Integrating and solving for P_0t_{50}, the values for 1:3, 1:2 and 1:1 mixture ratios stand as 1:2.0:9.4. The P_0t_{50} product thus should change much more rapidly with mixture ratio. The experimental data are again in reasonable agreement.

The temperature coefficient has been determined for the $2NH_3:1O_2$, and for $1NH_3:2O_2$ mixtures (Table II). Suitable plots give reasonably good straight lines from which activation energies have been calculated. Results vary somewhat but indicate a value in the neighborhood of 45,000 cal., for both rich and lean mixtures. There is thus some evidence for an underlying similarity in mechanism.

TABLE II

ACTIVATION ENERGY

°C.	625	650	675	700	725	$E_{act.}$ kcal.
$P^0_{NH_3}$ = 200 mm., $P^0_{O_2}$ = 100 mm.						
$[dP/dt]_0 \times 10^4$	52	69	109	213	361	42.2
t_{25}(sec.)	3850	1780	840	490	300	45.6
t_{50}(sec.)	11000	5860	2600	1500	800	46.9
$P^0_{NH_3}$ = 100 mm., $P^0_{O_2}$ = 200 mm.						
°C	525	550	575	600	625	
$[dP/dt]_0 \times 10^4$	36	80	206	495	750	48.0
t_{25}	1650	730	340	160	90	42.7
t_{50}	4200	2100	910	380	190	44.2

Without attempting to trace what the detailed process may involve, one additional fact may be added. Current experiments in a KCl-coated reaction vessel indicate that with ammonia-rich mixtures the rates are the same as given above for the uncoated vessel, and conform to the second-order kinetics. On the lean side, the rate is relatively low in the early stages of reaction, and varies with the $P_{NH_3} \times P_{O_2}$ product. After a time, however, the rate begins to increase, and thereafter roughly duplicates data for uncoated vessels. The behavior is not unlike that associated with "cool-flame" phenomena in hydrocarbon combustion, except that there appear to be no real discontinuities. Possibly this is again a case of slow accumulation of an intermediate, such accumulation being facilitated in the uncoated vessel.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Mechanism of Decomposition of Borine Carbonyl

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The rates of decomposition of BH_3CO and BD_3CO, by a nearly homogeneous reaction of the type $2BH_3CO \rightleftarrows B_2H_6 + 2CO$, become intelligible on the assumption that the rate-determining step is $BH_3 + BH_3CO \rightarrow B_2H_6 + CO$, the BH_3 groups being furnished from the initial equilibrium $BH_3CO \leftrightarrows BH_3 + CO$. This mechanism implies a rate equation of the form $2kKt = \frac{x}{a-x} - \ln\frac{a}{a-x} = f(x)$, which is confirmed by linear graphs of $f(x)$ *vs.* t for BH_3CO at 0–30° ($\log_{10} kK = 14.087 - 6000/T$) or for BD_3CO at 10–26° ($\log_{10} kK = 12.352 - 5370/T$). The corresponding ΔH values, 27.5 and 24.6 kcal., representing the sum of ΔH for the initial dissociation and ΔH for the activation of the rate-step, are rendered uncertain by a minor wall-reaction, small increases of kK with decreasing pressure, and the question of how well the first-step equilibrium is maintained. The equilibrium constants for the over-all decomposition are given by $\log_{10} K_{atm} = 7.104 - 1998/T$ ($\Delta F^\circ_T = 9142 - 32.5T$) for BH_3CO, and by $\log_{10} K_{atm} = 7.097 - 1850/T$ ($\Delta F^\circ_T = 8465 - 32.5T$) for BD_3CO, both in the range 25–80°. These imply that the decomposition-rate studies were not complicated by the reverse reactions, since the runs terminated at 8–25% decomposition.

The original description of borine carbonyl[1] included a preliminary study of the rate of the decomposition reaction $2BH_3CO \rightarrow B_2H_6 + 2CO$ (perfectly stoichiometric), with the suggestion that the first step might be the establishment of the equilibrium $BH_3CO \leftrightarrows BH_3 + CO$ as a very rapid process. The further suggestion that the rate-determining step might be $2BH_3 \rightarrow B_2H_6$ was not seriously inconsistent with the fairly rough original rate-data, but more recent studies have shown that a different theory of the rate-process is required.

