Bond Dissociation Energies from Equilibrium Studies

Part 1.— $D(CF_3$ —Br), $D(C_2F_5$ —Br) and $D(n-C_3F_7$ —Br)

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Received 26th October, 1966

The gas-phase equilibria:

 $\begin{array}{l} Br_2+CF_3H \rightleftharpoons HBr+CF_3Br & (1) \\ Br_2+C_2F_5H \rightleftharpoons HBr+C_2F_5Br & (2) \\ Br_2+n-C_3F_7H \rightleftharpoons HBr+n-C_3F_7Br & (3) \end{array}$

have been studied over the ranges 410-608°C (1), 359-569°C (2) and 340-528°C (3). Equilibria were approached from both sides. A third-law treatment of the values of K_1 gives $\Delta H_1^* = -4 \cdot 59 \pm 0.25$ kcal mole⁻¹ so that $\Delta H_f^*(CF_3Br) = \Delta H_f^*(CF_3H) + 11 \cdot 5 \pm 0.30$ kcal mole⁻¹, all at 298°K. The use of our previous value of $D(CF_3 - H)$ leads to $D(CF_3 - Br) = 69 \cdot 4 \pm 0.8$ kcal mole⁻¹. The third-law method cannot be applied to equilibria (2) and (3) but we estimate that $\Delta H_2^* = 5 \cdot 1 \pm 1 \cdot 0$ and $\Delta H_3^* = 5 \cdot 0 \pm 1 \cdot 0$ kcal mole⁻¹. Taking $D(C_2F_5 - H) = D(n \cdot C_3F_7 - H) = 103 \cdot 5 \pm 2 \cdot 0$, we obtain, $D(C_2F_5 - Br) = D(n \cdot C_3F_7 - Br) = 67 \cdot 0 \pm 2 \cdot 5$, all in kcal mole⁻¹ at 298°K. The various bond dissociation energies are compared with those of the corresponding alkanes and alkyl bromides.

Kinetic studies ¹ have yielded a value of the bond dissociation energy $D(CF_3-H)$ which we believe to be reliable to better than ± 1 kcal mole⁻¹. From this, other bond dissociation energies of the type $D(CF_3-R)$ can be calculated by combining the value of $D(CF_3-H)$ with enthalpies of reaction obtained from studies of equilibria; this technique has been used for hydrocarbons by Benson and co-workers.² In principle, the value of $D(CF_3-H)$ can also be used to obtain $\Delta H_f^{\circ}(CF_3)$ and hence bond dissociation energies of the type $D(CF_3-R)$. However, such calculations require accurate enthalpies of formation whereas many of these are in doubt for fluorine compounds ³ because of uncertainties in $\Delta H_f^{\circ}(HF, aq)$. The equilibrium method is unaffected by this difficulty.

This paper is the first of a series devoted to equilibria and it deals with the systems,

$$Br_2 + CF_3 H \rightleftharpoons HBr + CF_3 Br \tag{1}$$

$$Br_2 + C_2F_5H \rightleftharpoons HBr + C_2F_5Br \tag{2}$$

$$Br_2 + n - C_3 F_7 H \rightleftharpoons HBr + n - C_3 F_7 Br$$
(3)

The first of these was studied by Corbett, Tarr and Whittle ⁴ and their work has been checked using a larger temperature range and improved experimental methods.

EXPERIMENTAL

MATERIALS AND APPARATUS

All materials were prepared and purified as described elsewhere.4-6

Two similar apparatuses A and B were used each having a reaction vessel R.V. in an oven as shown in fig. 1. The cylindrical quartz R.V. were identical, with length 10.8 cm, diam.

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7 cm, vol. 199 ml. Each was connected via a graded seal to a Springham greaseless tap T_1 with Viton A diaphragm, immediately outside the oven. T_1 was connected through a second greaseless tap T_2 to a conventional high vacuum system. The volume of the side-arm of each vessel up to T_1 was 3.6 ml and the volume between T_1 and T_2 was 3.0 ml. Each oven had a cylindrical liner consisting either of phosphor bronze (A) or aluminium bronze (B); dimensions were, length 39 cm, ext. diam., 10.8 cm, int. diam., 7.0 cm. Each cylinder had two end-plugs of the same metal extending 13 cm inside the oven and 6.5 cm outside it. Each cylinder was wound with nichrome tape and was enclosed in an asbestos pipe, length



R.V. = reaction vessel with thermocouple well. [2], metal cylinder and end-plugs. Opening A is for Pt resistance thermometer of Sirect regulator; opening B is for thermocouple; dashed rectangle indicates asbestos pipe.

58 cm, ext. diam. 30 cm, filled with Vermiculite. Oven temperatures were measured with Chromel/Alumel thermocouples calibrated by means of a Pt/Pt--13% Rh thermocouple which had been calibrated to $\pm 1^{\circ}$ C by N.P.L.; hence temperatures quoted should be accurate to $\pm 1^{\circ}$ C. Oven B was controlled by a Sirect regulator (C.N.S. Instruments); at any given setting, no variation in temperature could be detected over many hours, i.e., the temperature was constant to $<\pm 0.2^{\circ}$ C. Oven A was controlled manually and the temperature varied by less than 1° in 3 h. With both ovens, the gradient along the R.V. was < 0.4° C.

Pressures of reactants and products were measured with a glass spiral gauge. In both measuring and analysis sections of the apparatus, Springham greaseless taps with Viton A diaphragms were used.

