

consistent with the above structure and suggests a mechanism for its reaction with hydrogen and diborane. Dissociation of B_4H_8CO to B_4H_8 retaining a vacant orbital 2112 structure¹⁹ could be the initial step in the

Table II. ^{11}B Spectral Data for B_4H_8CO and $B_4H_8PF_3$

		BH	BH (BHP)	BH ₂
B_4H_8CO	δ , ppm	+2.1	+58.7	+1.5
	J , cps	119	131	127
$B_4H_8PF_3$	δ , ppm	-0.7	+58.7	+3.9
	J cps	122	149	123

reaction. Interaction of the vacant orbital with hydrogen, followed by minor electronic and molecular rearrangement, would result in tetraborane(10). Substitution of deuterium for hydrogen in this reaction might

(19) J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

be expected to yield the bridge (μ), terminal (1) labeled molecule, $\mu, 1$ -dideuteriotetraborane(10). Similarly, in the reaction with diborane, initial bond formation between B_4H_8 and B_2H_6 might occur with formation of a boron hydrogen bridge bond at B_1 . Simultaneous or subsequent dissociation of the diborane followed by electronic and molecular rearrangement of the intermediate species would give rise to the final B_5H_{11} . The fact that $^{10}B^{10}B_4H_{11}$ did not have the ^{11}B isotope located specifically in either basal position, as might be inferred from this mechanism, may indicate that a rapid basal boron equilibration process exists for pentaborane(11), that an intermediate with four equivalent borons is formed, or that the intermediate species formed prior to pentaborane(11) can rearrange to the observed $^{10}B^{10}B_4H_{11}$ by two different mechanisms. Further study will be necessary to attempt to distinguish between these choices.

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Kinetics of the Decomposition of BH_3PF_3 and Related Compounds. A Revised Estimate of the Dissociation Energy of Diborane¹

Anton B. Burg and Yuan-Chin Fu

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received November 4, 1965

Abstract: Very sensitive infrared procedures were used to show that the compounds BH_3PF_3 , $BH_3 \cdot CF_3PF_2$, and $BH_3 \cdot (CF_3)_2PF$ all decompose to B_2H_6 and free phosphine ligand by the same mechanism as found earlier for BH_3CO , namely, the dissociation of BH_3L to BH_3 and free ligand L, followed by action of BH_3 to displace L from BH_3L . The same rate law applies also to the far more complicated case of $B_4H_8PF_3$. Extrapolation of early-stage rate data for BH_3PF_3 to zero time gave first-order rate constants for the initial dissociation at three temperatures. These results, taken with the over-all equilibria, led to $D(BH_3-BH_3) = 35.0$ kcal, consistent with but more precise than earlier estimates. The only systematic error here would arise from the reasonable assumption that $\Delta H = 0$ for activation of the reverse of the initial dissociation.

The thorough analysis by Garabedian and Benson,² of all data on the rates of decomposition of BH_3CO to CO and B_2H_6 ,^{3,4} confirmed the mechanism proposed by Burg³ and led to a considerably higher value for $D(BH_3-BH_3)$ than had been estimated by Bauer.⁵ Others have proposed still higher values.^{6,7}

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(2) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

(3) A. B. Burg, *ibid.*, **74**, 3482 (1952).

(4) Y. C. Fu and G. R. Hill, *ibid.*, **84**, 353 (1962).

(5) S. W. Bauer, *ibid.*, **78**, 5775 (1956).

(6) T. P. Fehlner and W. S. Koski, *ibid.*, **87**, 409 (1965).

However, all such estimates have been based upon assumptions sufficiently uncertain to allow fairly wide disagreement. A new approach to the problem was needed.

The compound BH_3PF_3 was reported as decomposing by a rate law at least roughly similar to that of BH_3CO .⁸ The present work abundantly confirms this mechanism, showing that BH_3PF_3 can be used for an independent development of data relating to $D(BH_3-BH_3)$. The great advantage here is the high sensitivity of the infrared method of observing the process; fortunately, the very intense P-F stretching peaks shown by PF_3

(7) E. J. Sinke, G. A. Pressley, Jr., A. B. Bayliss, and F. E. Stafford, *J. Chem. Phys.*, **41**, 2207 (1964).