The new data become orderly if it is assumed that the second step is $BH_3 + BH_3CO \rightarrow B_2H_6 + CO$, and that this step is so slow as not to have any serious effect upon the maintenance of equilibrium in the first step, $BH_3CO \leftrightarrows BH_3 + CO$. Thus if K is the equilibrium constant of the first step, and k the rate constant of the second, and it is noted that the total reaction yields two units of CO per unit of the rate-determining step, the rate equation is

$$\frac{dx}{dt} = 2kP_{BH_3CO}P_{BH_3} = \frac{2kK(P_{BH_3CO})^2}{P_{CO}} = \frac{2kK(a-x)^2}{x}$$

in which t is the time, a is the initial pressure, and x is the partial pressure of carbon monoxide (twice the observed increase of pressure, and equal to the loss of partial pressure of BH_3CO). Integrating between 0 and t, and 0 and x, gives the more usable form $2kKt = \frac{x}{a-x} - \log_e\frac{a}{a-x} = f(x)$.

It is recognized, of course, that this equation cannot describe the initial rate, because it implies that dx/dt is receding from infinity as the decomposition begins, and it is clear that the equilibrium $BH_3CO \leftrightarrows BH_3 + CO$ could not be maintained against a very rapid drain of BH_3 groups by the second step. Experimentally, it is very difficult to judge the nature of the early reaction, for the initial development of carbon monoxide is so fast even at 0° that the pressure a, corresponding to zero time, cannot be estimated directly. However, on termination of a run by freezing-out, the value of a may be determined from the measured volume of CO

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[1] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, 59, 780 (1937).

and the terminal pressure reading. Then the graph of $f(x)$ *vs.* t is linear through the origin, except that some very early points may deviate more than the experimental error. It is possible also to choose a in such a way that two widely separated points in the range 3–15% decomposition will determine a line through the origin; then all other points in that range will conform very well to the same line.

Thus it appears that the new theory of the rate-determining step applies well to the conveniently-measurable range of each rate experiment, although the estimate of the pressure at zero time cannot be made with sufficient accuracy to give any information about the first 1% of the decomposition process. The values of kK resulting from experiments in the range 0–30°, with initial pressures of 60 to 80 mm., conformed well to an equation of the type log $kK = B - A/T$, in which A ideally would determine the sum of ΔH for the dissociation step $BH_3CO \rightleftarrows BH_3 + CO$ and ΔH for the rate step $BH_3 + BH_3CO \rightarrow B_2H_6 + CO$. Then, if and when some means might be found for resolving this composite ΔH into its components, it would become possible to use the ΔH value for the over-all decomposition $2BH_3CO \rightleftarrows B_2H_6 + 2CO$ (as determined from equilibria) to estimate the ΔH of dissociation of diborane into BH_3 radicals.

The situation evidently lacks ideality, however, for the rates are mildly pressure-dependent and it is noted that the graph of log kK *vs.* $1/T$ is slightly concave-upward; furthermore, the decomposition is not strictly homogeneous, for a twenty-fold increase of surface:volume ratio (with greatly increased opportunity for diffusion to a Pyrex surface) increased the over-all rate, as well as causing definite deviations from the proportionality of $f(x)$ to time. It is possible that some of these slight discrepancies are due primarily to a heterogeneous component even when the surface is relatively small, but it is also possible that the initial dissociation equilibrium is somewhat disturbed by the rapid removal of BH_3 groups by the second-stage reaction, especially in the early range of the decomposition. The character and importance of the heterogeneous reaction cannot be evaluated without much more elaborate experimentation; for the present, however, it appears not to be more important than other experimental errors if the ratio of surface to volume is kept small.

Experimental Part

I. *Determination of Equilibrium Constants*

Small samples of diborane and carefully-measured large proportions of carbon monoxide were heated in Pyrex bomb-tubes for periods of time which preliminary experiments had shown to be ample for a near approach to equilibrium. Each tube was contained in a steel pipe in a thermostatic system having a long-range variation of less than 0.2°. The average temperature was read from a thermometer equally well protected from fluctuations.

A possible slow shift of the desired equilibrium, $2BH_3CO \rightleftarrows B_2H_6 + 2CO$, due to irreversible decomposition of the diborane, was minimized by establishing a high ratio of carbon monoxide to diborane, by including as much as one atmosphere pressure of hydrogen or deuterium in the original mixture, and by avoiding temperatures (*e.g.*, 100°) at which earlier experiments showed scattered results. Some of these experiments were matched by others in which the equilibrium was approached in the opposite direction, with check results.