PROCEDURE

Bromine was de-gassed and then admitted to the R.V. at a known pressure. This was followed by reactant RH, its pressure being obtained from the combined pressures of Br_2+RH . Tap T_1 was closed and the rest of the system was evacuated. After a suitable time, the R.V. was opened to the space between taps T_1 and T_2 . The sample thus removed was rejected as it was largely the contents of the side-arm. A second sample was immediately withdrawn in the same way and it was presumed to be representative of the contents of the R.V. This sample was analyzed by G.S.C. to determine the ratio [RH]/[RBr]. This procedure was repeated at suitable time intervals until the ratio [RH]/[RBr] had reached a constant value, i.e., until the mixture in the R.V. had reached equilibrium. At every temperature, separate experiments were done in which equilibrium was approached from the l.h.s. using Br_2+RH and from the r.h.s. using HBr+RBr.

ANALYSES

All equilibrium constants are calculated from analyses of equilibrium mixtures, i.e., the initial amounts of reactants are not involved (this differs from the procedure of ref. (4)). Details of analyses are as follows. For runs on equilibrium (1), the ratio $[CF_3H]/[CF_3Br]$ in the test samples was determined by G.S.C. using a 1.2 m alumina column preceded by 11

cm of Carbosorb (to remove Br_2+HBr), both at room temperature. At equilibrium the mixture in the R.V. was opened to a known volume V so that ~50 % of the products were removed. The SiF₄ content (if present) was measured by i.-r. and the sample was then rejected. The remainder of the mixture in the R.V. was frozen into V and the pressure was measured. The sample was then distilled from -120 to $-196^{\circ}C$ and the pressure of the residue, which contained only Br_2 , was measured. The distillate consisted of $HBr+CF_3H+CF_3Br+SiF_4$ (if present) and its total pressure was measured in V. The mixture was twice passed through Carbosorb to remove $HBr+SiF_4$ and the pressure of the residue gave the pressure of (CF_3H+CF_3Br) directly and ($HBr+SiF_4$) by difference. The equilibrium ratio [$CF_3H]_e/[CF_3Br]_e$ was already known by G.S.C. hence the separate pressures of CF_3H and CF_3Br could be calculated. In a similar way, the HBr pressure was obtained since the SiF₄ content of the mixture had been measured by i.-r.

For equilibrium (2) involving C_2F_5H , the analysis was similar except that C_2F_5H + $C_2F_5Br+HBr$ were separated from Br_2 by distillation at $-95^{\circ}C$. No SiF₄ was formed. For equilibrium (3), the G.S.C. analysis was modified, the ratio $[C_3F_7H]_e/[C_3F_7Br]_e$ being determined using a column consisting of 11 cm of Carbosorb at room temperature followed by 24 cm of silica gel at 66° C. The rest of the analysis utilized either of the following methods ; (i) a known fraction of the equilibrium mixture was treated with Carbosorb to remove HBr+Br₂ (no SiF₄ formed); the pressures before and after gave $(C_3F_7H+C_3F_7B_7)$ and (HBr+Br₂). Since the ratio $[C_3F_7H]_e/[C_3F_7Br]_e$ was found by G.S.C., the absolute amounts of each of these two are then known. The absolute amounts of HBr and Br_2 were obtained from the sum (HBr+Br₂) by assuming that [HBr]_e = $[C_3F_7Br]_e$, i.e., assuming that eqn. (3) is valid. (ii) Alternatively, a sample of the equilibrium mixture was distilled from -120 to The distillate consisting of all the HBr plus some C_3F_7H plus some C_3F_7Br was treated with Carbosorb and the HBr obtained by difference. The residue consisting of all Br_2 plus some C_3F_7H plus some C_3F_7Br was treated with Carbosorb to give the Br_2 by difference. Hence knowing the Br₂ and HBr content of the sample, we obtain the sum $(C_3F_7H+C_3F_7Br)$ which can be separated since the ratio of the last two is known by G.S.C. Method (i) was used for all but 2 runs, and method (ii) was used for these two runs and several of those which had already been analyzed by method (i). The results of the two methods always agreed to <1 %. No SiF₄ was formed in these experiments.

RESULTS

EQUILIBRIUM $Br_2 + CF_3H \rightleftharpoons HBr + CF_3Br$ (1)

This was studied by Corbett, Tarr and Whittle ⁴ (CTW) over the range 426-520°C using a Pyrex vessel. Equilibrium was approached from both sides. Eqn. (1) was stoichiometrically obeyed at all temperatures used and no other products were detected. Consequently mixtures of $CF_3H + Br_2$ or $CF_3Br + HBr$ were left in the oven for suitable times after which the Br_2 content was determined. The initial Br_2 content was known hence, using eqn. (1), the concentration of all other products in the equilibrium mixture could be calculated. Replicate experiments were done in which identical samples of a standard reaction mixture were left in the oven for progressively longer times before being analyzed. It was assumed that equilibrium had been reached when constant values of K were obtained.

We have now made a further study of equilibrium (1) using a R.V. made of silica instead of Pyrex and with the following improvements: (i) the temperature range has been increased to 410-608°C, (ii) the oven temperature was more accurately controlled (oven B was used for all runs), (iii) a given reaction mixture was periodically sampled until no further change in composition occurred, (iv) a total product analysis was done on each equilibrium mixture so that each K is based on measured values of all four components. This last modification is essential since above 540°C, traces of SiF₄ were formed; (v) enthalpies of reaction are calculated by a better method.

