

THE GAS PHASE THERMOCHEMISTRY OF THE REACTION:
 $\text{C}_2\text{F}_5\text{Br} + \text{I}_2 = \text{C}_2\text{F}_5\text{I} + \text{IBr}$

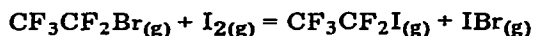
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ABSTRACT

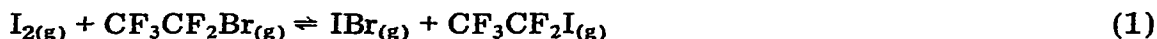
The gas phase equilibrium for the reaction



has been studied over the temperature range 620–670 K. A third law treatment of the data gave $\Delta H_{\text{r}}(1, 298) = 9.2 \pm 0.2 \text{ kcal mole}^{-1}$. This result is compared with other thermochemical data, and values for the heats of formation of $\text{C}_2\text{F}_5\text{Br}$, $\text{C}_2\text{F}_5\text{Cl}$ and $\text{C}_2\text{F}_5\text{H}$ are derived.

INTRODUCTION

As a part of a continuing study of the effects of fluorine substitution on heats of reaction and bond dissociation energies, we have undertaken equilibrium measurements for the reaction



The existence of equilibrium has been confirmed by approaching it from both sides of reaction (1). A third law treatment will be applied to the data to evaluate $\Delta H_{\text{r}}^0(1, 298)$. Ideal gas thermodynamic functions are well established for I_2 and IBr [1], while those for $\text{C}_2\text{F}_5\text{Br}$ and $\text{C}_2\text{F}_5\text{I}$ have been calculated for this work [2]. Since $\Delta H_{\text{f}}^0(\text{C}_2\text{F}_5\text{I}, \text{g}, 298)$ [3], $\Delta H_{\text{f}}^0(\text{IBr}, \text{g}, 298)$ [1], and $\Delta H_{\text{f}}^0(\text{I}_2, \text{g}, 298)$ [1] and the associated bond dissociation energies are known, $\Delta H_{\text{f}}^0(\text{C}_2\text{F}_5\text{Br}, \text{g}, 298)$ and $\text{DH}_{298}^0(\text{C}_2\text{F}_5\text{—Br})$ may be obtained.

EXPERIMENTAL

Research grade $\text{CF}_3\text{CF}_2\text{I}$ was obtained from the Pierce Chemical Company and $\text{CF}_3\text{CF}_2\text{Br}$ was obtained from the Penninsular Chemical Research Company. Both compounds were distilled under vacuum several times before use. Reagent grade I_2 was obtained from J.T. Baker Chemical Company and was

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resublimed just before use. Research grade Br_2 was obtained from Mallinckrodt Chemical Company and was distilled under vacuum.

The experimental apparatus has been described in detail elsewhere [4]. Basically, it consists of a heated 475 ml pyrex static reactor vessel connected to a "hot box" maintained between 98 and 108°C to facilitate the handling of up to 40 torr iodine. Pressure measurements are conducted inside the "hot box" using a Pace-Wiancko pressure transducer as a null device. Pressures are read either on a dibutylphthalate manometer ($P < 60$ torr) or on a mercury manometer ($P > 60$ torr). The "hot box" is connected to a series of cold traps to sample the reaction cell mixture for gas chromatographic analysis. The reaction cell was placed inside a wire wound aluminum block oven which was temperature controlled to $\pm 0.25^\circ\text{C}$ by means of a variable autotransformer and E.P.C. 1300 series proportional controller.

