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The Kinetics of the Pyrolysis of Carbon Monoxide Borane

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An infrared spectrometer study was carried out on the decomposition of carbon monoxide borane in a heated infrared cell. The concentration of each component, carbon monoxide borane and diborane, was followed by means of infrared spectrometric analysis, and the total pressure change was followed simultaneously by means of a pressure transducer attached to the heating cell. The effects of surface, photolysis by the infrared beam, the presence of diborane and the addition of carbon monoxide and hydrogen on the rate of the decomposition were observed. A mechanism for the decomposition of carbon monoxide borane is proposed. This mechanism involves as the slow step, $OCBH_3 \rightarrow BH_3 + CO$, and the equilibrium $BH_3 + BH_3 = B_2H_6$ is followed by the relatively rapid reactions $BH_3 + CO \rightarrow OCBH_3$ and $BH_3 + OCBH_3 \rightarrow B_2H_6 + CO$. The disappearance of $OCBH_3$ is expressed by the rate equation $\frac{-d(OCBH_3)}{dt} = \frac{2k_1(OCBH_3)^2}{(CO) + (OCBH_3)}$. This is confirmed by linear second order plots with the slopes inversely proportional to the sum of the existing $OCBH_3$ and CO pressures (constant for a given run) at 54 to 64°. Small amounts of hydrogen and higher boron hydrides are also formed as the result of the decomposition. The initial first order rate constant for the decomposition of $OCBH_3$ is expressed by the Eyring absolute rate equation $k' = 1.25 \times 10^{12}T \exp(-28{,}400/RT) \exp(10.2/R)$ min.$^{-1}$.

Burg[1,2] has studied the decomposition of carbon monoxide borane and has proposed a theory of the decomposition rate process. However, Bauer[3] suggested in his treatment of energetics of the boranes that the mechanism proposed by Burg was not correct because it was incompatible with other kinetic data for the reaction involving diborane and he proposed an alternate mechanism based on Burg's data. In view of this difference, it was believed that the investigation of the kinetics and mechanism of decomposition of carbon monoxide borane would be considerably aided by an application of infrared spectroscopy which permits direct measurement of the concentration of the reactants and products during the course of the reaction.

Experimental

Carbon monoxide borane was prepared from diborane and carbon monoxide in a Pyrex reaction tube. After heating for 20 minutes at 90–95°, the tube was attached to the vacuum line, and the contents were fractionated at low temperature.[4]

In the apparatus used for the kinetic studies, decompositions were carried out in a heatable infrared cell of 6.59 cm. length. The cell, which consisted of an inner cell and an outer cell, was constructed of a brass body and NaCl windows. The outer cell, which could be evacuated, was used to aid in maintaining constant temperature in the inner cell. The inner cell was first wrapped with copper wire to serve as a thermoregulator and then with a nichrome heating element on a separate layer. Two tubes from the top of the inner cell were attached to a stopcock, which was in turn connected to a U tube and to a pressure transducer respectively. The U tube was used to condense the sample before transferring it into the cell for the reaction. An iron-constantan thermocouple was fitted through one of the tubes into the cell. The temperature in the cell was maintained constant to ± 0.1°. The pressure transducer (Statham Laboratories, Model No. p24-2A-500-p10A) was used to measure the total pressure during the decomposition, and a Perkin–Elmer Model 21 infrared spectrometer (double beam) was used to monitor the concentration changes of $OCBH_3$, B_2H_6, and other species involved, as recorded in the spectra.

An $OCBH_3$ sample was condensed into the U tube attached to the cell at liquid nitrogen temperature. The cell was then placed in the sample beam of the infrared spectrometer and heated to a desired temperature. After the cell temperature became constant, the liquid nitrogen bath was removed from the U tube and the $OCBH_3$ sample was admitted to the cell to undergo reaction.

A quantitative analysis could be made from the spectra to determine the concentration of $OCBH_3$ and B_2H_6 during the reaction. The calibrated absorptivities for $OCBH_3$ and B_2H_6 at the various characteristic absorption peaks are collected in Table I. Carbon monoxide, though it has a characteristic absorption peak at 4.66 microns, did not contribute any appreciable peak in the range of pressure concerned (below 100 mm.) for the particular cell of 6.59 cm. length. However, the amount of CO would be determined since the quantity of CO produced was equal to the $OCBH_3$ which decomposed. The total pressure change was followed by measuring with a Leeds and Northrup potentiometer which was connected to a control unit (Statham Model CB 18) and then to the pressure transducer.