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TABLE 1.—EQUILIBRIUM CONSTANTS FOR Br2+CF3H≓HBr+CF3Br (1)

FORWARD REACTION

town SV	*ima	$[Br_2]_0$	[CF3H]0	[Br ₂]e	[CF3H]e	[HBr]e	[CF3Br]e	¥.,
temp. K	thie min	1	mm		μ mole			M 1
715·6	1170	44.8	69.7	19.4	109	167	161	12.6
825·0	135	45.2	60.0	20.8	46.3	87.7	86.5	7.87
826.3	245	46.1	54.1	19-1	31.3	72.6	72.5	8.79
855-2	120	45 ·8	63.1	25.1	31.5	82.1	72.8	7.54
875.1	160	45·2	56.3	31.9	19.5	73·9	56.6	6.72
881·0	120	48.6	50.0	28.2	19.5	67.4	58.9	7.22

BACK REACTION

4	•:	[HBr]₀	[CF ₃ Br] ₀	[Br ₂]e	[CF3H]e	[HBr]e	[CF3Br]e	F .
temp. K	time min	r	nm		μ mole			v 1
683·7	1560	50.8	59.7	40.9	50 ·1	162	187	16.5
715.7	1240	50.0	49.6	38.8	43.2	163	151	14.7
787·9	160	50·2	59.3	30.8	28.8	84.8	105	10 ∙0
825.5	125	52.1	53.6	29.0	24.4	80.0	83.1	9.41
827.4	130	48·9	54.6	30.0	26.3	78 .0	87.7	8.66
8 5 4·6	135	62.6	46.4	33.2	23.6	96·4	63.7	7.84
873·0	130	49 ·7	56 ·6	33.2	19.7	65.7	74·2	7.46

 $[]_0 = initial pressure at temperature of run.$ $[]_e = \mu mole of each product in a sample of equilibrium mixture.$

Table 2.—Third-law calculation of ΔH_1° at 298°K for $Br_2+CF_3H\rightleftharpoons HBr+CF_3Br_2$

FORWARD REACTION

BACK REACTION

т°К	log Kr	Δ(F.E.F.)	$-\Delta H_{298}^{\circ}$	Т°К	$\log K_T$	-Δ(F.E.F.)	- Δ <i>H</i> ² ₂₉₈
*701.4	1.139	1.407	4.64	683.7	1.218	1.463	4.81
715.6	1.099	1.379	4.79	*698.6	1.150	1.413	4.66
*742.5	1.065	1.329	4.60	715.7	1.168	1.379	4.81
*742.6	1.059	1.329	4.58	*734.9	1.101	1.342	4.69
*745.0	1.057	1.326	4.59	*751.7	1.100	1.312	4.77
*792.0	0.966	1.243	4.49	*763.2	1.063	1.294	4.70
*793.0	0.968	1.242	4.50	*763.8	1.072	1.292	4.73
825.0	0.896	1.189	4.36	787.9	1.002	1.250	4.60
826.3	0.944	1.184	4.55	*791.5	1.011	1.244	4.65
855.2	0.877	1.143	4.41	*791.7	1.007	1.244	4.63
875.1	0.827	1.114	4.29	825.5	0.974	1.188	4.67
881·0	0.859	1.106	4.44	827.4	0.938	1.185	4.53
				854.6	0.894	1.144	4.47
				873.0	0.873	1.118	4.46

average $\Delta H_{298}^{\circ} = -4.53 \pm 0.13$ kcal mole⁻¹ (forward reaction) = -4.65 ± 0.11 kcal mole⁻¹ (back reaction) $= -4.59 \pm 0.14$ kcal mole⁻¹ (all results)

* results of Corbett, Tarr and Whittle, ref. (4), Pyrex vessel.

F.E.F. = free-energy function.

Published on 01 January 1967. Downloaded by University of Chicago on 30/10/2014 08:15:40.

The new experimental results are given in table 1, K_1 being calculated from the expression $K_1 = [HBr][CF_3Br]/[Br_2][CF_3H]$. Using the data in table 2, we obtain the plot of log K_1 against 1/T shown in fig. 2 which also includes data from CTW. There is good agreement between results from the two studies and from forward and back reactions at any given temperature. Assuming that

$$\log K_1 = \Delta S_1^{\circ} / 2.303 R - \Delta H_1^{\circ} / 2.303 RT,$$
(4)

a least-squares treatment of our new results plus those of CTW gives, $\Delta H_1^\circ = -4.88 \pm 0.15$ kcal mole⁻¹ and $\Delta S_1^\circ = -1.64 \pm 0.20$ cal deg.⁻¹ mole⁻¹ at an average temperature of 509°C. Error limits given are statistical $(\pm \sigma)$ and do not indicate the true accuracy



FIG. 2.—Variation of Equilibrium Constant K_1 with temperature. Forward reaction, \bigcirc , this work; \bigcirc , ref. (4); back reaction, \square , this work; \blacksquare , ref. (4).

of the results since in eqn. (4) we neglect the temperature variation of ΔS_1° and ΔH_1° . The data in table 1 are better subjected to a third-law treatment⁷ hence we have calculated the enthalpy change at 298°K for reaction (1) using the equation,

$$\Delta H_{298}^{\circ} = T \left[\frac{\Delta G_T^{\circ}}{T} - \Delta \left(\frac{G_T^{\circ} - H_{298}^{\circ}}{T} \right) \right].$$
⁽⁵⁾

The first term on the right-hand side was evaluated using $\Delta G_T^{\circ} = -RT \ln K_1$ while the free-energy functions needed to evaluate the second term were obtained as follows: Br₂,⁸ HBr,⁹ CF₃H,¹⁰ CF₃Br.¹⁰ Values of ΔH_1° at 298°K are listed in table 2. The third-law procedure was not used by CTW, consequently we have applied eqn. (5) to their data and the results are included in table 2. The values of $\Delta H_{1,298}^{\circ}$ do not depend on whether they originate from forward or back reactions or from CTW or the present work. The final third-law result from all runs is,

 $\Delta H_1^\circ = -4.59 \pm 0.14$ kcal mole⁻¹ at 298°K.