(8) R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).

at 834, 853, and 867 cm^{-1} are far enough from the nearest P-F stretching peak of BH_3PF_3 (942 cm^{-1}) so that all three can be used for double-checked quantitative determinations of PF_3 as it is being released. Hence good rate curves can be drawn from observations at very early stages of the process, in contrast to the very uncertain early-stage BH_3CO data³ upon which Bauer based his estimates.⁵ Indeed, it proved possible to extrapolate our early-stage data at three low temperatures to first-order rates at zero time, and so to have a highly dependable basis for estimating $D(\text{BH}_3\text{-BH}_3)$. Similar work with BH_3CO would not have been possible because the infrared spectrum of CO is far too weak.

The new compound, $\text{BH}_3\cdot\text{CF}_3\text{PF}_2$, and the previously indicated $\text{BH}_3\cdot(\text{CF}_3)_2\text{PF}$ ⁹ also were found to decompose to B_2H_6 and free ligand in just the same manner, but a dependable study of the early-stage kinetics of either would have been far more difficult than for BH_3PF_3 . The same rate law applies also to the decomposition of $\text{B}_4\text{H}_8\text{PF}_3$,¹⁰ but its decomposition products are relatively difficult to interpret.

Experimental Methods

Preparation of Samples. The compounds BH_3PF_3 and $\text{B}_4\text{H}_8\text{PF}_3$ were made by the action of PF_3 in great excess upon B_2H_6 or B_5H_{11} .^{8,10} The similarly formed $\text{BH}_3\cdot\text{CF}_3\text{PF}_2$ and $\text{BH}_3\cdot(\text{CF}_3)_2\text{PF}$ could not be purified completely, for small proportions of CF_3PF_2 or $(\text{CF}_3)_2\text{PF}$ remained even after distillation in a high-vacuum reflux column and fractional condensation at -130 and -110° , respectively. Hence for kinetic runs on these, the effective zero times could be determined only by extrapolation from early points. This procedure was feasible because the presence or absence of diborane never affected our virtually irreversible kinetic process, the over-all rate of which was governed by the partial pressure of the free ligand. The same method was applied also to BH_3PF_3 samples which had suffered some slight decomposition during the usual distillation into the cold-tube attached to the infrared cell; however, for the very early-stage observations of BH_3PF_3 , this cold-tube was a small U-trap at -145° , through which the PF_3 impurity passed to a more distant trap at -196° .

The study of $\text{BH}_3\cdot(\text{CF}_3)_2\text{PF}$ was complicated by the unavoidable presence of $(\text{CF}_3)_2\text{PH}$ (a by-product of the synthesis), often in amounts comparable to $\text{BH}_3\cdot(\text{CF}_3)_2\text{PF}$ itself. However, $(\text{CF}_3)_2\text{PH}$ was only an inert diluent; and since its peaks at 749, 810, and 853 cm^{-1} were constant throughout any run, it was possible to determine the intensity of the 853- cm^{-1} peak of $(\text{CF}_3)_2\text{PF}$ by subtracting the intensity of the 853- cm^{-1} peak as calculated by reference to the 749- and 810- cm^{-1} peaks.

Infrared Technique. The infrared instrument for this work was the Beckman IR7, with interchangeable NaCl and CsI optics. The relative intensities of the pertinent bands were determined as $k = (100/PL) \log I_0/I$ for pressure P at 25° and path L , both in cm. For the standardization of any band, it was not necessary to determine the absolute base line for 100% transmittance, for I_0 and I could be based upon any two consistently measureable features of the same band. Then the arbitrary k values could be used to determine the partial pressure of any component during a kinetic run.