The infrared spectra were recorded shortly after the sample was admitted to the cell. The initial concentration was determined satisfactorily by extrapolating the $OCBH_3$ and B_2H_6 concentrations to zero time. This result was further checked against the initial total pressure which was also obtained by extrapolation.

The decomposition products were analyzed by a mass spectrometer (Consolidated Electrodynamics Model 21-620), which permitted the detection of small amounts of hydrogen and higher boron hydrides formed.

Results

One of the typical pressure–time curves is shown in Fig. 1. $OCBH_3$ and B_2H_6 curves were plotted from the results of the spectra analyses. The partial pressure of CO was calculated from the difference between the initial and final pressure of $OCBH_3$. The total pressure actually was measured experimentally. All the values were corrected to 25°.

The formation of hydrogen was not expected originally. However, the total pressure increased considerably more than could be calculated from the stoichiometric equation $2\ OCBH_3 = B_2H_6 + 2\ CO$. This pressure difference became greater with time as the reaction went on, hence it appeared that some other components were present besides the above. Mass spectrometric analysis of the final products gave evidence for the formation of hydrogen. By assuming that the difference of total pressure actually measured and that summed up from

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(1) A. B. Burg, *J. Am. Chem. Soc.*, **74**, 3482 (1952).

(2) A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

(3) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(4) (a) Appreciation is expressed to the University of Utah Research Fund for the Mass Spectrometer and Infrared Spectrometer used in this research. This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research & Development Command, under Contract No. AF 49(638)-28. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) Special efforts were not made to remove B_2H_6 completely from the $OCBH_3$ since it was expected that B_2H_6 had no appreciable effect upon the rate in the early stages of the process as suggested by Burg and Schlesinger. However, later it was found that this assumption was valid only when the initial concentration of B_2H_6 was low.

TABLE I

ABSORPTIVITIES FOR $OCBH_3$ AND B_2H_6

(Absorbance per mm. pressure per 6.59 cm. cell)

Compound	2.7 μ	3.54 μ	3.82 μ	4.12 μ	4.61 μ	6.23 μ
$OCBH_3$	0.00	0.00127 ± 0.00004	....	0.0100 ± 0.0002	0.0897 ± 0.0047	0.00
B_2H_6	.00277 ± .00002	.00	0.0165 ± 0.0004	.00	.00	.0545 ± 0.003

each component known from the spectra analysis was due to hydrogen, the dotted line shown in Fig. 1 was obtained. Besides the H_2, trace amounts of B_4H_{10}, B_5H_9 and B_6H_{10} also were detected, especially for the runs at high initial pressure and temperature.

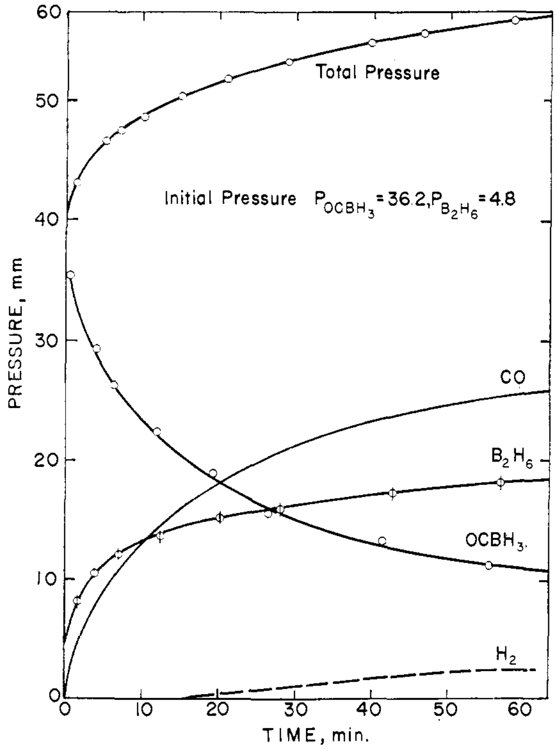

Fig. 1.—Pressure-time curve.