The values of ΔH_1° at 298°K in table 2 should be independent of the temperature at which K is measured. Actually they decrease by ~0.3 kcal mole⁻¹ as the temperature increases from 684° to 881°K. In view of this change, which is slightly larger than

experimental error, it is probably more realistic to write $\Delta H_1^{\circ} = -4.59 \pm 0.25$ kcal mole⁻¹.

A comparison of results from the "graphical method" using eqn. (4) and the thirdlaw method using eqn. (5) reveals a discrepancy. Thus, from eqn. (4), $\Delta H_1^\circ = -4.88 \pm 0.15$ kcal mole⁻¹ at the average temperature of 782°K which becomes $\Delta H_1^\circ = -5.93$ kcal mole⁻¹ after correction to 298°K using heat capacity data; ⁸⁻¹⁰ the corresponding third-law figure at 298°K is -4.59 kcal mole⁻¹. The discrepancy of 1.3 kcal mole⁻¹ indicates the error introduced by using the less reliable graphical method.

EQUILIBRIA
$$Br_2 + C_2F_5H \rightleftharpoons HBr + C_2F_5Br$$
 (2)

$$Br_2 + n \cdot C_3 F_7 H \rightleftharpoons HBr + n \cdot C_3 F_7 Br$$
(3)

Equilibrium (2) was studied over the range 359-569°C. Equilibrium constants were calculated from total product analyses which confirmed that eqn. (2) is obeyed to



FIG. 3.—Variation of Equilibrium Constants K_2 and K_3 with temperature. Curve A, $K = K_2$; curve B, $K = K_3$. O, forward reaction; \bullet , back reaction.

within 5 % or better. For equilibrium (3), the range was $340-528^{\circ}C$ and K_3 was calculated from product analyses using the assumptions given in the experimental section. The materials balance was good, e.g., the total bromine in all products at equilibrium equalled within 2 % the bromine content of the reactants. Values of K_2 and K_3 are given in tables 3 and 4 respectively and plots of log K_2 and log K_3 against 1/T are shown in fig. 3. For either equilibrium, the results from forward and back reactions are randomly distributed about the lines in fig. 3; this is strong evidence that true values of K_2 and K_3 have been obtained.

Above 516°C, the products of equilibrium (2) included traces of CF₃H and CF₃Br (always <0.5 %). These do not interfere with the determination of K_2 and they are probably formed as follows. The reaction between Br₂ and C₂F₅H is initiated by the step.

$$Br + C_2F_5H \rightarrow HBr + C_2F_5$$
,

TABLE 3.—Equilibrium constants for $Br_2+C_2F_5H \rightleftharpoons HBr+C_2F_5Br$

(2)

			FORWAR	D REACT	TION			
temp. °K	time min	[Br ₂] ₀	[C ₂ F ₅ H] ₀	[Br ₂]e	[C ₂ F ₅ H].	[HBr]e	[C ₂ F ₅ Br]e	K ₂
631.8	2700	44·9	53.5	10.7	44·3	158	171	57·0
654·3	1140	44 ·8	50 ·2	18.6	36.6	184	177	47.7
672·1	1320	52·2	54.5	23.9	28.4	175	160	41·2
706.9	210	48 ·3	49.9	27·9	26.8	163	149	32.6
* 713⋅8	200	45.5	51.8	24.5	71.1	237	218	29.6
741.5	120	45.6	54.4	18.3	51.8	159	153	25.7
*785-9	135	44.9	49 ·1	22.6	39.7	152	136	23.1
799 .6	50	45 ∙0	59.9	11.5	30.0	95.2	92.8	2 0·0
841.6	30	44·7	55.7	15.5	30-9	90 ∙6	81.8	15.5
			BACK	REACTIO	N			
temp. °K	time min	[HBr] ₀	[C ₂ F ₅ Br] ₀	[Br2]e	[C ₂ F ₅ H].	[HBr].	[C ₂ F ₅ Br].	K ₂
631.9	3990	54.7	44.0	45.4	44·5	269	228	49 ·8
654.5	1140	60.7	44.3	30.2	32.0	257	169	44.9
672.2	2760	51.8	48.6	35.1	29.6	224	181	39.0
706.8	1440	50.0	46.3	28.1	27.0	166	146	32.1
* 721·7	180	53.5	48 ∙0	45 ·4	44·5	269	228	30.3
741·6	110	49 ·1	42·9	28.0	28.5	162	132	27.0
*789.1	100	51.6	44·2	42.4	41 .6	233	172	22.7
799 ·5	50	53.5	49 ·8	21.4	21.0	107	96.3	22.8

* Pyrex reaction vessel: all other runs in quartz.