After the heating period, each bomb-tube was quickly immersed in liquid nitrogen (which then was cooled to −210° by pumping), and opened into the vacuum system. After removal of the non-condensable gases through traps at −196 and −210°, the borine carbonyl was separated from the diborane by fractional condensation at −150°, with subsequent distillation of the diborane from a tube at −160°; the small middle fraction was reworked in the same manner. In some cases a slight trace of less volatile material was trapped out at −120°; this included the previously-observed higher carbonyl[1] and probably higher boranes, in insignificant proportions.

The diborane and borine carbonyl were measured as gases in calibrated parts of the vacuum system, and the carbon monoxide was determined by subtraction from the original amount. The constant then was computed, for pressures in atmospheres, by means of the equation

$$K_{\text{atm}} = \frac{T V_{B_2H_6} V_{CO^2}}{273.2\, U V_{BH_3CO^2}}$$

in which U is the internal volume of the bomb-tube and V is the standard gas-volume of the indicated component. Similar experiments were done with B_2D_6, which was prepared as described elsewhere.[2]

The data and results of the acceptable equilibrium experiments on BH_3CO and BD_3CO are presented in Tables I and II.

TABLE I

DECOMPOSITION CONSTANTS OF BORINE CARBONYL

Vol. bomb, cc.	Time, hours	Temp., °K.	Volumes of components (cc. gases at S.C.) B_2H_6	BH_3CO	CO	K_{atm} Obsd.	Calcd.
46.62	3020	297.5	8.14	37.85	135	2.42	2.45
49.79	2230	297.5	14.10	82.6	235	2.50	2.45
94.7	82	316.7	28.40	103.1	421	5.80	6.20
47.07	140	326.7	8.76	31.6	205	9.37	9.68
125.2	126	326.7	9.72	48.9	500	9.72	9.68
46.18	39	335.7	15.20	60.8	365	14.6	14.2
47.90	39	335.7	15.90	58.14	346	14.4	14.2
47.65	16	349.5	4.17	36.00	539	25.1	24.4
49.10	17	350.9	1.78	22.80	527	25.0	25.7

TABLE II

DECOMPOSITION CONSTANTS OF DEUTEROBORINE CARBONYL

Vol. bomb, cc.	Time, hours	Temp., °K.	Volumes of components (cc. gases at S.C.) B_2D_6	BD_3CO	CO	K_{atm} Obsd.	Calcd.
46.62	434	309.7	5.84	41.6	409	13.1	13.3
46.18	427	309.8	8.84	49.6	444	14.7	13.4
46.18	121	320.5	7.37	44.4	482	22.0	21.1
49.79	136	320.7	9.81	60.0	575	21.3	21.3
47.90	70	333.0	19.00	48.2	408	34.6	34.8
47.90	31	348.6	9.84	32.1	496	62.6	62.6

The results for BH_3CO determine the equation $\log_{10} K_{atm} = 7.104 - 1998/T$, from which $\Delta F^\circ_T = 9142 - 32.51T$ cal. The corresponding equations for BD_3CO are $\log_{10} K_{atm} = 7.097 - 1850/T$ and $\Delta F^\circ_T = 8465 - 32.47T$. The respective standard free energies at 25.0° are −0.55 and −1.23 kcal., slightly favoring decomposition in both cases.

After a number of decomposition-rate experiments had been completed, it became feasible to use the equilibrium results to decide whether the reverse reaction could be neglected. For the case of nearest approach toward equilibrium, that of 13% decomposed BH_3CO at 0.10° (a = 40.77 mm.), K_{atm} was computed as 0.62 and from this the equilibrium partial pressures of the three components were calculated. Then from the tentative value of the constant kK, the reaction rate at equilibrium was calculated, and used to determine the rate constant for the reaction forming BH_3CO from B_2H_6 and CO. This reverse-rate constant then was used to calculate the rate of the formation reaction at the point of 13% decomposition. The result was only 1.0% of the forward rate—well within the general experimental error in the determination of kK. Hence it was concluded that the reverse reaction-rate could be neglected in

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(2) A. B. Burg, THIS JOURNAL, **74**, 1430 (1952).

this and all other decomposition-rate experiments terminating at points farther from equilibrium.