The free ligands PF_3 , CF_3PF_2 , and $(\text{CF}_3)_2\text{PF}$ all offered P-F stretching frequencies far enough from those of the BH_3 complexes for dependable observations of ligand appearance, undisturbed by the diminishing P-F stretching intensities of the complexes. For $\text{B}_4\text{H}_8\text{PF}_3$, however, P-F stretching was too close to that for PF_3 ; and even the PF_3 deformation at 487 cm^{-1} was not quite free of interference by the 444- and 556- cm^{-1} bands of $\text{B}_4\text{H}_8\text{PF}_3$. However, the PF_3 deformation at 347 cm^{-1} was quite adequately separated from the $\text{B}_4\text{H}_8\text{PF}_3$ band at 403 cm^{-1} to afford good measurements. For this low-frequency region, the cell was fitted with KBr

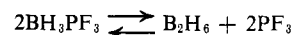
disks only 2 mm thick, and their small absorption was balanced by an equal thickness of KBr in the reference beam.

The infrared cells were so designed that the main beam-region could be equilibrated with the cell-chamber temperature while the sample resided in a cold-tube outside of the instrument. The decomposition process could be started by suddenly warming the sample from -196° , expanding it into the path of the beam; then by closing a stopcock just above the cell chamber, the observed process could be confined to the constant-temperature region. Cell path lengths of 11 and 81 mm permitted a wide choice of initial pressures and ranges of decomposition. The short-path cell was provided with a ballast volume within the constant-temperature region, to ensure uniform behavior of the sample.

For work over a range of temperatures, the cell body resided in a transit box within the instrument cell chamber, and was either heated by a fan blowing across electrically heated wires, or cooled by air which had been dehumidified at 7 atm pressure and 2° and passed through a copper coil at temperatures as low as -78° . By either arrangement, temperature constancy within 0.3° could be maintained.

Initial Sample Pressures. For each experiment, the effective initial pressure of the sample could be determined as the sum of the partial pressures of the BH_3 complex and the ligand, a sum which was constant throughout the course of a decomposition. In some cases the initial pressure was too high for infrared determination of both partial pressures. For these runs, the total BH_3 was determined as $(\text{CH}_3)_3\text{NBH}_3$ afterwards; and then the initial pressure could be calculated from the calibrated volume of the cell.

Equilibrium Measurements. The equilibrium constants at various temperatures for the over-all process



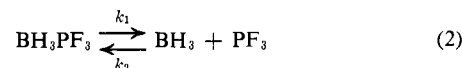
were determined by a procedure like that described earlier for BH_3CO .³ In the present case, the fraction passing a high-vacuum trap at -145° (B_2H_6 and PF_3) was measured as a gas and analyzed by conversion of the B_2H_6 part to $(\text{CH}_3)_3\text{NBH}_3$ for weighing.

Results

Main Kinetic Data for BH_3PF_3 . Our rate studies on BH_3PF_3 in the range 3–74% decomposition, at initial pressures from 9.1 to 308 mm and at temperatures ranging from 0 to 54.6° , were correlated by the equation

$$f(x) = \frac{2k_1k_3t}{k_2} = \frac{x}{1-x} - \ln(1-x) \quad (1)$$

as written by Garabedian and Benson.² This is equivalent to the equation given by Burg,³ with x redefined as the fraction of BH_3PF_3 decomposed at time t . It represents the integrated form of the rate equation based upon the process



with the assumption that k_3 is far smaller than k_2 . The very good linearity of the typical graphs shown in Figure 1 clearly demonstrates the validity of this mechanism. Only for the slow run at 0° , for which the scale is greatly magnified, do we see some of the expected deviation near the origin, as required by theory for a range in which k_3 is not solely rate determining.

From the slopes of all such lines, the values of k_1k_3/k_2 (designated as kK in the BH_3CO study)³ were

(9) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

(10) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

calculated and used to determine the energy equation

$$\log k_1 k_3 / k_2 = 15.84 - 29,300/4.578T \quad (4)$$

The validity of this equation is demonstrated in Table I.