FORWARD REACTION

22.4

19.7

94·2

78.5

TABLE 4.—EQUILIBRIUM CONSTANTS FOR $Br_2+n-C_3F_7H \rightleftharpoons HBr+n-C_3F_7Br$

49.3

(3)

16.8

temn °V	time min	[Br ₂] ₀	[C3F7H]0	[Br ₂].	[C3F7H].	[HBr].	[C ₃ F ₇ Br].	к.
temp. K	time mm	1	nm		μπ	nole		A 3
613.9	2730	50 ·8	58.6	15.1	55-3	187	187	41·8
648·1	2700	50.6	52·2	34.4	40.8	204	204	29.5
*648.3	1020	44·1	70 ·8	5.8	_	112		30.6
670·6	1080	48.8	53.7	31.0	49.3	190	190	24.2
689·8	255	51·2	49 ·1	45 ∙0	33-1	172	172	20.2
753.7	100	50.7	51.4	45.8	34.9	155	155	15.0
780 ·8	20	50 ·1	53.6	39.8	43.6	152	152	12.6
801·2	10	51·0	42·3	46.7	30.6	128	128	11.5
			BACK	REACTIC	N			
temp °K	time min	[HBr]0	[C ₃ F ₇ Br] ₀	[Br2]e	[C3F7H].	[HBr]e	[C3F7Br].	к.
temp. K	une ma	t	mm		μ mole			
614·2	4280	51.3	51.2	35.0	35·0	217	217	38.6
648·2	1380	45.6	55.7	34.9	34.9	176	202	29.9
670·2	315	50.7	54.0	37.3	37.3	193	186	25.9
689.7	270	51.0	53.0	30.5	39.5	180	180	20.7

* in these two experiments, the ratio $[C_3F_7H]_e/[C_3F_7Br]_e$ was measured but not the absolute amounts of each.

42.6

37.6

39.8

42.5

42.3

42.6

37.6

39.8

42.5

166

148

147

154

140

168

139

154

155

.....

15.4

14.5

14.3

13.3

12.2

56.7

50.7

52.7

51.5

50·9

841.8

725.5

753.9

778.7

776.1

*801.2

45

180

80

20

25

20

54·0

50.9

51·2

50.4

49.5

54·3

and at sufficiently high temperatures, there will be some cracking of the C_2F_5 radical, e.g.,

$$C_2F_5 \rightarrow CF_3 + CF_2$$
.

The CF₃ radicals so formed give rise to a mixture of CF₃H and CF₃Br, as observed, whereas CF₂ can give CF₂Br₂ and other products; the products from CF₂ were not detected but could have been present.

In the study of equilibrium (3), if a mixture of reactants was left at 500°C for a period much longer than that needed to reach equilibrium, the following products were formed in addition to those expected from reaction (3): CF_3Br , CF_3H , C_2F_5Br , C_2F_5H and CF_2BrCF_2Br (but no SiF₄). These extra products were formed in negligible amounts in the runs given in table 4. The presence of all the products can be explained by the following mechanism :

$$Br + CF_3CF_2CF_2H \rightarrow HBr + CF_3CF_2CF_2$$
(6)

$$CF_3CF_2CF_2 + Br_2 \rightarrow CF_3CF_2CF_2Br + Br$$
(7)

$$CF_3CF_2CF_2 + HBr \rightarrow CF_3CF_2CF_2H + Br$$
(8)

$${}_{\mathcal{A}} CF_3 + CF_2 = CF_2$$
 (9)

$$CF_3CF_2CF_2$$
 (10)

$$CF_3CF_2 \rightarrow CF_3 + CF_2. \tag{11}$$

Reactions (9)-(11) give either radicals or $CF_2 = CF_2$ each of which can react with either Br_2 or HBr to give all the observed products plus others which were not detected.

From a least squares treatment of the data in fig. 3 and tables 3 and 4, we obtain

$$\log K_2 = -(1.19 \pm 0.19)/2.303R + (5,760 \pm 140)/2.303RT,$$
(12)

$$\log K_3 = -(3.02 \pm 0.18)/2.303R + (6.310 \pm 1.30)/2.303RT,$$
(13)

so that, by analogy with eqn. (4),

$$\Delta H_2^\circ = -5.76 \pm 0.14 \text{ kcal mole}^{-1}; \qquad \Delta S_2^\circ = -1.19 \pm 0.19 \text{ cal deg.}^{-1} \text{ mole}^{-1}; \\ \Delta H_3^\circ = -6.31 \pm 0.13 \text{ kcal mole}^{-1}; \qquad \Delta S_3^\circ = -3.02 \pm 0.18 \text{ cal deg.}^{-1} \text{ mole}^{-1},$$

at mean temperatures of 746 and 707°K for equilibria (2) and (3) respectively. We showed that for equilibrium (1), there was a discrepancy of 1.3 kcal mole⁻¹ between ΔH_1° (graph) and ΔH_1° (third-law), both at 298°K. The third-law method is more reliable but we cannot use it for equilibria (2) and (3) as free-energy functions are not available for C₂F₅H, C₂F₅Br, C₃F₇H and C₃F₇Br. It is desirable to improve on the results of the graphical method and in principle the necessary thermodynamic data, i.e., ΔS , ΔH , ΔC_p , $\partial \Delta C_p/\partial T$, etc., can be extracted directly from the data in tables 3 and 4 by using the procedure of Clarke and Glew.¹¹ However, it is doubtful if our results are accurate enough for their treatment. In view of this, we have used semi-empirical procedures which we believe give better results than the graphical method although not as good as those based on the third law.