II. The Rates of Decomposition of Borine Carbonyl

Preliminary Measurements.—Before any elaborate experiments were planned, it was considered well to learn whether the rates of decomposition of BH_3CO and BD_3CO would be virtually independent of the wall-area and the starting pressure. The exploratory apparatus was a 150-ml. bulb (immersed in a dewar cylinder filled with water) with attached mercury manometer and a stopcock leading to the main vacuum system. The average temperature deviated no more than 0.2° from the standard 23.0°. In order to test for a surface effect, the bulb was filled with Pyrex helices having a surface area fifteen times that of the inner walls of the bulb–manometer system. Since the helices occupied approximately one-fourth of the space, the actual surface:volume ratio was approximately twenty times that of the bare bulb.

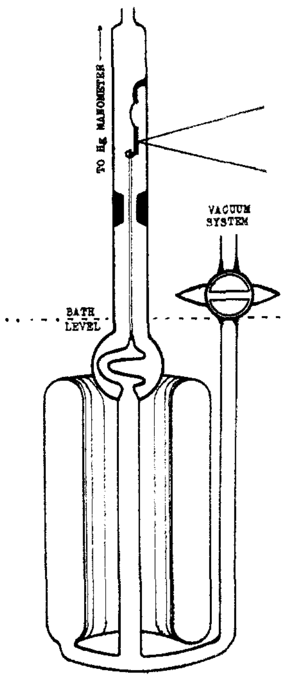

Fig. 1.—Optical-lever piezoscope.

At the start of each experiment the highly purified sample at −196° was warmed suddenly by immersing the container in water; as the vapor entered the reaction bulb, the stopcock was closed and the pressure read within 15 seconds. In all such experiments the pressures were read very frequently in the early stages, in order to obtain the best possible estimate of the true starting point; however, in many cases the early points were not consistent with the later readings, and were discarded on the ground that their purport varied extremely from one experiment to another.

These preliminary experiments showed that for a small surface:volume ratio the graphs of f(x) *vs.* t were strictly linear, but for a large surface:volume ratio most of the curves were noticeably concave-downward, especially in the early regions. For comparison purposes, only the later portions of these curves were used, and kK was determined by assuming a value of a which would give linearity through the origin. The results for both BH_3 and BD_3CO are given in Table III.

TABLE III

DECOMPOSITION OF BH_3CO AND BD_3CO-LARGE SURFACE AT 23°

BH_3CO		BD_3CO	
a (mm.)	$kK \times 10^{-8}$ (sec.$^{-1}$)	a (mm.)	$kK \times 10^{-8}$
12.30	133	....	...
44.24	93	45.25	269
50.20	95	53.42	243
68.4	80	65.4	255
103.5	72	93.0	235
150.1	75	151.9	195

Although there is some disorder, attributable to experimental errors, it is quite clear that the rate increases with decreasing initial pressure, in about the same proportion for both substances. The same trend (with less regularity) was evident in the curves before correction to linearity. The far more precise low-surface experiments with BH_3CO (described later) showed a similar pressure-dependence (average kK value 67 for a = 70, or 76 for a = 40). The larger surface increases the rate about 20 to 25% for BH_3CO, or about 40 to 50% (above kK = 165 at a = 60) for BD_3CO. However, if one extrapolates to zero surface, it appears that the catalytic effect of surface:volume ratios in the neighborhood of 1 cm.$^{-1}$ is well within the probable error of the best experiments.

Precision Rate Studies at Different Temperatures.—For more precise experiments over a range of temperatures, the entire bulb-manometer system was immersed in a bath at each of a number of temperatures held constant to 0.03°. To avoid the increased difficulty of precise reading of mercury levels, the new apparatus employed a pressure-indicator of the Jackson type.[3] In one form of the apparatus, this was mounted vertically upon a 300-ml. bulb, and the motion of the pointer (linear with pressure to 0.01 mm.) was followed across the fixed reference point by means of a horizontal traveling microscope. However, the observations sometimes were uncertain on account of refraction by the slight vertical striations in the glass tube which surrounded the pointer; also vibration was very troublesome. Hence, although some difficult but very satisfactory runs were made by means of this apparatus, it was considered well to modify it to the form shown in Fig. 1.

