# Bond Dissociation Energies from Equilibrium Studies

Part 2.— $D(CF_3$ — $CF_3)$  and Enthalpy of Formation of  $C_2F_6$ 

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Reveived 11th January, 1967

Equilibrium constants have been measured for the system

 $C_2F_6+Br_2 \rightleftharpoons 2CF_3Br$ 

over the range 621-722°C. Equilibrium was approached from both sides. Using a third-law method  $\Delta H_2^\circ = 3.66 \pm 0.14$  kcal mole<sup>-1</sup> at 298°K. This is combined with results from our previous work to give  $D(CF_3 - CF_3) = 96.5 \pm 1.0$  kcal mole<sup>-1</sup>. We also obtain

$$\Delta H_f^{\circ}(C_2F_6) - 2 \ \Delta H_f^{\circ}(CF_3H) = 12.0 \pm 0.6 \text{ kcal mole}^{-1}$$
(10)

(2)

(1)

and the relevance of this result to published enthalpies of formation of  $C_2F_6$ ,  $CF_3H$  and HF,aq. is discussed. There are now six determinations of  $\Delta H_f^{\circ}(HF,aq.)$  which indicate that the value in N.B.S. circ. 500 needs revision. A revised value is proposed and is used to obtain  $\Delta H_f^{\circ}(CF_3H)$ . When the latter figure is combined with  $\Delta H_f^{\circ}(C_2F_6)$ , the result is in excellent agreement with that in eqn. (10). Our value of  $D(CF_3-H)$  is combined with enthalpies of formation to give  $\Delta H_f^{\circ}(CF_3)$  $= -112.6 \pm 1.2$ ,  $D(CF_3-F) = 129.3 \pm 2.0$  and  $D(CF_3-CH_3) = 99.7 \pm 2.0$  kcal mole<sup>-1</sup>.

In part 1,<sup>1</sup> we reported on the thermodynamics of the gas-phase equilibrium  $Br_2 + CF_3H \rightleftharpoons HBr + CF_3Br.$ 

The measured enthalpy of reaction was combined with the bond dissocation energy  $D(CF_3 - H)$  to yield a value of  $D(CF_3 - Br)$ . These studies have been extended to include the equilibrium

$$Br_2 + C_2 F_6 \rightleftharpoons 2CF_3 Br. \tag{2}$$

From the measured  $\Delta H_2^\circ$  and our previous results, we obtain a value for the bond dissociation energy  $D(CF_3 - CF_3)$ .

### EXPERIMENTAL

#### MATERIALS

 $C_2F_6$  from Peninsular ChemResearch, Florida, was de-gassed, passed twice through Carbosorb and given two bulb-to-bulb distillations. Other materials were as before.<sup>1</sup> No impurities could be detected by i.-r. or gas-solid chromatography (G.S.C.) in any of the reactants.

#### APPARATUS AND PROCEDURE

This was essentially as in part 1; however, one oven only was used, the temperature of of which was controlled to better than  $\pm 0.2^{\circ}$ C using a Sirect regulator. In each run, the silica reaction vessel was filled with a reactant mixture at a suitable temperature and samples were removed periodically for analysis; about 7 % of the contents were removed each time (this includes purging of dead space). Each sample was analyzed by G.S.C. using a 1.2 m column of alumina preceded by 11 cm of Carbosorb to remove Br<sub>2</sub>. When the ratio [CF<sub>3</sub>Br]/[C<sub>2</sub>F<sub>6</sub>] became constant, it was presumed that equilibrium had been reached and the

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limiting value of the ratio gave  $[CF_3Br]_e/[C_2F_6]_e$ . The contents of the reaction vessel were then passed through a liquid-nitrogen trap, the only non-condensible gas being CO which was pumped away. The trap was next warmed to  $-120^{\circ}C$  and a fraction was distilled off which consisted of  $C_2F_6+CF_3Br+SiF_4+CF_4+CO_2$ . This was analyzed for  $C_2F_6$  and  $CF_3Br$  by i.-r. using the 14 and  $13\mu$  peaks respectively. The ratio  $[CF_3Br]_e/[C_2F_6]_e$  so obtained always agreed to better than 2 % with the G.S.C. result. The fraction not volatile at  $-120^{\circ}C$  was entirely  $Br_2$ , the pressure of which was measured in a known volume. The bromine materials balance was always complete within experimental error, i.e., the sum of  $[Br_2]_e + [CF_3Br]_e$  equalled the bromine initially present whether in the form of  $Br_2$  or  $CF_3Br$ or both (after allowing for samples removed before equilibrium was reached).