First, we have used the additivity rules for calculating ΔS and ΔC_p proposed by Benson and Buss ¹² and applied by Benson ¹³ to the analogue of equilibrium (1) involving CHCl₃. The Benson method (B.M.) assumes that the entropy of a given molecule is a sum of contributions each of which is characteristic of a given bond, e.g.,

$$S^{\circ}(C_2F_5H) = 5S^{\circ}_{C-F} + S^{\circ}_{C-C} + S^{\circ}_{C-H} - R \ln \sigma,$$

where the last term is a symmetry contribution. The bond entropies are calculated

using suitable reference molecules. It follows from the method that in an equilibrium such as (2), the C—F and C—C contributions cancel, so that

$$\Delta S_2^\circ = S_{C-Br}^\circ - S_{C-H}^\circ + S_{HBr}^\circ - S_{Br_2}^\circ.$$
⁽¹⁴⁾

In a similar way, ΔC_p can be calculated for any given reaction.

The B.M. was tested by applying eqn. (14) to equilibrium (1) for which accurate entropies exist. At 500°C, the Benson terms S_{C-Br}° and S_{C-H}° have values of 26.01 and 12.67 cal deg.⁻¹ mole⁻¹ respectively hence, using literature values ⁸, ⁹ of $S_{Br_2}^{\circ}$ and S_{HBr}° , we have $\Delta S_1^{\circ} = 0.43$ cal deg.⁻¹ mole⁻¹. For comparison, using known entropies ¹⁰ of CF₃H and CF₃Br, we have $\Delta S_1^{\circ} = 0.06$ cal deg.⁻¹ mole⁻¹ at 500°C. As a further test, eqn. (14) was used to calculate ΔS_1° at the appropriate temperature for every run on equilibrium (1) including those of CTW. Substituting each ΔS_1° and K_1 (observed) into eqn. (4) then gives a ΔH_1° at that temperature which was corrected to 298°K using ΔC_p calculated by the B.M. The final mean value was $\Delta H_{1,298^{\circ}K}^{\circ} =$ -4.38 ± 0.60 kcal mole⁻¹ (error limits are estimated) which agrees well with the thirdlaw result of -4.59 kcal mole⁻¹ and is an improvement on the graphical figure of -5.93 kcal mole⁻¹.

In view of this, the B.M. was applied to equilibria (2) and (3) and the results are given in table 5. We also include in the table, ΔH_2° and ΔH_3° at 298°K from the graphical method (G.M.). These are derived by correcting the results in eqn. (12) and (13) to 298°K using ΔC_p estimated by the B.M. The corrections are insensitive to the values of ΔC_p used.

FABLE	5.—Comparison	OF	ΔH_{298}° obtained	BY	DIFFERENT	METHODS
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	$-\Delta H_{298}^{\circ}$, kcal mole ⁻¹					
reaction		graph	Benson method	estimated	recommended	
$Br_2 + CF_3H \rightleftharpoons HBr + CF_3Br$	(1)	5·93 ±0·21	4·4 ±0·6	(4.59)	$4{\cdot}59\pm\!0{\cdot}25$	
$Br_2 + C_2F_5H \rightleftharpoons HBr + C_2F_5Br$	(2)	$6{\cdot}35\pm\!0{\cdot}14$	5.2 ± 0.7	5.0	5.1 ± 1.0	
$Br_2+n-C_3F_7H \rightleftharpoons HBr+n-C_3F_7Br$	(3)	6.87 ± 0.13	4·5 ±0·7	5.5	5·0 ±1·0	

Values of ΔH_1° in last 2 columns are from third-law calculation. Values of ΔH_2° and ΔH_3° in next to last column calculated using $\Delta H_1^{\circ} = -4.59$ as a reference.

The B.M. is not expected to work as well for equilibria (2) and (3) as it does for (1). For all three equilibria, we must calculate S_{C-H}° and S_{C-Br}° from $S_{CH_4}^{\circ}$ and $S_{CBr_4}^{\circ}$ so that errors may be introduced by neglect of restricted rotation in the substituted ethanes and propanes. Comparison of results of the B.M. and G.M. in table 5 shows that the progressive change in ΔH° (G.M.) from CF₃H to C₃F₇H no longer occurs with results from the B.M. It is probable that the G.M. gives fairly reliable *differences* in ΔH° , e.g., $\Delta H_1^{\circ} - \Delta H_2^{\circ}$, even if the *absolute* values of ΔH° are not correct, consequently we can take ΔH_1° (G.M.) $- \Delta H_2^{\circ}$ (G.M.) and ΔH_1° (G.M.) $- \Delta H_3^{\circ}$ (G.M.) and combine these differences with the reliable third-law result for ΔH_1° to give the "estimated" ΔH in column 3 of table 5.

The B.M. apparently gives a poor result for ΔH_3° at 298°K probably because of the assumption that $\Delta S_1^\circ = \Delta S_2^\circ = \Delta S_3^\circ$ at any given temperature. We find experimentally that $K_2 = 34.5$ and $K_3 = 20.4$ at 700°K and, if ΔS_2° were equal to ΔS_3° , the difference in K would correspond to ΔH_2° more negative than ΔH_3° by 0.7 kcal mole⁻¹; in fact, using the G.M., ΔH_2° is *less* negative than ΔH_3° by 0.5 kcal mole⁻¹. We therefore believe that much of the difference between K_2 and K_3 arises from a difference in ΔS_2° and ΔS_3° which cannot be accurately calculated at present.