Examination of the disappearance of $OCBH_3$ shows, at a given temperature, that the rate of the disappearance is second order after a period of a few minutes to one quarter hour depending on the initial $OCBH_3$ and B_2H_6 pressures and the reaction temperature. Considering the second order part of the rate

$$\frac{-\mathrm{d}\,P_{OCBH_3}}{\mathrm{d}t} = k_{exp}P^2_{OCBH_3}$$

when $1/P_{OCBH_3}$ is plotted against the time a linear plot is obtained. The slope of this line gives the rate constant k_{exp} in the above equation. However, it was also found that the k_{exp} value was dependent upon the initial $OCBH_3$ pressure. Figure 2 shows the plots for various initial $OCBH_3$ pressures at an average temperature of 60.2°. When the k_{exp} values are plotted against the reciprocal of the initial $OCBH_3$ pressures, linear plots were obtained for different temperatures as shown in Fig. 3. The slope of each line is expressed as k'_{exp} and given in the last column of Table II.

A plot of the logarithm of k'_{exp}/RT *versus* $1/T$ is linear, and the slope gives the value 28.4 kcal. per mole for the heat of activation in the 54 to 64° temperature range.

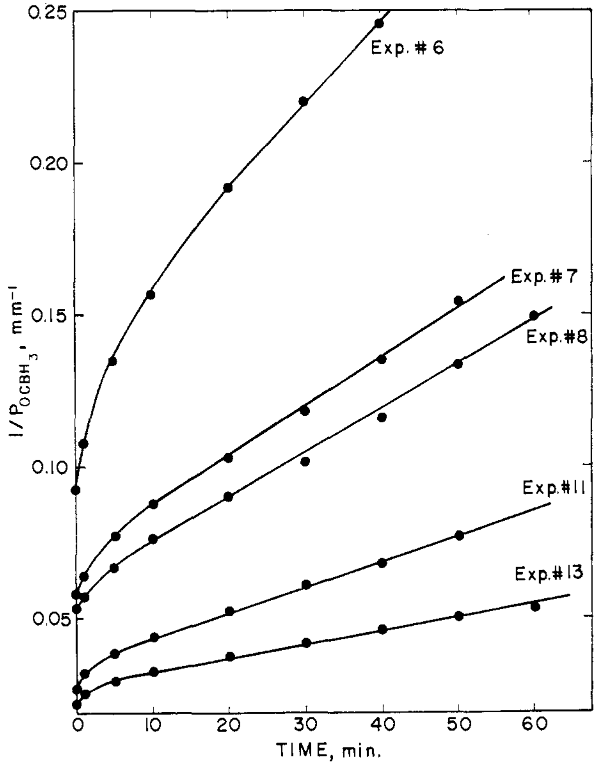

Fig. 2.—Second order plots of $OCBH_3$ disappearance at 60.2°.

The non-linear part of the second order plot for the initial period of the decomposition and the different slopes of the plot at various pressures for a given temperature suggest that the decomposition is not a simple bimolecular collision of two $OCBH_3$'s. It is interesting to notice that Burg[1] also found that the rate constant applied to his mechanism increased as the initial pressure decreased. To determine the exact mechanism, the effects of component partial pressures, of variation in surface area, and of photolysis were observed.

An experiment was performed in which the surface to volume ratio of the cell was increased about four times by putting 5 g. of copper powder (200 mesh) in the cell. The rate increased only about 30%, demonstrating that the reaction was essentially homogeneous as far as the copper surface is concerned. Other evidences for homogeneity are the reproducibility of the results and the fact that higher pressures do not cause a decrease in the rate.

The possibility of the photolytic effect of the infrared beam was tested by performing the experi-