#### RESULTS

Equilibrium (2) is more difficult to study than equilibrium (1) because of the chemical inertness of  $C_2F_6$ , e.g., there is no measurable reaction between  $Br_2$  and  $C_2F_6$  below 550°C. In the early stages of the work, if the temperature were high enough to make reaction (2) occur at a reasonable rate, then large quantities of other products were formed, notably CO,  $CF_4$ ,  $SiF_4$  and, after long periods,  $CO_2$ . As the work continued, these products became less important and ultimately were less than 25 % of the products of the runs in which  $K_2$  was measured. We assume that the decline was caused by conditioning of the reaction vessel. At all stages, bromine was present only as  $Br_2$  or  $CF_3Br$  and, since the system probably reaches equilibrium via  $CF_3$  radicals, we may write the following overall reaction for the production of the main spurious products,

$$SiO_2 + 4CF_3 \rightarrow SiF_4 + 2CO + 2CF_4.$$
(3)

Fortunately these products neither interfere with the analysis for  $Br_2$ ,  $C_2F_6$  and  $CF_3Br$  nor affect our determination of  $K_2$  provided that reaction (2) or its reverse has reached true equilibrium.

The equilibrium was studied over the range 621-722°C. At 621°C, equilibrium was reached after ~33 days for a forward reaction, hence experiments at lower temperatures were impracticable. At 722°C, equilibrium was attained in ~5 h. Above 722°C, reaction (3) was so fast that reaction (2) never reached equilibrium. Equilibrium constants were calculated from  $K_2 = [CF_3Br]^2/[Br_2][C_2F_6]$ . Each concentration was measured in any given mixture at equilibrium i.e., the initial concentrations of reactants were not utilized and the stoichiometry of eqn. (2) was not assumed. At any given temperature, equilibrium was approached from either side and the values of  $K_2$  obtained from both forward and back reactions are given in table 1.  $K_2$  is practically independent of whether equilibrium is approached from left or right. Since the reactions are slow, particularly at lower temperatures, time was saved by making up reactant mixtures which were about half-way to equilibrium, i.e., for a forward reaction some  $CF_3Br$  was added to the  $Br_2 + C_2F_6$  and vice versa for a back reaction.

A plot of log  $K_2$  against 1/T gives a line with no apparent curvature. Assuming that

$$\log K_2 = \Delta S_2^{\circ}/2.303 \mathbf{R} - \Delta H_2^{\circ}/2.303 \mathbf{R}T,$$

we obtain by least squares

$$\Delta S_2^{\circ} = 5.85 \pm 0.70$$
 cal deg. <sup>-1</sup> mole <sup>-1</sup>;  $\Delta H_2^{\circ} = 5.14 \pm 0.66$  kcal mole <sup>-1</sup>;

at a mean temperature of 944°K (error limits are  $\pm \sigma$  unless otherwise stated). On correction to 298°K, using published data on heat capacities,<sup>2-4</sup>  $\Delta H_{2,298^{\circ}K}^{\circ} = 4.62 \pm 0.66$  kcal mole<sup>-1</sup>. However, the results in table 1 are better subjected to a third-law

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treatment since  $\Delta S_2^\circ$  and  $\Delta H_2^\circ$  vary with temperature. Hence we have calculated  $\Delta H_2^{\circ}$  at 298°K from each value of  $K_2$  using the eqn.,

$$\Delta H_{298}^{\circ} = -RT \ln K_2 + T\Delta [-(G_T^{\circ} - H_{298}^{\circ})/T].$$

The appropriate free-energy functions are from the following sources :  $C_2F_6$ , Carney et al.<sup>2</sup>; CF<sub>3</sub>Br, Gelles and Pitzer<sup>3</sup>; Br<sub>2</sub>, Evans et al.<sup>4</sup> The values of  $\Delta H_{298}^{\circ}$  in table 1 are independent of whether they are derived from forward or back reactions and of the temperature of the reaction. Also, there is no significant variation in  $\Delta H_{298}^{\circ}$ if the runs are arranged in chronological order. Hence the final mean value of  $\Delta H_2^\circ = 3.66 \pm 0.14$  kcal mole<sup>-1</sup> at 298°K seems reliable.