In order to initiate an equilibrium study, bromine was measured into the reaction cell. Addition of a larger pressure of iodine converted essentially all Br_2 to IBr ($K_{\text{eq}} \cong 38$) [1]. The desired mixture of $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_3\text{CF}_2\text{I}$ was then expanded into the reaction cell and the total pressure measured. After sufficient time was allowed for the reaction mixture to approach equilibrium, the contents of the cell were passed through an Ascarite trap submerged in ice water to remove I_2 and IBr . The remaining halocarbon mixture was then expanded into a second trap and subjected to gas-liquid chromatographic analysis. A 0.6×305 cm column (6 mm inner diameter) packed with 30% 2,4-dimethylsulfolane on 60/80 Chromosorb W was run at room temperature (25–29°C) with a helium flow rate of 30 ml min^{-1} . The air peak occurred at 1.5 min after injection and the retention times relative to air for $\text{CF}_3\text{CF}_2\text{I}$ and $\text{CF}_3\text{CF}_2\text{Br}$ were 11.0 and 1.9, respectively. Accuracy of the gas-liquid chromatographic analysis was $\pm 2\%$ and was determined from standard mixtures analyzed under simulated experimental conditions. Peak areas were determined by the peak width at half-height method.

RESULTS AND DISCUSSION

Data for the equilibrium study of reaction (1) are presented in Table 1. Assuming all Br_2 initially present is converted to IBr , the initial pressure of IBr is given as twice the pressure of Br_2 introduced. The pressure of I_2 remaining after formation of IBr is then

$$P_{\text{I}_2}^{\text{i}} = P_{\text{I}_2}^0 - P_{\text{Br}_2}^0$$

where $P_{\text{I}_2}^0$ is the pressure of iodine introduced. After reaction, the final, or equilibrium pressures of IBr ($P_{\text{IBr}}^{\text{e}}$) and I_2 ($P_{\text{I}_2}^{\text{e}}$) are given by

$$P_{\text{IBr}}^{\text{e}} = P_{\text{IBr}}^{\text{i}} + \Delta P_{\text{RI}} \quad (2)$$

$$P_{\text{I}_2}^{\text{e}} = P_{\text{I}_2}^{\text{i}} - \Delta P_{\text{RI}} \quad (3)$$

where

$$\Delta P_{\text{RI}} = P_{\text{T}} \left[1 + \left(\frac{P_{\text{RBr}}}{P_{\text{RI}}} \right)^{\text{e}} \right]^{-1} - P_{\text{T}} \left[1 + \left(\frac{P_{\text{RBr}}}{P_{\text{RI}}} \right)^{\text{i}} \right]^{-1}$$

and $P_{\text{T}} = P_{\text{RBr}} + P_{\text{RI}}$.

TABLE 1

Experimental data for $\text{CF}_3\text{CF}_2\text{Br}_{(\text{g})} + \text{I}_{2(\text{g})} \rightleftharpoons \text{CF}_3\text{CF}_2\text{I}_{(\text{g})} + \text{IBr}_{(\text{g})}$.

T (K)	Run No.	$P_{\text{I}_2}^0$ (torr)	$P_{\text{Br}_2}^0$ (torr)	P_{T} (torr)	$(P_{\text{RBr}}/P_{\text{RI}})^i$	Time (h)	$(P_{\text{RBr}}/P_{\text{RI}})^c$
618	1	20.23	0	25.77 *		5.0	31.56
	2	20.15	0	26.35 *		12.5	37.28
	3	20.58	1.96	4.46	32.87	5.0	104.61
	4	20.04	0.46	5.65	96.35	9.0	25.82
	5	20.96	0.54	5.08	96.35	5.0	26.27
	6	20.93	1.92	5.46	96.35	12.2	157.48
	8	19.96	1.42	5.97	96.35	10.5	117.71
	9	21.77	0.81	5.15	96.35	5.7	51.05
	10	20.23	2.00	5.15	28.35	9.9	154.36
	11	19.42	1.12	5.88	28.35	12.4	86.20
	12	19.00	1.00	6.00	28.35	13.4	71.05
	24	9.53	0.54	19.38	118.21	1.0	94.40
	25	9.68	0.51	10.43	118.21	1.0	106.85
640	19	18.92	1.00	19.23	24.37	0.3	50.68
	20	9.69	1.04	21.04	24.37	0.3	81.78
	21	19.62	0.54	3.62	71.05	0.3	39.18
	22	20.23	0.54	19.77	118.21	0.3	50.69
	23	9.58	0.58	12.04	118.21	0.3	87.17
667	13	18.84	0.96	18.81	28.35	1.0	60.52
	14	19.27	0.96	4.12	28.35	1.0	41.16
	15	18.88	0.46	5.27	96.35	1.0	31.43
	16	19.12	0.54	15.50	71.05	1.0	39.79
	17	18.96	0.50	15.69	71.05	0.5	33.54
	18	18.69	0.50	15.39	71.05	0.3	31.57

* $P_{\text{T}} = P_{\text{RBr}}$.