Table I. Summary of BH_3PF_3 Decomposition Rates

Temp, °C	P_0 , mm	Total time, min	% decompn	$10^5 k_1 k_3 / k_2$, sec ⁻¹ Obsd	Calcd
0.0	170	180	3.4	2.9	2.6
0.0	210	172	3.5		
0.0	308	168	3.3		
5.0	60	143	4.4	5.9	6.7
21.2	13.2	234	22.5	125	125
28.5	9.1	190	33.0	396	417
35.0	31.5	161	44.5	1,120	1,170
37.0	10.6	187	50.5	1,410	1,590
37.0	23.2	70	35.2		
37.2	28.5	185	50.2		
43.5	19.0	118	59.8	4,260	4,220
48.3	10.7	152	76.2	9,100	8,520
54.6	24.9	62	73.9	20,700	20,400

The Early Low-Temperature Data. In the temperature range -10.3 to 0° it was possible to make good observations of the progress of the decomposition between 0 and 1%, demonstrating very considerable deviations from the simple rate law based upon $k_3 \ll k_2$. However, on the basis of the complete rate equation given by Garabedian and Benson,² namely

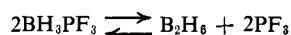
$$-\frac{d(\text{BH}_3\text{PF}_3)}{dt} = \frac{2k_1 k_3 (\text{BH}_3\text{PF}_3)^2}{k_2 (\text{PF}_3) + k_3 (\text{BH}_3\text{PF}_3)} \quad (5)$$

it is apparent that zero time would require a first-order rate law, since $(\text{PF}_3) = 0$ so that $k_3(\text{BH}_3\text{PF}_3)$ would cancel out. As expected, the simplified first-order rate equation $2k_1 = x/t$ showed " k_1 " variable with time, but ΔH_{act} could be estimated as 23.5 kcal from pseudo- k_1 values obtained by extrapolations to zero time. Alternatively, graphs of $(x/2 + 2x^2/3)$ vs. t/x (according to eq 3 of Garabedian and Benson)² gave $2k_1 k_3 / k_2$ as slopes and $-k_3/k_2$ as intercepts at $t/x = 0$, leading to the k_1 values (in sec⁻¹ $\times 10^{-5}$) 0.29 at -10.3° , 0.63 at -5.6° , and 1.56 at 0.0° . The equation

$$\log k_1 = 13.94 - 23,450/4.578T \quad (6)$$

gives these as 0.288, 0.632, and 1.56.

Over-all Equilibria. The values of K in atm for the equilibrium



are shown with an equation, the experimental data, and the calculated values in Table II.

Decomposition Rates for $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$. The new compound $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$ showed important infrared absorption at 2445, 1220, 1180, 928, 921, and 773 cm^{-1} . As it decomposed, bands characteristic of B_2H_6 and CF_3PF_2 appeared, indicating the equation

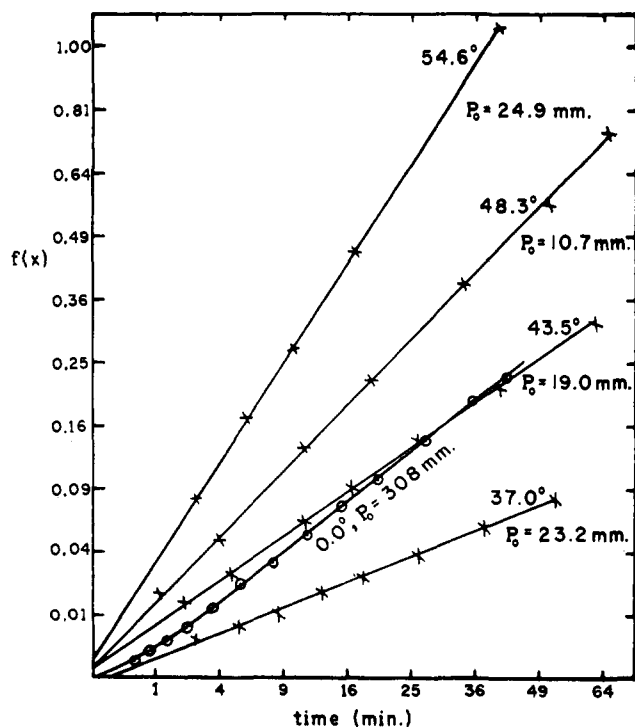
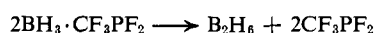