		in of	nitial pressu reactants in	res mm	[Br <sub>2</sub> ]•	[C <sub>2</sub> F <sub>6</sub> ]•	[CF3Br].		
°C	time h	Br <sub>2</sub>	$C_2F_6$	CF3Br		µmole		<i>K</i> <sub>2</sub>	∆ <i>H</i> <sup>2</sup> 98
620.8	792f	45.9	53.1	35.9	134	100	123	1.09	3.66
622·3	138 <i>b</i>	24.5	32.2	56.8	78.5	68.6	80.2	1.18	3.53
637.4	307 <i>f</i>	53·2	49.3	23.7	117	61.6	84.6	0.99	3.90
638.6	210b	27.2	28.1	59.6	103	63·2	82.4	1.06	3.79
648.0	120 <i>f</i>	45.1	57.6	29.3	<b>94</b> .8	92.3	95.0	1.03	3.88
647.9	115b	29.3	34.9	60.4	112	84·0	107	1.22	3.57
652·9	89 <i>f</i>	45.7	51.7	28.5	109	85·1	<del>9</del> 9·0	1.06	3.84
652·9	67b	26.9	32.1	62.5	111	87.7	109	1.23	3.58
659.8	91 <i>f</i>	47.1	49.5	22·2	95.4	62.7	84·0	1.14	3.78
659·8	50b	27.3	34.5	68·2	113	93.7	113	1.21	3.62
673-2	46 <i>f</i>	40.6	<b>49</b> ∙0	25.4	106	86.4	106	1.24	3.63
673·2	24b	32.9	34.8	<b>50</b> ·0	96.2	77.5	<b>95</b> .8	1.25	3.61
687.5	46 <i>f</i>	<b>44</b> ·6	55-3	48·9	130	85.8	126	1.43	3.57
687.5	20 <i>b</i>	29·2	38-9	81.5	129	100	122	1.20	3.74
697.9	20 <i>f</i>	45.3	41·9	18.4	104	57.6	88·3	1.32	3.60
<b>698</b> ∙0	16b	29.6	27.9	67.8	124	72.7	106	1.27	3.67
707•3	20f	50.0	<b>48</b> •7	28.7	139	61.4	110	1.43	3.47
707•3	23b	31.0	36.6	71-2	120	<b>5</b> 6·0	101	1.49	3.40
722.0	5f	45.8	54·2	25.0	94.3	60.8	81.5	1.24	3.80
722.0	3 <i>b</i>	28.7	33.2	62.8	98·3	77·8	106	1.47	3.47

TABLE 1.—EQUILIBRIUM CONSTANTS FOR THE REACTION  $Br_2+C_2F_6 \rightleftharpoons 2CF_3Br$ 

(2)

mean  $\Delta H_{298}^{\circ} = 3.66 \pm 0.14$  kcal mole<sup>-1</sup>.

Initial pressures are at temperature of run. [ ]<sub>e</sub> = amounts of products in  $\mu$ mole in a sample of equilibrium mixture. In column 2, f and b indicate forward and back reactions respectively.

The principal systematic, as distinct from random, errors lie in the free-energy functions used and in the measurement of temperature and equilibrium constants. The free-energy functions are quoted to 0.01 cal deg.<sup>-1</sup> mole<sup>-1</sup> but even an error of 0.1 cal deg.<sup>-1</sup> mole<sup>-1</sup> in  $\Delta$ (F.E.F.) causes an error in  $\Delta H^{\circ}_{2,298}$  of only 0.1 kcal mole<sup>-1</sup> The absolute values of the temperatures quoted in table 1 should be accurate to  $\pm 1^{\circ}$ and such an error causes an error in  $\Delta H^{\circ}_{2,298}$  of ~0.1 % at an average temperature of ~900°K; this is negligible. Systematic errors in  $K_2$  should be  $\leq 4$  % which is equivalent to an error in  $\Delta H_{2,298}^{\circ}$  of 0.07 kcal mole<sup>-1</sup> at 900°K. Thus the sum of the obvious systematic errors is about the same as the standard deviation given above.

#### DISCUSSION

### BOND DISSOCIATION ENERGY $D(CF_3-CF_3)$

From this and previous work,<sup>1</sup> we obtain for equilibria (1) and (2),  $\Delta H_1^\circ = -4.59 \pm 0.25$ ,  $\Delta H_2^\circ = 3.66 \pm 0.14$  kcal mole<sup>-1</sup> (unles otherwise stated, all data refer to gases at 298°K). It follows from eqn. (1) and (2) that

$$D(CF_3 - CF_3) = \Delta H_2^\circ + 2D(CF_3 - Br) - D(Br - Br)$$
(4)

$$= \Delta H_2^{\circ} - 2\Delta H_1^{\circ} + D(Br - Br) + 2D(CF_3 - H) - 2D(H - Br).$$
(5)

Taking D(Br-Br) = 46.09, D(H-Br) = 87.54 (calculated from data in ref. (5)), and  $D(CF_3-H) = 106.3 \pm 0.5$  kcal mole<sup>-1</sup>,<sup>6</sup> we have from eqn. (5)

$$D(CF_3 - CF_3) = 96.5 \pm 1.0 \text{ kcal mole}^{-1}$$

The error limits arise mainly from the uncertainty of ~  $\pm 0.5$  kcal mole<sup>-1</sup> in  $D(CF_3 - H)$ .