Table 2 gives the values for $-RT \ln Q$ in which Q is the ratio of the partial pressures of the products to reactants for both the initial, Q_i , and the equilibrium, Q_e , reaction mixtures. One expects that $Q_e = K_p$ for this reaction, but the $-RT \ln Q_e$ values in Table 2 show that there is in the order of 10–20% scatter in Q_e . In order to show that Q_e does indeed approximate K_p , the initial pressure ratios of $(P_{\text{RBr}}/P_{\text{RI}})^i$ were adjusted so that reaction (1) took place in both directions, thus assuring that the Q_i values bracketed K_p .

The Gibbs free energy change, ΔG_r^0 , can be determined to within ± 0.5 kcal mole $^{-1}$ from these data, and if the free energy functions are known, $\Delta H_r^0(298)$ may be evaluated. The ideal gas thermodynamic functions for IBr and I_2 are known [1], and those for the two halocarbons have been calculated for this work [2]. Table 3 summarizes the important thermochemical data.

Experimental values of ΔH_i and ΔH_e at 298.15 K are given in Table 2. They were obtained by subtracting $\Delta(G^0 - H_{298}^0)$ from the appropriate $-RT \ln Q$ values. The ΔH_i values are upper or lower limits to ΔH_r depending on whether the reaction of the initial mixture proceeds to the right or left, respectively. For example, in Run 3 of Table 2, the reaction obviously pro-

TABLE 2

Results of the equilibrium study of $\text{CF}_3\text{CF}_2\text{Br}_{(\text{g})} + \text{I}_{2(\text{g})} = \text{CF}_3\text{CF}_2\text{I}_{(\text{g})} + \text{IBr}_{(\text{g})}$

T (K)	$\Delta(G^0 - H_{298}^0)$ (kcal mole ⁻¹)	Run No.	$-RT\ln Q_i$ (kcal mole ⁻¹)	$-RT\ln Q_i$ (kcal mole ⁻¹)	ΔH_i * (kcal mole ⁻¹)	ΔH_e ** (kcal mole ⁻¹)
618	-0.96	1	∞	8.17	∞	9.13
		2	∞	8.54	∞	9.50
		3	6.20	7.66	>7.16	8.62 ***
		4	9.36	7.54	<10.32	8.50 ***
		5	9.23	7.47	<10.19	8.43 ***
		6	7.58	8.17	>8.52	9.13
		8	7.92	8.17	>8.88	9.13
		9	8.75	8.17	<9.71	9.13
		10	5.97	8.11	>6.91	9.07
		11	6.69	8.14	>7.65	9.10
		12	6.81	8.02	>7.77	8.98
		24	8.46	8.14	<9.42	9.10
		25	8.57	8.42	<9.53	9.38
640	-1.00	19	6.85	8.08	>7.85	9.08
		20	5.87	7.91	>6.87	8.91
		21	9.08	8.28	<10.08	9.28
		22	9.76	8.44	<10.76	9.44
		23	8.68	8.25	<9.68	9.25
667	-1.04	13	7.39	8.67	>8.43	9.67
		14	7.42	7.94	>8.46	8.98
		15	10.02	8.38	<11.06	9.42
		16	9.43	8.46	<10.47	9.50
		17	9.51	8.22	<10.55	9.26
		18	9.49	8.09	<10.53	9.13
Ave						9.22 \pm 0.2

* $\Delta H_i = -RT\ln Q_i - \Delta(G^0 - H_{298}^0)$; > or < indicates that ΔH_r is greater or less than ΔH_i .

