Exchange Rates.—Because of the fact that only a small fraction of each of the hydrocarbons is converted to the anion, the e.s.r. spectra of the anions were necessarily observed in the presence of excess hydrocarbon. For the systems naphthalene negative ion–naphthalene[19] and anthracene negative ion–anthracene[20] rapid oxidation reduction exchange reactions which conceal the hyperfine splittings occur. Since for the ions here described well resolved hyperfine structure was observed in the presence of neutral hydrocarbons at about 1 *M* the exchange rates are considerably lower than for the naphthalene and anthracene systems. At temperatures in the range −50 to −80° the second-order rate constants for oxidation reduction exchange are less than 5×10^5 l. mole^{-1} sec.$^{-1}$.

ST. LOUIS, MISSOURI

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[19] R. L. Ward and S. I. Weissman, THIS JOURNAL, **79**, 2086 (1957).

[20] E. de Boer, unpublished observation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. JOSEPH'S COLLEGE, AND THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Lower Hydrides of Phosphorus. III. The Interaction of Biphosphine and Diborane[1]

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Diborane and boron trifluoride react with biphosphine to produce the compounds $P_2H_4 \cdot B_2H_6$ and $P_2H_4 \cdot 2BF_3$, respectively The compound formed with diborane is more stable than biphosphine toward decomposition, with the elimination of phosphine, but the compound with boron trifluoride eliminates phosphine at temperatures above −118°. When biphosphine is treated with diborane at room temperature, both phosphine and hydrogen are evolved leading to defective solids containing boron, phosphorus and hydrogen.

Previous communications have been concerned with the decomposition of biphosphine *in vacuo* at room temperature[2a] and in liquid ammonia at its boiling point.[2b] In both cases phosphine is eliminated and solid hydrides of indefinite composition are produced.

In the present study we have examined the interaction of biphosphine with the Lewis acids, boron trifluoride and diborane. The compounds $P_2H_4 \cdot 2BF_3$ and $P_2H_4 \cdot B_2H_6$ are formed, respectively. The compound formed with boron trifluoride is considerably less stable than biphosphine itself and decomposes rapidly at −78° to yield both boron trifluoride and phosphine. The compound with diborane, on the other hand, is more stable than biphosphine. It may be formed at −35° where biphosphine decomposes at a measurable rate. Apparently it may also be formed at room temperature under pressure of excess diborane. Removal of excess diborane then causes the elimination of diborane, phosphine and hydrogen, leaving a defective solid containing boron, phosphorus and hydrogen. When the compound is heated rapidly to 0° dissociation and decomposition occur together.

The greater stability of $P_2H_4 \cdot B_2H_6$ as compared with $P_2H_4 \cdot 2BF_3$, or P_2H_4 itself, may be attributed to the availability of electrons in the B–H linkage to back-bond to available d-orbitals in phosphorus. An interaction of this kind would tend to augment the sigma dative bonding[3] and probably increase the electron density of the P–P bond, leading to increased stability. An opposite effect might be expected here with boron trifluoride. The electronegative fluorine atoms probably would permit only sigma dative bonding, thus rendering the phosphorus atoms more positive and reducing the electron density of the P–P bond.

The greater chemical stability of $B_2H_6 \cdot P_2H_4$ as compared with P_2H_4 is demonstrated further by its behavior toward HCl. Thus HCl has been shown to effect a rapid decomposition of P_2H_4 into PH_3 and a yellow solid hydride at temperatures as low as −125°,[4] whereas HCl does not react with $P_2H_4 \cdot B_2H_6$ at a measurable rate at −78°.

Experimental

1. **Reagents and Procedure.**—Diborane was prepared by allowing a slurry of lithium aluminum hydride in anhydrous di-*n*-butyl ether to react with the di-*n*-butyl etherate of boron trifluoride. The diborane as produced was swept from the reaction vessel with nitrogen through two traps cooled to −78 and −119°, respectively. It was collected in a trap covered with liquid air then transferred to a two liter storage vessel equipped with a Stock valve and a manometer. Biphosphine was prepared and purified as described previously.[1]

Reactants were measured out by volume as gases in a calibrated section of the vacuum apparatus. Condensable products were separated by fractional condensation and characterized by standard methods. The analyses of mixtures of diborane and phosphine were carried out by hydrolyzing the diborane and measuring the hydrogen formed in the hydrolysis, along with residual phosphine. Results on mixtures were checked by molecular weight determinations.