The magnitude of  $D(CF_3-CF_3)$  was discussed by Tschuikow-Roux<sup>7</sup> who quotes values ranging from 64 to 140 kcal mole<sup>-1</sup>. Some are indirect in that they involve thermochemical calculations which often utilize other dubious bond dissociation energies and enthalpies of formation. However, the present work yields a value of  $D(CF_3-CF_3)$  which is derived from our previous value of  $D(CF_3-H)$  which in turn depends almost entirely on kinetic data. The only bond dissociation energies used in determining  $D(CF_3-H)$  and  $D(CF_3-CF_3)$  are D(Br-Br) and D(H-Br), both of which are accurately known. No enthalpies of formation of fluorine compounds are involved. The only direct determination of  $D(CF_3-CF_3)$  was made by Tschuikow-Roux,<sup>8</sup> (T-R) using a shock tube. For the reactions

$$C_2F_6 \rightleftharpoons 2CF_3$$
 (6, -6)

$$CF_3 + H_2 \rightarrow CF_3H + H$$
 (7)

he obtained  $\frac{1}{2}E_6 + E_7 - \frac{1}{2}E_{-6} = 56 \pm 2 \text{ kcal mole}^{-1}$ . Taking  $E_7 - \frac{1}{2}E_{-6} = 8.8 \text{ from}$ Pritchard *et al.*<sup>9</sup>,  $E_6 = 94.4 \text{ kcal mole}^{-1}$ . Now  $D(CF_3 - CF_3) = E_6 - E_{-6}$  and T-R used  $E_{-6} = 1.2 \text{ kcal mole}^{-1}$  to give a final result of  $D(CF_3 - CF_3) = 93 \pm 4 \text{ kcal mole}^{-1}$ . However, this needs the following modifications. Ayscough and Polanyi <sup>10</sup> also have measured  $E_7 - \frac{1}{2}E_{-6}$ , the result being 9.5 kcal mole<sup>-1</sup>. The value of 8.8 given above has been modified by Pritchard and Foote <sup>11</sup> to 8.6 hence we shall use the mean figure of 9.1 kcal mole<sup>-1</sup>. From this,  $E_6$  becomes 94 kcal mole<sup>-1</sup>. There is good evidence <sup>12</sup> that  $E_{-6} = 0$  so that  $D(CF_3 - CF_3) = 94 \pm 4 \text{ kcal mole}^{-1}$  at a mean temperature of 1450°K or  $96 \pm 4 \text{ kcal mole}^{-1}$  after correction to 298°K using literature data for  $C_2F_6^2$  and  $CF_3$ .<sup>13</sup> Our result agrees well with this revised value of  $D(CF_3 - CF_3)$  from the work of T-R although the error limits of the latter figure are large. We believe that the present work has provided a reliable determination of  $D(CF_3 - CF_3)$  which supersedes previous figures.

ENTHALPIES OF FORMATION OF  $C_2F_6$  and related molecules

For equilibria (1) and (2), we may write,

$$\Delta H_1^\circ = \Delta H_f^\circ(\mathrm{HBr}) + \Delta H_f^\circ(\mathrm{CF}_3\mathrm{Br}) - \Delta H_f^\circ(\mathrm{Br}_{2,g}) - \Delta H_f^\circ(\mathrm{CF}_3\mathrm{H})$$
  
$$\Delta H_2^\circ = 2\Delta H_f^\circ(\mathrm{CF}_3\mathrm{Br}) - \Delta H_f^\circ(\mathrm{Br}_{2,g}) - \Delta H_f^\circ(\mathrm{C}_2\mathrm{F}_6).$$

At 298°K,  $\Delta H_f^{\circ}(Br_2,g)^5 = 7.39$  and  $\Delta H_f^{\circ}(HBr)^5 = -8.70$  kcal mole<sup>-1</sup> hence using the  $\Delta H_1^{\circ}$  and  $\Delta H_2^{\circ}$  given earlier,

$$\Delta H_{f}^{\circ}(CF_{3}H) = \Delta H_{f}^{\circ}(CF_{3}Br) - 11.50 \pm 0.30, \qquad (8)$$

$$\Delta H_f^{\circ}(C_2F_6) = 2\Delta H_f^{\circ}(CF_3Br) - 11.05 \pm 0.20.$$
(9)

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From eqn. (8) and (9),

$$\beta = \Delta H_f^{\circ}(C_2 F_6) - 2\Delta H_f^{\circ}(CF_3 H) = 12.0 \pm 0.6, \tag{10}$$

all in kcal mole<sup>-1</sup>.