** $\Delta H_e = -RT\ln Q_e - \Delta(G^0 - H_{298}^0)$; an estimate of ΔH_r .

*** Not used in average.

ceeds to greater partial pressures for the reactants so that $Q_i > K_p$ and therefore $\Delta H_r^0 > \Delta H_i$, as indicated in Table 2. Similarly, in Run 4, $Q_i < K_p$ so that $\Delta H_r^0 < \Delta H_i$.

The average value for ΔH_e is 9.2 ± 0.2 kcal mole⁻¹ and this value is consistent with the upper and lower limits set by the ΔH_i values so that we can conclude that

$$\Delta H_r^0(1, 298) = 9.2 \pm 0.2 \text{ kcal mole}^{-1}$$

This result may be combined with the relevant data from Table 3 to obtain

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{I}, \text{g}, 298) - \Delta H_f^0(\text{CF}_3\text{CF}_2\text{Br}, \text{g}, 298) = 14.35 \pm 0.2 \text{ kcal mole}^{-1}$$

and

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{Br}, \text{g}, 298) = -254.4 \pm 1 \text{ kcal mole}^{-1}$$

TABLE 3

Summary of thermochemical data

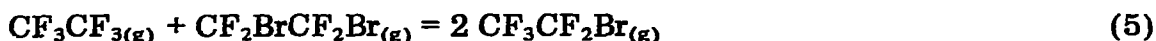
Compound	ΔH_f^0 (g, 298) (kcal mole ⁻¹)	$(G^0 - H_{298}^0/T)$ (cal K ⁻¹ mole ⁻¹)		
		600 K	700 K	800 K
CF ₃ CF ₂ I	-240.0 ± 1 ^a	-94.655 ^b	-97.388	
CF ₃ CF ₂ Br		-92.672 ^b	-95.386	-98.100
CF ₃ CF ₂ Cl			-92.945 ^b	-95.644
CF ₃ CF ₂ H		-84.953 ^c	-87.387	-89.838
Br ₂	+7.39 ± 0.03 ^d	-60.363 ^d	-61.096	-61.806
IBr	+9.77 ± 0.02 ^d	-63.597 ^d	-64.336	
I ₂	+14.92 ± 0.01 ^d	-64.025 ^d	-64.767	
Cl ₂	0.0		-55.643 ^d	-56.334
ClBr	+3.5 ± 0.3 ^d		-59.740 ^d	-60.440
HBr	-8.71 ± 0.1 ^d	-48.837 ^d	-49.422	-49.992
C ₂ F ₄	-157.4 ± 0.7 ^d			
C ₂ F ₆	-320.9 ± 1.5 ^c			

^a Ref. 3.^b Ref. 2.^c Ref. 10.^d Ref. 1.

This latter value can be compared with earlier results of Lacher et al. [5] on the heat of addition of bromine to tetrafluoroethylene using the principles of group additivity [6,7]. Benson et al. [6,7] have shown that the change in the thermodynamic properties (heat capacity, entropy, and enthalpy) for reactions such as (4) can be assumed to be zero to a very good approximation.



In reaction (4) N and N' are polyvalent nuclei (the same or different) and R and S are atoms. Deviations in the enthalpy of reaction have been observed in a few cases in which the polarity of RN and SN' are very different [2,8]. However, recent work has shown that these deviations can be accounted for as the energy of the dipole-dipole interactions between the different groups; and as the difference in polarity of the RN and SN' groups diminishes, the energy of interaction approaches zero [9]. For the cases to be considered in this work, the polarities of the groups are similar enough to justify the assumption that $\Delta H_r(4, T) = 0$. The results of Lacher et al. [5] yield $\Delta H_f^0(\text{CF}_2\text{BrCF}_2\text{Br}, \text{g}, 298) = -188.3 \pm 1$ kcal mole⁻¹ (see Table 3). This may be combined with our results and $\Delta H_f^0(\text{C}_2\text{F}_6, \text{g}, 298)$ [10] to obtain $\Delta H_r(5, 298) = +0.4 \pm 2$ kcal mole⁻¹.