Figure 1. Representative rate curves for the decomposition of BH_3PF_3 . For graphical convenience the linear plot is $\sqrt{f(x)}$ vs. \sqrt{t} , magnifying the early regions. Thus the lines drawn through the X points seem to miss the origin, but the deviations actually are within the small error of estimating t_0 . For the 0.0° curve (circled points) the linear plot is $20\sqrt{f(x)}$ vs. $0.5\sqrt{t}$ so that the ordinate numbers should be divided by 400 and the abscissa numbers multiplied by 4, for true comparison with the other curves. This 0.0° curve illustrates the genuine deviation of the very early points from linearity, an effect not noticed for the faster runs at higher temperatures.

The kinetic runs used samples containing 3-5% of CF_3PF_2 impurity. Since the initial rates would be governed by this rather than by the presence or absence of diborane, it was reasonable to run the $f(x)$ vs. t curves through the origin, thus determining the zero time t_0 by extrapolation. On this basis the curves

Table II. Decomposition Constants for BH_3PF_3
($\log K_{\text{atm}} = 8.670 - 2592/T = 8.670 - 11,870/4.578T$)

Temp, °K	Time, hr	Tube			K , atm		
		vol, ml	Std gas volumes, cc BH_3PF_3	B_2H_6	PF_3	Obsd	Calcd
297.76	674	45.7	43.4	6.03	114.0	0.99	0.91
305.96	408	46.5	41.6	10.05	102.5	1.47	1.55
314.16	330	55.9	35.6	11.30	116.2	2.48	2.58
323.96	163	47.3	29.3	11.10	120.6	4.72	4.61
334.16	163	47.4	34.5	14.60	160.2	8.13	8.09

were indeed linear (conforming to the same mechanism as for BH_3CO or BH_3PF_3), with precision essentially the same as in Figure 1. The composite rate constants from eight experiments at four temperatures are shown with the resulting energy equation in Table III.

Decomposition Rates for $\text{BH}_3 \cdot (\text{CF}_3)_2\text{PF}$. The main infrared absorption peaks for $\text{BH}_3 \cdot (\text{CF}_3)_2\text{PF}$ appeared

at 2432, 907, and 697 cm^{-1} , with the usual very intense C-F stretching bands in the range 1120–1200 cm^{-1} not easily distinguished in the presence of the $(\text{CF}_3)_2\text{PH}$ and $(\text{CF}_3)_2\text{PF}$ impurities. However, it was possible to demonstrate the same kind of dissociation as for BH_3PF_3 and $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$, and to deal with rate data in

Table III. Summary of $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$ Decomposition Rates
($\text{Log } k_1k_3/k_2 = 11.02 - 24,474/4.578T$)

Temp, °C	P_0 , mm	Total time, min	% decompn	$-10^3k_1k_3/k_2$, sec $^{-1}$	Obsd	Calcd
24.9	8.7	164	6.9	12.9	12.4	
25.0	20.9	228	7.6			
37.4	10.6	97	10.6	56.5	64.2	
37.5	17.6	92	10.5			
45.2	10.9	69	15.6	173	169	
45.2	25.6	96	18.0			
53.5	9.5	58	20.3	440	446	
53.3	28.3	72	23.3			

the same manner. Again the $f(x)$ vs. t graphs were linear with the usual precision. The rates, shown with the energy equation in Table IV, were about 20 times as fast as for BH_3PF_3 , or 400 times as fast as for $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$, at the same temperatures.

Table IV. Summary of $\text{BH}_3 \cdot (\text{CF}_3)_2\text{PF}$ Decomposition Rates
($\text{Log } k_1k_3/k_2 = 11.70 - 21,536/4.578T$)

Temp, °C	P_0 , mm	$(\text{CF}_3)_2\text{PH}$, mm	Total time, min	% decompn	$10^3k_1/k_3/k_2$, sec $^{-1}$	Obsd	Calcd
16.2	6.1	6.6	84	49	2.74	2.80	
26.7	6.8	7.2	72	66	10.5	10.4	
35.6	6.6	6.5	44	75	28.2	29.3	