In the last column of table 5 are given recommended figures for ΔH_2° and ΔH_3° which are a compromise between those from the B.M. and those which are "estimated", column 3. Calculation of more accurate values of ΔH_2° and ΔH_3° must await the determination of the necessary free energy functions.

DISCUSSION

BOND DISSOCIATION ENERGIES AND ENTHALPIES OF FORMATION

We consider first reaction (1) for which,

$$\Delta H_{298}^{\circ} = D(Br - Br) + D(CF_3 - H) - D(H - Br) - D(CF_3 - Br)$$
(15)

$$= \Delta H_{f}^{\circ}(\mathrm{HBr}) + \Delta H_{f}^{\circ}(\mathrm{CF}_{3}\mathrm{Br}) - \Delta H_{f}^{\circ}(\mathrm{Br}_{2}) - \Delta H_{f}^{\circ}(\mathrm{HBr})$$
(16)

(unless otherwise stated, all bond dissociation energies and enthalpies of formation refer to gases at 298°K). From standard tables,¹⁴ D(Br-Br) = 46.09, D(H-Br) = 87.54, $\Delta H_f^{\circ}(Br_2,g) = 7.39$ and $\Delta H_f^{\circ}(HBr) = 8.70$ kcal mole⁻¹. Combining these figures with our third-law result of $\Delta H_1^{\circ} = -4.59$ kcal mole⁻¹ leads to,

$$D(CF_3 - Br) = D(CF_3 - H) - 36.86 \pm 0.30 \text{ kcal mole}^{-1},$$
(17)

$$\Delta H_{f}^{\circ}(\mathrm{CF}_{3}\mathrm{Br}) = \Delta H_{f}^{\circ}(\mathrm{CF}_{3}\mathrm{H}) + 11.5 \pm 0.30 \text{ kcal mole}^{-1}.$$
 (18)

With ¹ $D(CF_3-H) = 106.3 \pm 0.5$ kcal mole⁻¹, we have

$$D(CF_3-Br) = 69.4 \pm 0.8 \text{ kcal mole}^{-1}$$
.

The only direct determination of $D(CF_3$ —Br) is that of Sehon and Szwarc ¹⁵ using a pyrolysis method which gave $D(CF_3$ —Br) = 64.5 kcal mole⁻¹. However, the kinetics were not entirely satisfactory possibly because of the following difficulty. The authors pyrolyzed CF₃Br with excess toluene and assumed that the CF₃ and Br produced were converted to CF₃H and HBr respectively by reaction with toluene; the benzyl radicals so produced should then give dibenzyl and the overall reaction should be

$$CF_{3}Br + 2C_{6}H_{5}CH_{3} \rightarrow CF_{3}H + HBr + (C_{6}H_{5}CH_{2})_{2}.$$
 (19)

However, large conversions of CF₃Br were used, e.g., 12 % at 1021°K and 64 % at 1090°K and we now see from our present work that equilibrium (1) could have been set up. If so, the Br₂ formed would at once react with toluene so that in effect there is an alternative overall reaction to (19), i.e.,

$$CF_3Br + C_6H_5CH_3 \rightarrow CF_3H + C_6H_5CH_2Br.$$
(20)

The rate of decomposition of CF_3Br was calculated from the HBr produced hence the rate constant could be in error if there were any appreciable contribution from reaction (20); in that case, Br atoms produced from CF_3Br could end up as benzyl bromide rather than HBr. This could explain why the observed rate constants were not independent of the pressure of toluene.

An independent estimate of $D(CF_3$ —Br) comes from the activation energies of the reactions,

$$CH_3 + CF_3Br \rightleftharpoons CH_3Br + CF_3. \qquad (21, -21)$$

Tompkinson and Pritchard ¹⁶ obtained $E_{21} = 12.5 \pm 1.0$ and Alcock and Whittle ¹⁷ btained $E_{-21} = 8.3 \pm 0.6$ kcal mole⁻¹ so that $\Delta H_{21}^{\circ} = 12.5 - 8.3 = 4.2$ kcal mole⁻¹ and

$$D(CF_3 - Br) = D(CH_3 - Br) + 4.2 \text{ kcal mole}^{-1}$$

Taking $D(CH_3-Br) = 69.5$ (see later) gives $D(CF_3-Br) = 73.7$ kcal mole⁻¹. This is unexpectedly high and Pritchard *et al.*¹⁸ suggest that there may be an anomaly in

the determination of E_{21} and similar activation energies. However, this result does indicate a higher value of $D(CF_3-Br)$ than that obtained by Sehon and Szwarc.

The enthalpy of formation of CF₃Br has not been measured but may be calculated from eqn. (18). Neugebauer and Margrave ¹⁹ give $\Delta H_f^{\circ}(CF_3H) = -162\cdot60\pm0\cdot65$, so that $\Delta H_f^{\circ}(CF_3Br) = -151\cdot1\pm0.8$ kcal mole⁻¹. However, if Cox and Harrop's ³ revised $\Delta H_f^{\circ}(CF_3Br) = -156\cdot4$ kcal mole⁻¹ (the relation in eqn. (18) is independent of this correction).