TABLE II

DECOMPOSITION OF $OCBH_3$ AND k_{exp} FOR THE SECOND ORDER PLOT

Exp. no.	Temp., °C.	Initial pressure, mm. $OCBH_3$	B_2H_6	t_{end}, min.	Decomp. at end, %	$k_{exp} \times 10^{-4}$, $mm.^{1-} min.^{-1}$	$k'_{exp} \times 10^2$, $min.^{-1}$
			Av. temp., 54.0				
1	54.0	13.6	1.6	60	61.0	9.85	
2	54.1	23.3	3.0	50	49.6	6.10	1.37
3	54.0	29.7	4.0	60	47.8	3.82	
4	54.0	44.7	2.1	50	47.4	3.11	
			Av. temp., 60.2°				
5	60.0	8.4	3.1	60	67.7	38.77	
*6	60.0	10.8	3.9	50	66.0	28.40	
7	60.5	17.2	2.1	50	62.2	16.46	3.19
8	60.2	18.2	6.8	60	64.2	14.97	
*9	60.5	33.5	6.1	60	66.0	9.44	
10	60.5	36.2	4.8	60	69.6	10.33	
11	60.5	36.7	5.4	50	64.6	8.78	
*12	60.0	36.8	2.2	60	67.1	8.89	
13	60.0	46.0	7.2	60	59.1	4.35	
			Av. temp., 64.1°				
14	64.1	17.6	6.0	50	76.1	33.32	
15	64.0	22.5	3.0	70	79.6	23.17	5.21
16	64.4	41.0	17.0	50	72.2	10.36	
17	63.9	120	8.0	60	75.8	4.17	

ment in which the decomposition was carried out without the presence of the infrared beam except for the moments when it was necessary to record a peak of the $OCBH_3$ spectrum. The experiments 6, 9 and 12 (marked with *) in Table II are the runs carried out in this manner. Comparison of the experiments 11 and 12, in which the initial $OCBH_3$ pressure and the reaction temperature were nearly the same, shows that the decomposition rates were identical. Therefore, the photochemical effect of the infrared beam on the decomposition of $OCBH_3$ was not significant.

The experimental results shown in Table II indicate that the presence of B_2H_6 at low concentrations does not affect the rate appreciably, since the k_{exp} value is dependent only upon the initial $OCBH_3$ concentration for a given temperature. However, it was shown that appreciable concentrations of B_2H_6 increased the initial rate and the percentage of decomposition considerably. In examining the infrared spectra it was found that the absorption peaks corresponding to B_4H_{10} appeared and then diminished gradually as the reaction proceeded. It is apparent that the B_2H_6 decomposes simultaneously to form higher boron hydrides. These in turn affect the rate of the decomposition of $OCBH_3$. Indeed, in some runs where a small amount of B_4H_{10} was present initially, a great increase of the rate was observed.

TABLE III

EFFECTS OF THE ADDITION OF CO

Exp. no.	Temp., °C.	Initial pressure, mm. OC-BH_3	B_2H_6	CO	OC-BH_3 + CO	t_{end}, min.	Decomp. at end, %	$k_{exp} \times 10^4$, $mm.^{-1}$ $min.^{-1}$
18	60.6	47.8	12.5	30.7	78.5	60	43.1	2.62
19	61.0	38.2	10.0	52.4	90.6	60	39.0	2.85
20	60.6	25.3	3.4	27.9	53.2	60	41.3	4.38
21	60.4	30.2	6.5	17.3	47.5	60	49.0	5.03
22	60.6	24.6	13.5	7.5	32.1	60	49.6	8.01

Further investigation indicated that the initial addition of CO depressed the rate. The results are given in Table III. The plot of k_{exp} *versus* the reciprocal of the sum of the initial $OCBH_3$ and CO pressures for the average temperature of 60.6° was found to be linear. It was also found that the second order plots became linear almost as soon as the reaction started. This is shown in Fig. 4. A run to determine the effect of H_2 on the rate indicated no appreciably change in rate or in the time required to reach second order dependence.

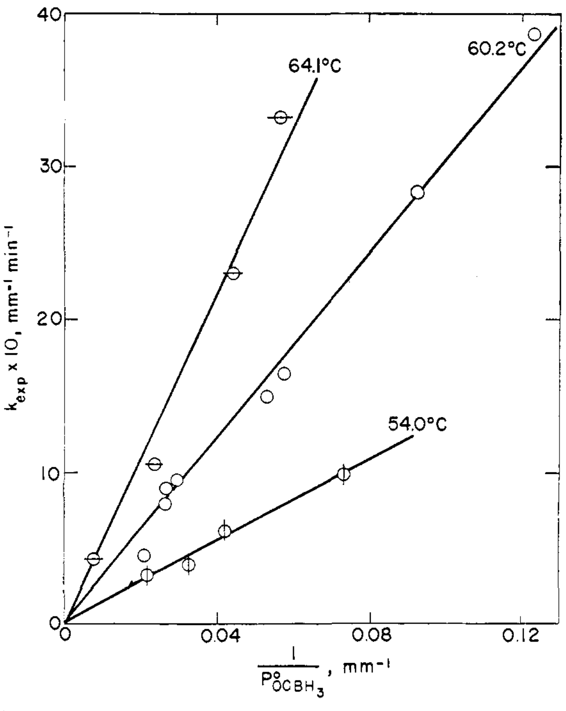

Fig. 3.—Experimental second order rate constant *vs.* reciprocal of the initial $OCBH_3$ pressure.