The Decomposition of $\text{B}_4\text{H}_8\text{PF}_3$. The dissociation of $\text{B}_4\text{H}_8\text{PF}_3$ is not very directly observable, for many secondary products are formed very rapidly. For example, a 0.268-mmole sample of $\text{B}_4\text{H}_8\text{PF}_3$ was 63% decomposed in a closed glass tube during 25 min at 25°. Then the volatile products were separated from the remaining $\text{B}_4\text{H}_8\text{PF}_3$, and the components were identified by their infrared spectra and determined, in parts per 100 $\text{B}_4\text{H}_8\text{PF}_3$ consumed, as follows: 16 H_2 , 80 PF_3 , 14 BH_3PF_3 , 22 B_2H_6 , 16 B_4H_{10} , and 14 B_5H_{11} . No B_5H_9 could be found. All components except hydrogen were returned to the same tube and the process was continued for 63 hr, eliminating the $\text{B}_4\text{H}_8\text{PF}_3$. Now the total H_2 was 36 per 100 $\text{B}_4\text{H}_8\text{PF}_3$, and the other products were 69 PF_3 , 20 BH_3PF_3 , 18 B_2H_6 , 11 B_4H_{10} , and 4 B_5H_9 . The reason for the disappearance of B_5H_{11} , while B_4H_{10} remained, is not clear. Apparently both were formed in amounts far above the equilibrium values and then slowly decomposed. Also, there was far more BH_3PF_3 than would have been in equilibrium with the observed B_2H_6 and PF_3 ; it must have been formed directly from BH_3 fragments derived from the B_4H_8 unit. As far as PF_3 formation was concerned, the reaction was fairly clean: no more than 11% of this ligand was incorporated in the nonvolatile solid products.

The rate studies on $\text{B}_4\text{H}_8\text{PF}_3$ also gave quite linear graphs when plotted in the same manner as the other runs. Since the basis was the observation of liberated PF_3 , it would appear that the ultimate incorporation of a little PF_3 in the nonvolatile solid (and its use to make BH_3PF_3) did not have much effect upon the results. The rates over a range of temperatures are shown with an energy equation in Table V.

Table V. Summary of $\text{B}_4\text{H}_8\text{PF}_3$ Decomposition Rates
($\text{Log } k_1k_3/k_2 = 11.36 - 20,556/4.578T$)

Temp., °C	P_0 , mm	Total time, min	% decompn	$10^3k_1k_3/k_2$, sec $^{-1}$	Obsd	Calcd
-2.2	12.0	74	26.6	6.15	6.19	
0.0	21.9	64	27.8			
0.0	44.2	61	27.7	8.1	8.4	
10.4	13.6	62	47.4			
25.0	12.3	37	66.0	197	199	

Discussion

The Reaction Mechanism. The rate equation (5) on integration becomes

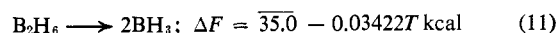
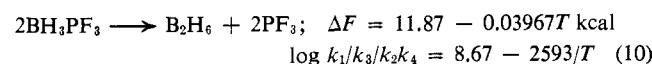
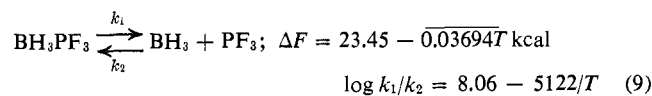
$$\frac{2k_1k_3t}{k_2} = \frac{x}{1-x} + (1 - k_3/k_2) \ln(1-x) \quad (7)$$

Thus again it is apparent that $k_3 \ll k_2$ reduces the rate law to eq 1. However, at zero time the process governed by k_3 , namely reaction 3, cannot begin for lack of free BH_3 . Hence at that point, eq 5 reduces to a first-order rate law, describing the dissociation reaction (2) as the rate-determining step, namely

$$-\frac{d(\text{B}_4\text{H}_8\text{PF}_3)}{dt} = 2k_1(\text{B}_4\text{H}_8\text{PF}_3) \quad (8)$$

The observed very rapid deviation from this first-order law shows that k_3 is indeed far smaller than k_2 , so that our low-temperature observations describe a transition from the first-order law to eq 1, almost entirely within the first 1% of decomposition. For this reason, most of our runs (with the first observations beyond 1%) failed to show any significant deviation of the $f(x)$ vs. t curves from linearity through the origin.