Eqn. (8) and (9) cannot be checked because  $\Delta H_f^{\circ}(CF_3Br)$  is unknown. However. eqn. (10) can be used to check existing enthalpies of formation of  $C_2F_6$  and  $CF_3H$ provided that they have been determined independently of each other. Accordingly we evaluate the left-hand side of eqn. (10), denoted by  $\beta$ , using various published  $\Delta H_{f}^{2}$ . Many previously accepted enthalpies of formation of fluorine compounds are now uncertain because they depend on  $\Delta H_{i}^{2}(HF,aq)$  which is in doubt.<sup>14</sup> However, the evaluation of  $\beta$  in eqn. (10) is not necessarily affected by this uncertainty, e.g., suppose a value of  $\Delta H_{f}^{\circ}(C_{2}F_{6})$  is obtained using  $\Delta H_{f}^{\circ}(HF,aq.)$  and that the latter is subsequently amended by  $\delta$  kcal mole<sup>-1</sup>. This correction changes  $\Delta H_f^{\circ}$  $(C_2F_6)$  by 6 $\delta$ . Similarly  $\Delta H^{\circ}_{\ell}(CF_3H)$  would change by 3 $\delta$  so that  $\beta$  in eqn. (10) would change by  $6\delta - 2(3\delta)$ , i.e., the evaluation of  $\beta$  is unaffected by the change in  $\Delta H_{f}^{\circ}(HF,aq)$ . This is true provided that both determinations of  $\Delta H_{f}^{\circ}$  for  $C_{2}F_{6}$  and  $CF_3H$  involve  $\Delta H_f^{\circ}(HF,aq)$  and also provided that the correction  $\delta$  changes  $\Delta H_f^{\circ}$ (HF, aq.) by the same amount at the various dilutions used. This is so for the correction proposed by Cox and Harrop.14

We now evaluate  $\beta$  using the following data, all of which are based on the "old" value <sup>15</sup> of  $\Delta H_{f}^{\circ}(\text{HF},aq.)$ . From combustion measurements, Neugebauer and Margrave <sup>16</sup> obtained  $\Delta H_{f}^{\circ}(\text{CF}_{3}\text{H}) = -162\cdot6\pm0.7$  kcal mole<sup>-1</sup>; this is the only determination. Kirkbride and Davidson <sup>17</sup> measured the enthalpy of reaction of C<sub>2</sub>F<sub>6</sub> with potassium from which they obtained  $\Delta H_{f}^{\circ}(\text{C}_{2}\text{F}_{6}) = -303$  kcal mole<sup>-1</sup>. The gas-phase reaction,

$$C_2F_6 + \frac{2}{3}NF_3 \rightarrow 2CF_4 + \frac{1}{3}N_2,$$
 (11)

was studied by Sinke <sup>18</sup> who obtained  $\Delta H_{11}^{\circ} = -103.9 \pm 1.0$  kcal mole<sup>-1</sup> using a calorimetric method. From this, he calculated that  $\Delta H_f^{\circ}(C_2F_6) = -318$  kcal mole<sup>-1</sup> using  $\Delta H_f^{\circ}$  for CF<sub>4</sub> and NF<sub>3</sub> from ref. (5). All these data involve the old value of  $\Delta H_f^{\circ}(\text{HF}, aq.)$  and hence may fairly be used to determine  $\beta$ . The values of  $\beta$  so obtained are compared in table 2 with our result given in eqn. (10).

TABLE 2.—EVALUATION OF  $\beta = \Delta H_f^{\circ}(C_2F_6) - 2\Delta H_f^{\circ}(CF_3H)$  using published enthalpies of formation

∆ <i>H<sub>f</sub></i> (CF <sub>3</sub> H)	ref.	$\Delta H_{f}^{\circ}(C_{2}F_{6})$	ref.	β
-162.6	16	- 303	17	22
-162.6	16	-318	18	7.0
-166.8	а	-321.0	а	12·6 ±2·1
	Ь		Ь	$12.0 \pm 0.6$

a, after correction of results in ref. (16) and (18), see present text; b, "experimental" result, present work;  $\Delta H_f^{\circ}$  and  $\beta$  are in kcal mole<sup>-1</sup>.

A third value of  $\beta$  can be calculated from recent data which gives a value of  $\Delta H_f^{\circ}(C_2F_6)$  which is independent of  $\Delta H_f^{\circ}(HF,aq.)$  and which also leads to a more reliable value of  $\Delta H_f^{\circ}(CF_3H)$ . We still obtain  $\Delta H_f^{\circ}(C_2F_6)$  from Sinke's value of  $\Delta H_{11}^{\circ}$  but the subsidiary values of  $\Delta H_f^{\circ}$  for NF<sub>3</sub> and CF<sub>4</sub> are modified as follows.