Equations analogous to (15) and (16) can be derived for reactions (2) and (3) and, using the recommended values of ΔH_{298}° in table 5, we have :

$$D(C_2F_5-Br) = D(C_2F_5-H) - 36.4 \pm 1.0, \qquad (22)$$

$$D(CF_{3}CF_{2}CF_{2}-Br) = D(CF_{3}CF_{2}CF_{2}-H) - 36.5 \pm 1.0,$$
(23)

$$\Delta H_f^{\circ}(C_2F_5Br) = \Delta H_f^{\circ}(C_2F_5H) + 11.0 \pm 1.0, \qquad (24)$$

$$\Delta H_f^{\circ}(\mathbf{n}-\mathbf{C}_3\mathbf{F}_7\mathbf{B}\mathbf{r}) = \Delta H_f^{\circ}(\mathbf{n}-\mathbf{C}_3\mathbf{F}_7\mathbf{H}) + 11\cdot\mathbf{1}\pm\mathbf{1}\cdot\mathbf{0},\tag{25}$$

all in kcal mole⁻¹. None of the ΔH_f° in eqn. (24) and (25) is known.

Values of $D(C_2F_5-H)$ and $D(n-C_3F_7-H)$ can be estimated in two ways. Pritchard and Thommarson ²² used activation energies of the reactions

$$C_2F_5 + CH_4 \rightleftharpoons C_2F_5H + CH_3$$

$$n-C_3F_7+CH_4 \rightleftharpoons n-C_3F_7H+CH_3$$

to obtain

$$D(C_2F_5-H) = D(CD_3-H) - (1.1 \pm 1.7),$$

 $D(n-C_3F_7-H) = D(CD_3-H) - (0.4 \pm 2.2)$ kcal mole⁻¹.

Using ²³
$$D(CH_3 - H) = 103.8$$
 kcal mole⁻¹ and assuming $D(CD_3 - H) = D(CH_3 - H)$, we have

 $D(C_2F_5-H) = 102.7 \pm 2.0$ and $D(n-C_3F_7-H) = 103.4 \pm 2.5$ kcal mole⁻¹.

These figures are slightly greater than those in ref. (22) because a more recent $D(CH_3-H)$ has been used.

The photobromination of C_2F_5H and $n-C_3F_7H$ was studied by Coomber and Whittle ⁶ who obtained activation energies for

$$Br + C_2F_5H \rightarrow HBr + C_2F_5 \tag{26}$$

$$Br+n-C_{3}F_{7}H \rightarrow HBr+n-C_{3}F_{7}; \qquad (27)$$

subsequently their results were slightly amended.¹ Since E_{-26} and E_{-27} are not known, the values of E_{26} and E_{27} yield only upper limits of D(C-H). Taking $E_{26} = 18.9$ and $E_{27} = 18.7$ together with D(H-Br) = 88.0 at 200°C, we have $D(C_2F_5-H) = 106.9 - E_{-26}$ and $D(n-C_3F_7-H) = 106.7 - E_{-27}$ kcal mole⁻¹. Probably, E_{-26} and E_{-27} are both ≥ 3 kcal mole⁻¹ hence the final result that $D(C_2F_5-H) = D(n-C_3F_7-H) = 103.5$ kcal mole⁻¹ seems a resonable compromise based on our work and that of Pritchard and Thommarson. The error limits are $\sim \pm 2$ kcal mole⁻¹. On introduction of these figures into eqn. (22) and (23),

$$D(C_2F_5-Br) = D(n-C_3F_7-Br) = 67.0\pm 2.5$$
 kcal mole⁻¹.

These results are compared with other related bond dissociation energies in table 6; D(R-H) increases when a given alkyl group is fully fluorinated whereas D(R-Br) is unchanged, within experimental error.

* The JANAF tables 20 give $\Delta H_{f}^{\circ}(CF_{3}H) = -165 \cdot 1 \pm 1.6$ kcal mole⁻¹ which is based on a value of $\Delta H_{f}^{\circ}(HF, aq)$ intermediate between the "old " value 21 and that of Cox and Harrop.

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TABLE 6.—SOME BOND DISSOCIATION ENERGIES

R	D(RH)	D(R-Br)	R	D(R—H)	D(R-Br)
CH ₃	103.8	69.5	CF ₃	1 06·3	6 9 •4
C_2H_5	98·3	67.7	C_2F_5	103·5	67
$n-C_3H_7$	98.9	68-5	$n-C_3F_7$	103.5	67

 $D(CH_3-H)$, $D(C_2H_5-H)$ and $D(n-C_3H_7-H)$ from ref. (23). $D(CH_3-Br)$, $D(C_2H_5-H)$ Br) and $D(n-C_3H_7-Br)$ are calculated from corresponding D(R-H) together with $\Delta H^{\circ}_{,(RH)}$ from ref. (24) and $\Delta H_f^{\circ}(\text{RBr})$ as follows: $\Delta H_f^{\circ}(\text{CH}_3\text{Br}, g) = -9.0$;^{25, 26} $\Delta H_f^{\circ}(\text{C}_2\text{H}_5\text{Br}, g) =$ -15.0; this is a weighted mean of -14.79 ²⁵ and -15.6; ²⁷ $\Delta H_{f}^{\circ}(n-C_{3}H_{7}Br) = -19.82$, ²⁸ all in kcal mole⁻¹; other data from ref. (14).

We thank Prof. H. O. Pritchard for showing us results before publication and the S.R.C. for a grant to J. W. C.

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