Thermochemical Results. Making the reasonable assumption of zero ΔH of activation for the reverse of the dissociation of BH_3PF_3 into BH_3 and PF_3 (eq 2), and accepting the literature estimate of the entropy of dissociation of diborane,¹¹ we can use the results from Table II with eq 6 to write the mutually consistent equations



(11) A. Shepp and S. H. Bauer, *J. Am. Chem. Soc.*, **76**, 265 (1954).

where k_4 concerns the reversal of eq 3 and each overlined value is derived by combining the other two equations.

Various other results now can be derived. For example, from eq 4 and 6

$$\begin{aligned}\log k_3/k_2 &= 15.84 - 6400/T - 13.94 + 5122/T \\ &= 1.90 - 1289/T\end{aligned}$$

From this, k_3/k_2 at 300°K is calculated as roughly 4×10^{-3} , reconfirming the assumption $k_3 \ll k_2$. Similarly, eq 4 and 9 combine to give

$$\log k_3 = 7.78 - 1278/T$$

while eq 4 and 10 give

$$\log k_4 = 7.17 - 3807/T$$

Hence the equilibrium constant for reaction 3 is given by

$$\begin{aligned}\log k_3/k_4 &= 0.61 + 2529/T; \\ \Delta F &= -11.53 - 0.00279T \text{ kcal}\end{aligned}$$

This result is consistent with our evidence that reversal did not appreciably affect our results even at late stages of the over-all reaction.

Other derivations from these thermochemical equations are obvious.

It is interesting that our first-order activation-energy equation for BH_3PF_3 is nearly the same as that of Fehlner and Koski⁶ for BH_3CO , namely

$$\log k_1 = 13.94 - 23,450/4.578T \text{ for } \text{BH}_3\text{PF}_3$$

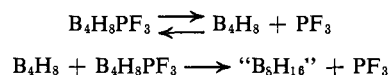
vs.

$$\log k_1 = 13.90 - 23,100/4.578T \text{ for } \text{BH}_3\text{CO}$$

Our new 35.0-kcal value for $D(\text{BH}_3\text{-BH}_3)$ (eq 11) probably has a random error less than 0.5 kcal. It is quite consistent with the estimates by Garabedian and Benson (35 ± 3 kcal)² and Fehlner and Koski (37 ± 4 kcal).⁶ If, contrary to expectations, k_2 were related to a positive ΔH of activation, our estimate would be lower. However, arguments omitting eq 6, and applying somewhat less rigorous assumptions to our main rate data, would lead to values about 1 kcal higher.

The Other Decompositions. The rate studies on $\text{BH}_3 \cdot \text{CF}_3\text{PF}_2$ and $\text{BH}_3 \cdot (\text{CF}_3)_2\text{PF}$ conformed well to the BH_3PF_3 mechanism but could not be used in the same way for an independent estimate of $D(\text{BH}_3\text{-BH}_3)$ because the unavoidable presence of the free ligands made it impossible to extrapolate into the region of zero time.

The conformity of $\text{B}_4\text{H}_8\text{PF}_3$ to the BH_3PF_3 mechanism would suggest further attempts to obtain useful thermochemical results concerning polyboranes, but the process here is so much more complicated as to discourage such efforts. The decomposition is some 300 times as fast as for BH_3PF_3 , making it more difficult to study the very early stages of the reaction; and in any case, if we write



there remains great doubt about the character of the second step. For example, the rate law for the appearance of PF_3 would seem the same if B_4H_8 were decomposing rapidly to produce a fragment which displaces PF_3 more slowly from $\text{B}_4\text{H}_8\text{PF}_3$, or if an intact B_4H_8 were to remove a fragment from $\text{B}_4\text{H}_8\text{PF}_3$, leaving a $\text{B}_2\text{H}_7\text{PF}_3$ which loses PF_3 much more rapidly.

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