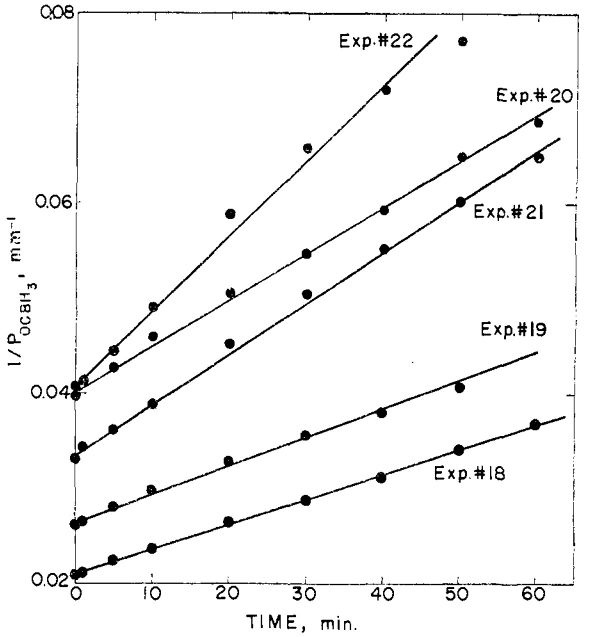

Fig. 4.—Effect of the addition of CO on the second order plot of $OCBH_3$ disappearance.

Discussion

The inverse pressure dependence of the rate on the sum of CO + $OCBH_3$ demonstrates that the reaction does not follow a simple bi-molecular path. The mechanisms proposed by Bauer[3] and by Burg,[1] while not correct in detail, proved to be good bases for the mechanism proposed below which does account for all of the experimental observations.

The $OCBH_3$ decomposes initially by a first order reaction

$$OCBH_3 \longrightarrow BH_3 + CO\ (k_1) \qquad (1)$$

The equilibrium reaction

$$BH_3 + BH_3 = B_2H_6\ (K_{eq}) \qquad (2)$$

is followed by simultaneous reactions

$$BH_3 + CO \longrightarrow OCBH_3\ (k_2) \qquad (3)$$

$$BH_3 + OCBH_3 \longrightarrow B_2H_6 + CO\ (k_3) \qquad (4)$$

Bauer's suggestion that k_2 does involve an activation energy is employed in equation 3. Neglecting the later steps to account for the formation of H_2 and higher boron hydrides for the moment and assuming that the k_2 and the k_3 are of the same order of magnitude, it can be shown that the rate is

$$\frac{-d\,(OCBH_3)}{dt} = \frac{2k_1\,(OCBH_3)^2}{(CO) + (OCBH_3)}$$

This agrees with the experimental rate equation

$$\frac{-d\ P_{OCBH_3}}{dt} = \frac{k'_{exp}}{P^0_{OCBH_3}}\,P^2_{OCBH_3}$$

The postulated rate equation is further justified by observation that k_{exp} decreases as CO is added. It is obvious that the denominator remains constant, in a given run, regardless of the amount of CO added initially. The slope of the linear plot obtained from Table III gives k'_{exp} as 2.69×10^{-2} min.$^{-1}$ for the average temperature of 60.6°. This value, however, is somewhat smaller than the value of 3.19×10^{-2} min.$^{-1}$ for 60.2°, as shown in Table II. It may be that the difference could be caused by a slight difference in the actual magnitudes of k_2 and k_3.

Comparison of the rate equation with the experimental equation reveals that

$$2\,k_1 = k'_{exp}$$

Hence, the activation energy (28.4 kcal./mole) obtained from the plot of log k'_{exp}/RT *versus* $1/T$ is the activation energy of the first step shown in equation 1. The entropy of activation is then found to be 10.2 e.u.