Sinke <sup>10</sup> measured the enthalpy of explosion of NF<sub>3</sub>+H<sub>2</sub> mixtures and obtained  $\Delta H_{f}^{\circ}(NF_{3}) = -31.44 \pm 0.30$  kcal mole<sup>-1</sup>. Walker <sup>20</sup> measured  $\Delta H$  for

$$S+2NF_3 \rightarrow SF_6+N_2$$

and combined his result with  $\Delta H_f^{\circ}(SF_6)$  from O'Hare *et al.*<sup>21</sup> to get  $\Delta H_f^{\circ}(NF_3) = -31.75 \pm 0.20$  kcal mole<sup>-1</sup>. Ludwig and Cooper <sup>22</sup> measured  $\Delta H$  for

$$B + NF_3 \rightarrow BF_3 + \frac{1}{2}N_2$$

and combined their result with  $\Delta H_f^{\circ}(BF_3)$  from Johnson *et al.*<sup>23</sup> to give  $\Delta H_f^{\circ}(NF_3) = -31.95 \pm 1.30$  kcal mole<sup>-1</sup>. We shall use as a "best" value,  $\Delta H_f^{\circ}(NF_3) = -31.6 \pm 0.3$  kcal mole<sup>-1</sup>.

Armstrong and Domalski<sup>24</sup> measured the enthalpy of reaction between graphite and fluorine from which  $\Delta H_f^{\circ}(CF_4) = -222 \cdot 87 \pm 0.38$  kcal mole<sup>-1</sup>. They <sup>24</sup> also measured  $\Delta H$  for

$$C_2F_4$$
 (polymer) + 2 $F_2 \rightarrow 2CF_4$ 

and obtained a result slightly different from their previous one.<sup>25</sup> Their final value was combined with  $\Delta H$  for

$$C_2F_4$$
 (polymer) +  $O_2 \rightarrow CF_4 + CO_2$ 

from work by Good *et al.*<sup>26</sup> to give  $\Delta H_f^{\circ}(CF_4) = -223 \cdot 1 \pm 0.5$  kcal mole<sup>-1</sup>. The best value seems to be  $\Delta H_f^{\circ}(CF_4) = -223 \cdot 0 \pm 0.5$  kcal mole<sup>-1</sup>. When these best values of  $\Delta H_f^{\circ}$  for NF<sub>3</sub> and CF<sub>4</sub> are combined with Sinke's value <sup>18</sup> of  $\Delta H$  for reaction (11), we obtain  $\Delta H_f^{\circ}(C_2F_6) = -321 \cdot 0 \pm 1.5$  kcal mole<sup>-1</sup>. This result and all quantities used to obtain it are independent of  $\Delta H_f^{\circ}(HF, ag.)$ .

To calculate  $\beta$  using this new result, we require  $\Delta H_{f}^{\circ}(CF_{3}H)$  accurately but the only available value involves  $\Delta H_{f}^{\circ}(HF,aq.)$ . From the review given below, we conclude that  $\Delta H_{f}^{\circ}(HF,21H_{2}O) = -77.0\pm0.2$  kcal mole<sup>-1</sup> and this, when combined with the combusion results of Neugebauer and Margrave <sup>16</sup> gives  $\Delta H_{f}^{\circ}(CF_{3}H) = -166.8\pm0.7$  kcal mole<sup>-1</sup>. The new values of  $\Delta H_{f}^{\circ}$  for  $C_{2}F_{6}$  and  $CF_{3}H$  lead to  $\beta = 12.6\pm2.1$  kcal mole<sup>-1</sup> which is the third result given in table 2.

Of the three values of  $\beta$  in table 2, the first is in poor agreement with our "experimental" result in eqn. (10) and this confirms previous suggestions <sup>27, 28</sup> that Kirkbride and Davidson's <sup>17</sup>  $\Delta H_f^{\circ}(C_2F_6)$  is not sufficiently negative. However the third value of  $\beta$ , which is based on the latest thermochemical data, is in excellent agreement with our experimental result.