In this system, the 12-cm. long gage-pointer engaged an inner edge of a glass loop attached to the lower edge of a glass frame carrying a mirror. The frame hung from a short Pyrex filament which acted as a spring, bending with the motion of the pointer. A light beam was reflected off the mirror in such a manner as to focus cleanly upon a vertical meter-scale at a distance of 3 m., permitting better than 0.02 mm. (Hg) precision of measurement. The calibration was linear over a wide range and the readings were not sensitive to vibrations below the direct-sensory level.

In this modified apparatus the gas occupied the space (280 cc.) between concentric cylindrical walls 12 mm. apart —a container-shape which should permit more efficient removal of heat during the early part of the decomposition, without an unallowable increase of wall area. However, this change did not improve the consistency of the initial points with the main curve; in fact, the results were altogether in agreement with those from the bulb-type apparatus.

In some experiments it was possible to estimate the initial pressure (a) from a few readings taken very soon after the start, but in most cases the results showed greater consistency if a were so chosen that a graph of f(x) *vs.* t gave the best straight line through the origin and a group of typical early and late points. The intermediate points then also determined the same line, the slope of which gave a value for kK. The correctness of this interpretative procedure was demonstrated by four experiments (using the optical-lever system) in which the decomposition was terminated by suddenly passing the reaction mixture into a series of U-tubes at −196° and drawing the CO off through a quick-acting Toepler pump into a measuring tube. By previous calibration of the reaction-chamber against the same measuring tube, the partial pressure of the CO in the mixture at the

TABLE IV

DECOMPOSITION OF BH_3CO AT 0.00°

Time, min.	$p_{mm.}$	1000 f(x) Obsd.	1000 f(x) Calcd.
0	(74.50)	...	...
10	74.54	0.001	0.017
15	74.63	.007	0.026
20	74.72	.017	0.034
25	74.76	.025	0.043
40	74.92	.064	0.068
50	75.03	.103	0.085
60	75.07	.119	0.103
200	75.48	.358	0.342
450	75.93	.78	0.77
700	76.28	1.21	1.20
980	76.56	1.66	1.67
1620	77.12	2.72	2.77
1690	77.21	2.92	2.89
1890	77.34	3.23	3.23
1995	77.40	3.38	3.41
2000	77.40	3.38	3.42

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(3) T. E. Phipps, M. L. Spealman and T. G. Cooke, *J. Chem. Ed.*, **12**, 318 (1935).

terminal point could be estimated closely; then *a* was obtained by subtracting half the partial pressure of the CO from the terminal pressure-reading. The detailed rate-data of one such experiment are given in Table IV, and the three others are shown in Fig. 2. This figure includes also two runs which were interpreted by the linearization method —one from data obtained by the traveling microscope (16.90°) and one by the optical lever (13.28°) with the bath darkened by india ink, proving no photochemical effect in the other experiments.

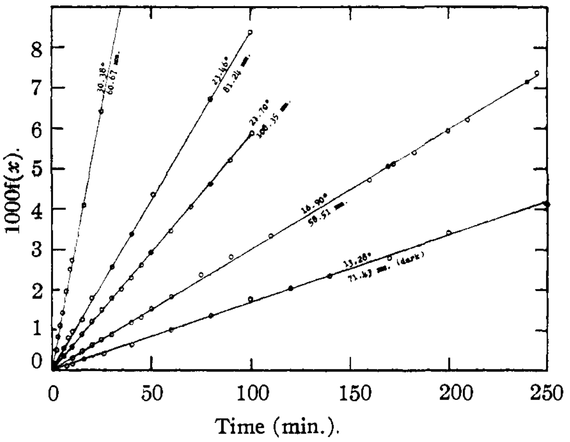

Fig. 2.—Rate curves for the decomposition of borine carbonyl.

Table V presents a summary of twelve runs with BH_3CO. Those at 0, 13.28, 21.70, 23.46 and 30.38° were done by means of the optical lever system, with CO pump-off except at 13.28°. The seven others were done by the microscope method, with estimation of *a* from early points or by the linearity principle. It is noted that the average deviation of 1000 f(*x*) from the best line increases sharply with the extent of the reaction. The reason is that this function becomes more and more sensitive to errors of pressure-reading as the process becomes slower; thus at the end of the experiment at 22.94°, the rate of change of 1000 f(*x*) was 0.16 per 0.01 mm. of pressure. The trend still was linear, but the points near the end could not be taken very seriously.