The scheme presented in the above is analogous to that proposed by Burg[1] except that he assumes the reaction $OCBH_3 \rightarrow BH_3 + CO$ to be in a rapid equilibrium, which apparently is not the case in this system. The equilibrium condition (2) was introduced from the consideration that the rate of association of BH_3 to B_2H_6 is greater than the rate of reactions 3 and 4. By accepting this condition, one can specify the concentration of BH_3 at each instant from the known concentration of B_2H_6. The concentration of BH_3 is so small, however, that its rate of change may be set equal to zero without serious error.

The departure from linearity in the early range of the reaction is suggestive of a complication in the mechanism during that period. The observation that the presence of appreciable B_2H_6 increases the initial rate of $OCBH_3$ decomposition may possibly give an explanation. Whatever the reaction step which causes the complication may be, it is apparently strongly inhibited by CO. The experimental results also indicate that the non-linear period is shorter at higher temperature.

The evidence of formation of H_2 and higher boron hydrides suggests the following steps may be the possible course of the decomposition in the later stage, though they are minor

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2 \qquad (5)$$

$$B_3H_7 + B_2H_6 \longrightarrow \text{higher hydrides} + H_2 \qquad (6)$$

Values of the rate constant k_1 are listed in Table IV. The temperature dependence of k_1 may be expressed by the Eyring absolute rate equation

$$k_1 = 1.25 \times 10^{12}T\,e^{-28,400/RT}\,e^{10.2/R}\ \text{min.}^{-1}$$

Table IV

Initial First Order Rate Constants

Temp., °C.	$k_1 \times 10^3$, min.$^{-1}$
54.0	6.85
60.2	15.96
64.1	26.57

The thermodynamics of the system may then be treated as follows. Since the B-C bond energy is calculated to be 18.8 kcal. by Bauer and McCoy[5] based on Burg's[1] equilibrium data of $OCBH_3$, reaction 3 (rate constant is k_2) has an activation energy of 9.6 kcal. From the known value of the entropy change ($\Delta S° = 33.17$ e.u.)[6] for $BH_3 + CO = OCBH_3$, the entropy of activation of reaction 3 is

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(5) R. M. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

(6) A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).

TABLE V

HEAT AND ENTROPY OF ACTIVATION

	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	Temp. range	Ref.
$OCBH_3 \rightarrow BH_3 + CO$	10.2	28.4	327 to 337°K.	This paper
$BH_3 + CO \rightarrow OCBH_3$	−23.0	9.6	327 to 337°K.	This paper
$B_2H_6 \rightarrow BH_3 + BH_3$	....	28.4	....	Bauer[8]
$BH_3 + BH_3 \rightarrow B_2H_6$	....	0	....	Assumed by Bauer[8]

calculated to be −23.0 e.u. Table V summarizes the values of heat and entropy of activation.

A rough calculation indicates, at 60°, that the equilibrium constant for $OCBH_3 = BH_3 + CO$ is of the order of 10^{-5} (K_p, atm.), and that k_2 is approximately 1.6×10^3 atm.$^{-1}$ min.$^{-1}$. It is obvious that k_2 is much larger than k_1 and the decomposition of carbon monoxide borane to borane and carbon monoxide (eq. 1) is the slow step of the process.

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Phosphorus Nitrogen Chemistry. IV. The Reactions of Dimethylaminophosphines with Boron Trihalides and Trialkyls[1,2]

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The reactions of $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$ with $B(CH_2CH_3)_3$, $B(CH_3)_3$, BF_3 and BCl_3 have been investigated. Evidence indicates that $B(CH_2CH_3)_3$ forms liquid 1:1 adducts at room temperature. $B(CH_3)_3$ forms solid 1:1 adducts at −46°. The reactions with BF_3, BCl_3 and excess $B(CH_3)_3$ were complex and slow. Analysis of the products yields $(CH_3)_2NBY_2$, where Y is CH_3, F or Cl, in all cases except the $P[N(CH_3)_2]_3$–$BCH_3)_3$ case. The data indicate that the reaction $(CH_3)_xP[N(CH_3)_2]_{3-x} + (3 - x)BY_3 \rightarrow (3 - x)(CH_3)_2NBY_2 + (CH_3)_xPY_{3-x}$ where x is 0, 1 or 2, proceeds to some extent in all cases, and over 75% in the $P[N(CH_3)_2]_3$-BF_3, $P[N(CH_3)_2]_3$-BCl_3 and $(CH_3)_2PN(CH_3)_2$–$B(CH_3)_3$ cases. Secondary reactions between $(CH_3)_xPY_{3-x}$ and the reactants led to an investigation of $(CH_3)PCl_2$ and $(CH_3)_2PCl$ with BCl_3. Solid 1:1 adducts were found at 0° which were slightly dissociated at room temperature. A possible reaction mechanism indicated by the data is considered.