#### ENTHALPY OF FORMATION OF HF, aq.

Cox and Harrop <sup>14</sup> suggested that the values of  $\Delta H_{j}^{\circ}(\mathrm{HF},aq.)$  in N.B.S. circ. 500 should all be more negative by 1.76 kcal mole<sup>-1</sup>. In this paper, we particularly need  $\Delta H_{j}^{\circ}(\mathrm{HF},21\mathrm{H}_{2}\mathrm{O})$  in order to re-calculate  $\Delta H_{j}^{\circ}(\mathrm{CF}_{3}\mathrm{H})$  from the combustion data of Neugebauer and Margrave. From N.B.S. circ. 500,  $\Delta H_{j}^{\circ}(\mathrm{HF},21\mathrm{H}_{2}\mathrm{O}) = -75.64$ kcal mole<sup>-1</sup> but the results of more recent work are as follows : (1) Cox and Harrop <sup>14</sup> obtained  $-77.40\pm0.14$  kcal mole<sup>-1</sup>. (2) Cox and Harrop <sup>14</sup> used published data on the hydrolysis of SiF<sub>4</sub> to obtain a result equivalent to  $\Delta H_{j}^{\circ}(\mathrm{HF},21\mathrm{H}_{2}\mathrm{O}) = -77.0\pm0.4$ kcal mole<sup>-1</sup>. (3) Johnson *et al.*<sup>23</sup> measured  $\Delta H_{j}^{\circ}(\mathrm{BF}_{3})$  by direct union of the elements and they compared their result with an independent determination <sup>29</sup> which involved  $\Delta H_{j}^{\circ}(\mathrm{HF},aq.)$ . Hence they obtained  $\Delta H_{j}^{\circ}(\mathrm{HF},3\mathrm{H}_{2}\mathrm{O})$  from which we calculate that  $\Delta H_{j}^{\circ}(\mathrm{HF},21\mathrm{H}_{2}\mathrm{O}) = -77.0\pm0.10$  kcal mole<sup>-1</sup>. (4) Sinke <sup>30</sup> measured  $\Delta H$  for  $\mathrm{NF}_{3} + \frac{3}{2}\mathrm{H}_{2} + aq. \rightarrow 3(\mathrm{HF},123\mathrm{H}_{2}\mathrm{O}) + \frac{1}{2}\mathrm{N}_{2}$ 

from which  $\Delta H_{f}^{\circ}(\text{HF},123\text{H}_{2}\text{O}) = -77.03\pm0.12$  (using the recommended value of  $\Delta H_{f}^{\circ}(\text{NF}_{3})$  given above) so that  $\Delta H_{f}^{\circ}(\text{HF},21\text{H}_{2}\text{O}) = -76.97\pm0.12$  kcal mole<sup>-1</sup>. (5) Cox, Gundry and Head <sup>31</sup> studied a combustion reaction which produces CF<sub>4</sub> and obtained  $\Delta H_{f}^{\circ}(\text{CF}_{4}) = -225.63\pm0.65$  kcal mole<sup>-1</sup> using Cox and Harrop's data <sup>14</sup> on  $\Delta H_{f}^{\circ}(\text{HF},aq)$ . However, if we accept the value of  $\Delta H_{f}^{\circ}(\text{CF}_{4})$  given earlier in this

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paper which is independent of  $\Delta H_f^{\circ}(\text{HF},aq.)$ , we can reverse the calculation of Cox, Gundry and Head to obtain  $\Delta H_f^{\circ}(\text{HF},21\text{H}_2\text{O}) = -76.74\pm0.15$  kcal mole<sup>-1</sup>. (6) We derived above a value of  $\Delta H_f^{\circ}(\text{C}_2\text{F}_6)$  which was independent of  $\Delta H_f^{\circ}(\text{HF},aq.)$  and on combining this with our experimental results in eqn. (10), we obtain  $\Delta H_f^{\circ}(\text{CF}_3\text{H}) = -166.5\pm0.8$  kcal mole<sup>-1</sup>. Combining this result with the data of Neugebauer and Margrave <sup>16</sup> on the combustion of CF<sub>3</sub>H then leads to  $\Delta H_f^{\circ}(\text{HF}, 21\text{H}_2\text{O}) = -76.9\pm0.3$  kcal mole<sup>-1</sup>.

To sum up, there are 6 determinations of  $\Delta H_{3}^{\circ}(\text{HF},21\text{H}_{2}\text{O})$  which are in the range -76.74 to -77.40 kcal mole<sup>-1</sup> whereas the N.B.S. circ. 500 value is -75.64 kcal mole<sup>-1</sup>. Thus, suggestions by Cox and Harrop<sup>14</sup> and by others that the N.B.S. circ. 500 value needs revision are confirmed and we propose that a more acceptable result is

$$\Delta H_f^{\circ}(\text{HF}, 21\text{H}_2\text{O}) = -77.0 \text{ kcal mole}^{-1};$$

this is probably accurate to better than  $\pm 0.2$  kcal mole<sup>-1</sup>. This result implies that any given value of  $\Delta H_f^{\circ}(\text{HF},n\text{H}_2\text{O})$  in N.B.S. circ. 500 or N.B.S. Tech. Note 270-1 becomes more negative by 1.4 and 0.7 kcal mole<sup>-1</sup> respectively. The concordancy of the above results also provides strong support for the enthalpies of formation of  $C_2F_6$ ,  $CF_4$  and  $CF_3$ H used in this paper.

