ s at 1300 K using mixture C are also shown in Table III. Reaction (5) is sensitive for the formation of HBr, C_2F_6 , and CF_3H , and also for CF_3Br consumption. The expression $k_5 = 1.1 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ gives good predictions for the CF_3Br , CF_3H , and C_2F_6 concentrations, as shown in Figure 2. However, the calculated [HBr] are lower than the observed ones, as shown in Figures 1 and 3. On the other hand, the rate constant expression $k_5 =$ $2.2 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ gives good agreement between the observed HBr concentration and the calculated one, as shown in Figures 1 and 3, but the calculated CF_3Br and CF_3H concentrations at lower temperatures are somewhat lower and higher, respectively, than the observed ones. Values smaller than the expression $k_5 = 1.1 \times 10^{13}$ $\exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ brought about a larger discrepancy between the calculated CF₃H concentrations and the observed ones. Hence, we adopted the expression $k_5 = 2.2 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1}$ s⁻¹ for reaction (5): the expression $k_5 = 1.1 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3$



Figure 3. Comparison of the calculated [HBr] with those observed at 100 μ s, 200 μ s, and 400 μ s with mixture B. Δ : observed [HBr] at 100 μ s; Δ : observed [HBr] at 200 μ s; Δ : observed [HBr] at 400 μ s; ---: calculated lines as in Figure 1; and ---: calculated lines as in Figure 1.

 $mol^{-1} s^{-1}$ seemed to be a minimum value for reaction (5). A comparison of the present k_5 expression with reported ones is shown in Figure 4. The present value of k_5 at about 1100 K is similar to that of the Westbrook [2] and the extrapolated values of our k_5 are similar to those of Fagarash et al. [13], and Ayscough et al. [9], as shown in Figure 4.

Bopp et al. [18] studied the reaction of H₂ and Br₂ over the temperature range of 1400–2000 K and modeled their results well using $k_{11} = 1.39 \times 10^{14} \exp(-19.6 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate constant is smaller than that of Baulch et al. [15] by a factor of about 1.4. Results calculated by using Bopp et al.'s value scarcely differed from our final calculated results: the yield of products varied within 1%. The calculated results were also similar to those obtained by using Table IV even when the rate constant of reactions (13) was changed to that recommended by Kerr and Moss [19]: the yield of products varied within 1%. From the description above, we can see that the influence of reactions (11) and (13) upon [CF₃H], [C₂F₆], and [HBr] is small.

Tsai and McFadden [20] recently evaluated $k_6 = 5.5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K from experiments in a gas flow system using photoionization mass spectrometry. When this expression was used in calculations, the calculated yield of C₂F₄ was considerably larger than the observed one. To match the calculated [C₂F₄] to observed one, we had to use a quarter of its value when $k_3 = 4.4 \times 10^{14} \exp(-9.46 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_5 = 2.2 \times 10^{13} \exp(-12 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ were used.



Figure 4. Comparison of the reported rate constants k_5 with that used for an interpretation of our data. ——:: this work; — - —: reported by Westbrook [2]; -----: reported by Skinner and Ringrose [1]; —---:: reported by Kibby and Weston [12]; ———: reported by Ayscough et al. [9]; —---:: reported by Fagarash et al. [13]; and •—•: Berces et al. [14].

Tsai and McFadden [20] also evaluated $k_{15} = 2.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for reaction CF₂ + H \rightarrow CF + H₂ (15). On the other hand, Ryan and Plumb [21] reported $k_{15} = 9.6 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. If we used the value of Tsai and McFadden for reaction (15), $k_{15} = 2.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, the CF concentration reached 16% of the initial concentration of CF₃Br at 2000 μ s at 1300 K. The CF is considered to form C₂F₂ by the following reaction

(16) $CF + CF + M \longrightarrow C_2F_2 + M \qquad \Delta H_0 = -116 \text{ kcal/mol}$

The rate constant for reaction (16) may be assumed from the behavior of the similar reaction $CF_2 + CF_2 + M \rightarrow C_2F_4 + M$, $\Delta H_0 = -69$ kcal/mol: the value assumed for reaction (16) was 1.0×10^{16} cm⁶ mol⁻² s⁻¹. When we added this reaction to Table IV and simulated the yield at 1300 K for mixtures A and B, C_2F_2 of about 2-4% of the initial concentration of CF_3Br was produced. However, under our experimental conditions, products other than CF_3Br , C_2F_6 , C_2F_4 , and CF_3H were not detected. Hence, the rate constant of reaction (15) is inferred to be much smaller than 2.3×10^{13} cm³ mol⁻¹ s⁻¹.

Bibliography

- [1] G. B Skinner and G. H. Ringrose, J. Chem. Phys., 43, 4129 (1965).
- [2] C.K. Westbrook, Comb. Sci. Tech., 34, 201 (1983).
- [3] Y. Hidaka, S. Shiba, H. Takuma, and M. Suga, Int. J. Chem. Kinet., 17, 441 (1985).
- [4] Y. Hidaka, T. Nakamura, A. Miyauchi, T. Shiraishi, and H. Kawano, Int. J. Chem. Kinet., 21, 643 (1989).
- [5] Y. Hidaka, T. Nakamura, and H. Kawano, Chem. Phys. Letters, 154, 573 (1989).
- [6] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, JANAF ThermoChemical Tables, third ed., NSRDA-NBS, J. Phys. Chem. Ref. Data, 14 (1985).
- [7] Y. Hidaka, T. Nakamura, and H. Kawano, Chem. Phys. Letters, 187, 40 (1991).
- [8] K. Glanzer, M. Maier, and J. Troe, J. Phys. Chem., 84, 1681 (1980).
- [9] P. B. Ayscough, J. C. Polanyi, and E. W. R. Steacie, Can. J. Chem., 33, 743 (1955).
- [10] G.O. Pritchard, H.O. Pritchard, H.I. Schiff, and A.F. Trotman-Dickenson, Trans. Faraday Soc., 52, 849 (1956).
- [11] J.C. Amphlett and E. Whittle, Trans. Faraday Soc., 63, 2695 (1967).
- [12] C. L. Kibby and R. E. Weston, Jr., J. Chem. Phys., 49, 4825 (1968).
- [13] M.B. Fagarash, F.B. Moin, and V.I. Ocheret'ko, Kinetics and Catalysis, 9, 762 (1968).
- [14] T. Berces, F. Marta, and I. Szilagyi, J. Chem. Soc. Faraday I, 68, 867 (1972).
- [15] D. L. Baulch, J. Duxbury, S.J. Grant, and D.C. Montague, J. Phys. Chem., Ref. Data, 10, Supple. 1 (1981).
- [16] I. Weeks and E. Whittle, Int. J. Chem. Kinet., 15, 1329 (1983).
- [17] N. Selamoglu, M. J. Rossi, and D. M. Golden, Chem. Phys. Lett., 124, 68 (1986).
- [18] J. M. Bopp, A. C. Johnson, R. D. Kern, and T. Niki, J. Phys. Chem., 86, 805 (1982).
- [19] J.A. Kerr and S.J. Moss, CRC Handbook of Bimolecular and Termolecular Gas Reactions, CRC Press, Inc., Boca Raton, 1981, Vol. II, p. 24.
- [20] C. Tsai and D. L. McFadden, J. Phys. Chem., 93, 2471 (1989).
- [21] K.R. Ryan and I.C. Plumb, Plasma Chem. Plasma Proc., 4, 141 (1984).
- [22] W.C. Gardiner, Jr., J. Phys. Chem., 81, 2367 (1977).

Received August 27, 1992 Accepted June 2, 1993