Previously a study[4] of the thermal decomposition of borine adducts of $(CH_3)_2PN(CH_3)_2$ led to the production of N–B and P–B products. Working with trimethylborane and triethylborane, 1:1 adducts were formed in this study with the dimethylaminophosphines, $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$ and $(CH_3)_2PN(CH_3)_2$; however, in the case of the trimethylborane adducts and excess trimethylborane, further reaction ensued. Preliminary experiments showed that such reactions proceed much faster with boron trichloride in the initial stages as evidenced by the rapid take up of the gaseous trichloride by tris-dimethylaminophosphine. Fractionation of the product mixture in this case led to the isolation of dimethylaminoboron dichloride, phosphorus trichloride and small amounts of an oil.

To ascertain the variety and extent of the reactions occurring as well as correlate the behavior involved as far as possible, a more thorough investigation was conducted in which the reactions of the dimethylaminophosphine series with trimethylborane, boron trichloride and boron trifluoride were studied systematically.

Experimental and Results

Apparatus.—High vacuum systems equipped with mercury-float valves were used for part of this study. In general transfer operations outside the line and weighings were performed with the aid of a dry box. Samples of the phosphines, after purification in the vacuum line, were weighed without exposure to air directly into ampoules fitted with break tips and sealed and stored until ready for use. A special "reaction section" previously described[5] was used to study pressure-composition diagrams and to carry out the reactions in the systems described below.

In all tables reporting pressure–composition data, the mole fractions refer to condensed phase values. All ratios of quantities referred to in reaction mixtures are given in terms of moles.

Materials.—The purification of tank boron trifluoride and trichloride (Matheson) was described previously.[6] Vapor pressures of boron trifluoride samples at −111.7° were 297 mm. and for boron trichloride, 477 mm. at 0°.

Trimethylborane was prepared by a method described by Brown.[7] After fractionation the vapor pressure at −78.5° was 30.6 mm. (literature value,[8] 32 mm. at −78.4°).

Triethylborane (Callery Chemical Co.) was fractionated just prior to its use since increases in pressure were noted on storing.[8] The fractionated material exhibited a vapor pressure of 12.2 mm. at 0° (literature value[7,8] 12.4 mm., 12.5 mm. at 0°). The pressure would rise to about 16 mm. at 0° after 24 hr. and to as high as 40 mm. at 0° after a month of storage at room temperature.[8]

Tris-dimethylaminophosphine, $P[N(CH_3)_2]_3$, was prepared by the dimethylamine reaction with phosphorus trichloride in ether solution, similar to that described by Burg and Slota.[9] After distillation and fractionation in the line using −8°, −78° and −196° traps, the −8° trap contained the product having a vapor pressure of 2.2 mm. at 20° (literature,[9] 2.8 mm. at 20°) and a boiling point of 161° at 736.4 mm. (literature,[9] 163.5 at 760 mm.).

Dimethylaminodimethylphosphine, $(CH_3)_2PN(CH_3)_2$, was prepared and fractionated according to the procedure of Burg and Slota.[9] Vapor pressure at 0° was 12.2 mm. (literature,[9] 12.53 mm. at 0°).

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(1) Previous paper in the series: R. R. Holmes, *J. Am. Chem. Soc.*, **83**, 1334 (1961). Presented before the Inorganic Division at the 140th Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

(2) This paper represents part of the work submitted by Raymond P. Wagner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(3) Research assistant (1959–1961), National Science Foundation Grant.

(4) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **82**, 2145 (1960).

(5) H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 6275 (1953).

(6) H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).

(7) H. C. Brown, *ibid.*, **67**, 374 (1945).

(8) A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921). These authors observed similar behavior and showed that small amounts of C_2H_6 and H_2 were produced.

(9) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).