TABLE V

RATES OF DECOMPOSITION OF BH_3CO

Temp., °C.	*a*, mm.	t_{end}, min.	Dec. at end, %	Terminal 1000 f(*x*)	Av. dev. 1000 f(*x*)	kK (sec.$^{-1}$) × 10^8 Obsd.	Calcd.
0.00	74.50	2000	7.8	3.38	0.02	1.42	1.32
0.10	40.77	4325	12.9	8.95	.05	1.67	1.35
11.18	73.03	400	9.1	4.72	.03	10.0	9.7
13.28	71.43	420	11.0	7.05	.03	13.8	13.8
16.90	58.51	250	11.3	7.50	.03	24.8	25.2
21.70	108.35	101	10.1	5.89	.02	48.5	54.7
22.94	40.29	360	21.7	32.6	.17	75.5	66.7
23.42	79.24	100	11.8	8.35	.02	69.6	72.0
23.46	81.24	100	11.9	8.38	.02	69.1	72.3
28.86	67.00	72	15.6	15.65	.06	169	166
29.69	27.65	34	12.9	10.07	.03	246	188
30.38	60.67	60	15.6	15.05	.05	209	209

Table VI summarizes six BD_3CO experiments, the first four of which were done by the optical-lever method and the last two by the preliminary bulb–Hg-manometer method at pressures far enough apart to show the increase of rate at lower pressures.

TABLE VI

RATES OF DECOMPOSITION OF BD_3CO

Temp., °C.	*a*, mm.	t_{end}, min.	Dec. at end, %	Terminal 1000 f(*x*)	Av. dev. 1000 f(*x*)	kK (sec.$^{-1}$) × 10^8 Obsd.	Calcd.
9.70	50.25	250	10.7	7.00	0.035	23.3	23.3
14.71	59.95	160	12.9	9.92	.05	51.5	49.9
20.26	62.68	67	12.0	8.51	.02	106.5	112.5
25.86	51.08	54	15.8	15.07	.05	247	247
23.1	31.95	180	23.5	39.4	.15	184	168
23.0	63.50	240	25.4	47.8	.25	166	166

Figure 3 demonstrates the nearly linear relation between log *kK* and 1/*T* for all experiments at similar pressures of BH_3CO or BD_3CO. The effect of pressure is evident in the position of the points representing the experiments starting at 40.77, 108.35, 40.29 and 27.65 mm.; also since the point representing the experiment at 16.90° (58.51 mm.) is low in spite of the lower-than-average pressure, while that corresponding to 0.00° (74.50 mm.) is slightly above the line, the true line evidently would have a slight upward-concavity.

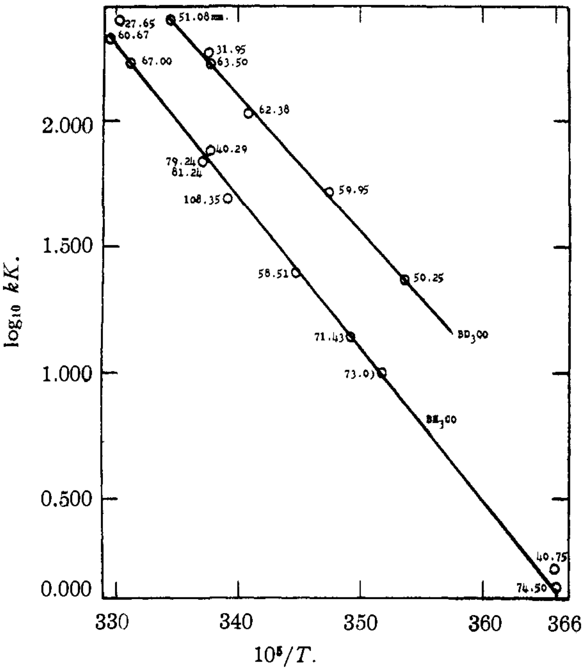

Fig. 3.—Log *kK* *vs.* 1/*T* for BH_3CO and BD_3CO.

The line drawn for BH_3CO corresponds to $\log_{10} kK = 14.087 - 6000/T$, which implies the value 27.5 kcal. for the composite ΔH. The corresponding line for BD_3CO is $\log_{10} kK = 12.352 - 5370/T$, implying that $\Delta H = 24.6$ kcal. The possible experimental errors are such that the true ΔH values are not necessarily different.

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