#### BOND DISSOCIATION ENERGIES RELATED TO $D(CF_3 - CF_3)$

If is of interest to compare our present value of  $D(CF_3-CF_3)$  with  $D(CH_3-CH_3)$ and  $D(CF_3-CH_3)$ . Taking <sup>32</sup>  $D(CH_3-H) = 104\cdot0\pm1\cdot0$  kcal mole<sup>-1</sup> and using standard  $\Delta H_f^\circ$ , we have  $\Delta H_f^\circ(CH_3) = 34\cdot0\pm1\cdot0$  so that  $D(CH_3-CH_3) = 88\cdot2\pm2\cdot0$ kcal mole<sup>-1</sup>. Kolesov *et al.*<sup>33</sup> studied the combustion of  $CF_3CH_3$  and obtained  $\Delta H_f^\circ(CF_3CH_3) = -174\cdot1\pm0\cdot4$  kcal mole<sup>-1</sup> using  $\Delta H_f^\circ(HF,aq.)$  from N.B.S. circ. 500. Using the new value proposed above, the corrected result is  $\Delta H_f^\circ(CF_3CH_3) = -174\cdot1-3(1\cdot4) = -178\cdot3\pm0\cdot4$  kcal mole<sup>-1</sup>. Now

$$D(CF_{3}-CH_{3}) = D(CF_{3}-H) + \Delta H_{f}^{\circ}(CH_{3}) - \Delta H_{f}^{\circ}(H) + \Delta H_{f}^{\circ}(CF_{3}H) - \Delta H_{f}^{\circ}(CF_{3}CH_{3})$$
(12)

and introduction into this eqn. of the data above, including our corrected value of  $\Delta H_f^{\circ}(CF_3H)$ , gives

$$D(CF_3-CH_3) = D(CF_3-H) - 6.6 \pm 1.5 \text{ kcal mole}^{-1}$$
. (13)

This result is *independent* of  $\Delta H_{f}^{\circ}(\text{HF},aq.)$  since whatever value is used cancels in the difference  $\Delta H_{f}^{\circ}(\text{CF}_{3}\text{CH}_{3}) - \Delta H_{f}^{\circ}(\text{CF}_{3}\text{H})$  in eqn. (12). Introducing our previous result <sup>6</sup> that  $D(\text{CF}_{3}\text{--H}) = 106\cdot3$  kcal mole<sup>-1</sup> into eqn. (13) gives  $D(\text{CF}_{3}\text{--CH}_{3}) = 99\cdot7 \pm 2\cdot0$  kcal mole<sup>-1</sup>. If this figure is correct, then CF<sub>3</sub>CH<sub>3</sub> contains one of the strongest known C—C single bonds in a saturated molecule.

The only other determination of  $D(CF_3-CH_3)$  was by Steele and Stone <sup>34</sup> using an electron impact method, the result being  $D(CF_3-CH_3) = 88$  kcal mole<sup>-1</sup>. This is based on an appearance potential of 13.9 eV for  $CF_3^+$  from  $CF_3CH_3$  together with an ionization potential of 10.15 eV for the  $CF_3$  radical. There is some evidence <sup>7</sup> that  $I(CF_3) = 9.35$  eV which would change Steele and Stone's result to  $D(CF_3-CH_3)$ = 106 kcal mole<sup>-1</sup>, a value which is closer to 99.7 kcal mole<sup>-1</sup> obtained above. However, until a reliable value of  $I(CF_3)$  is available, the electron-impact results must be treated with reserve.

Enthalpies of formation of  $CF_3H$  and  $CF_4$  were given above from which  $D(CF_3 - F)$  is obtained as follows. Using  $D(CF_3 - H) = 106.3$  kcal mole<sup>-1</sup> together with

## $\Delta H_f^{\circ}(CF_3H)$ , we have $\Delta H_f^{\circ}(CF_3) = -112.6 \pm 1.2 \text{ kcal mole}^{-1}$ . Hence

# $D(CF_3 - F) = \Delta H^{\circ}_{f}(CF_3) + \Delta H^{\circ}_{f}(F) - \Delta H^{\circ}_{f}(CF_4)$

= -112.6 + 18.9 - (-223.0) = 129.3 kcal mole<sup>-1</sup>.

This result is probably accurate to  $\pm 2$  kcal mole<sup>-1</sup>. ( $\Delta H_f^{\circ}(F)$  is from ref. (5).)

We thank Dr. H. A. Skinner for valuable discussions and for acquainting us with recent thermochemical data. We also thank the S.R.C. for a grant to J. W. C.

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