This is in excellent agreement with the value expected from group additivity showing that our results are consistent with those of Lacher et al. [5].

Coomber and Whittle [11] have determined the equilibrium constants for reaction (6) over the temperature range 730–830 K. A Van 't Hoff plot

of their data gave $\Delta H_r^0(6, 298) = -10.3 \pm 0.6 \text{ kcal mole}^{-1}$.



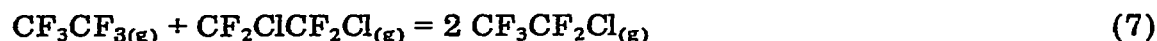
We have calculated the ideal gas, thermodynamic properties for both $\text{CF}_3\text{CF}_2\text{Br}$ and $\text{CF}_3\text{CF}_2\text{Cl}$ so that the enthalpy of reaction (6) may be obtained from Coomber and Whittles' [1] data with the free energy functions summarized in Table 3 (a "Third Law" value). This gave: $\Delta H_r^0(6, 298) = -9.5 \pm 0.1 \text{ kcal mole}^{-1}$. We favor the third law value because of the excellent fit to the data. This value and the heats of formation of Table 3 yield

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{Cl}, g, 298) - \Delta H_f^0(\text{CF}_3\text{CF}_2\text{Br}, g, 298) = -13.0 \pm 0.1 \text{ kcal mole}^{-1}$$

and

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{Cl}, g, 298) = -267.4 \pm 1 \text{ kcal mole}^{-1}$$

This result may also be compared via group additivity with the heat of addition of chlorine to tetrafluoroethylene measured by Lacher et al. [12]. The heat of chlorination yields (see Table 3): $\Delta H_f^0(\text{CF}_2\text{ClCF}_2\text{Cl}, g, 298) = -214.6 \pm 0.7 \text{ kcal mole}^{-1}$. This, combined with the result for $\text{CF}_3\text{CF}_2\text{Cl}_{(g)}$, yields for reaction (7); $\Delta H_r^0(7, 298) = +0.7 \pm 0.2 \text{ kcal mole}^{-1}$. This, too, is in excellent agreement with group additivity [6,7].



Coomber and Whittle [13] have also determined the equilibrium constants for reaction (8) over the temperature range 630–840 K.



Their Van 't Hoff plot resulted in $\Delta H_r^0(8, 298) = -6.4 \pm 0.2 \text{ kcal mole}^{-1}$ while a "Third Law" treatment using the free energy function summarized in Table 3 gave $\Delta H_r^0(8, 298) = -7.5 \pm 0.1 \text{ kcal mole}^{-1}$. Both methods fit the observations quite well, however, we prefer the "Third Law" approach as do Coomber and Whittle (however, free energy functions had not yet been determined for $\text{CF}_3\text{CF}_2\text{H}$ and $\text{CF}_3\text{CF}_2\text{Br}$) so that we shall adopt $\Delta H_r^0(8, 298) = -7.5 \pm 0.1 \text{ kcal mole}^{-1}$. This value leads to

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{H}, g, 298) - \Delta H_f^0(\text{CF}_3\text{CF}_2\text{Br}, g, 298) = -8.6 \pm 0.1 \text{ kcal mole}^{-1}$$

and

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{H}, g, 298) = -263.0 \pm 1 \text{ kcal mole}^{-1}$$

This latter value is less stable by $1.0 \text{ kcal mole}^{-1}$ than the value adopted by Chen et al. [10] which is due entirely to the change in $\Delta H_r^0(8, 298)$.

The values for the heats of formation that have been determined or selected in this work are

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{Br}, g, 298) = -254.4 \pm 1 \text{ kcal mole}^{-1}$$

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{Cl}, g, 298) = -267.4 \pm 1$$

and

$$\Delta H_f^0(\text{CF}_3\text{CF}_2\text{H}, g, 298) = -263.0 \pm 1$$

The values for C_2F_5Br and C_2F_5Cl have been shown to be consistent with the results of Lacher et al. [5,12] for the heats of addition of Br_2 and Cl_2 to C_2F_4 .

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