2. **Reaction of Biphosphine and Diborane at Low Temperature.**—A measured excess of diborane was added to a given amount of biphosphine. The course of the reaction was followed by measuring the unreacted diborane. The latter was removed at −78° where the vapor pressure of biphosphine is less than one mm.[1] Although biphosphine melts at -92°,[3] reaction with diborane occurs below this temperature. The reactions were allowed to continue at the temperatures indicated in Table I until it was established that the consumption of diborane was negligible over a 24 hr. period. The final molar ratios show that $P_2H_4 \cdot B_2H_6$ was formed. This is a white solid, stable at −78° and possessing no appreciable vapor pressure.

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[1] Presented before the Inorganic Division, American Chemical Society, 132nd National Meeting, New York City, September, 1957.

[2] (a) E. C. Evers and E. H. Street, Jr., THIS JOURNAL, **78**, 5726 (1956); (b) E. H. Street, Jr., D. M. Gardner and E. C. Evers, *ibid.*, **80**, 1819 (1958).

[3] W. A. G. Graham and F. G. A. Stone, *Chem. Ind.*, 319 (1956).

[4] R. Royen and K. Hill, *Z. anorg. allgem. Chem.*, **229**, 97 (1936).

TABLE I

REACTION OF B_2H_6 WITH P_2H_4 AT LOW TEMPERATURES

Exp. no.	Reactants, mmoles P_2H_4	Reactants, mmoles B_2H_6	Reaction time, hr.	Temp., °C.	Mmoles B_2H_6 reacted	Molar ratio B_2H_6/P_2H_4
1	1.83	5.19	4	−118	1.18	0.64
			24	− 78	1.88	1.03
			96	− 78	1.91	1.04
2[a]	2.11	3.67	5	−118	1.11	0.53
			29	− 78	2.08	.99
3[a]	2.16	3.77	18	− 78	1.50	.70
			39	− 78	1.67	.77
			63	− 78	1.74	.81
4[a]	2.25	4.41	20	− 78	1.83	.82
			42	− 78	1.88	.84
			44	− 35	2.21	.98

[a] Deuterated biphosphine was employed in these reactions since it was prepared for use in connection with infrared studies[5] and was available at the time this study was initiated. No difference in chemical activity was noted between protonated and deuterated biphosphine in this study.

3. **Thermal Decomposition of $P_2H_4 \cdot B_2D_6$.**—When the solid white product is warmed to −40°, a clear liquid forms and the pressure increases slowly with time. On heating to 0°, bubbles form in the liquid, the latter turns yellow and a yellow solid is deposited on the walls of the reaction vessel from the vapor phase. This could only have come from the decomposition of biphosphine.[2] Evidently the compound dissociates to some extent at 0° and the biphosphine undergoes an irreversible decomposition, concomitantly, with the evolution of phosphine. The pressure in the vessel continues to increase with time, but only condensable products are released. After warming to room temperature and standing for some time, the liquid solidifies and hydrogen is liberated.

The analysis of the gases obtained on warming the product from expt. 3 of Table I to room temperature is presented below. The hydrogen (0.71 mmole) was removed after cooling the mixture with liquid air. When the vessel was warmed back to −127°, volatile products were collected (gas aliquot no. 1). The remaining gases were removed after the vessel was warmed to 25° (aliquot no. 2). In each case the molecular weight of the gas mixture was determined; then the gas mixture was analyzed. The following results were obtained. Gas aliquot no. 1, mmoles: PD_3, 0.506; B_2H_6, 0.511; mol. wt. exptl., 32.7; calcd., 32.4. Aliquot no. 2, mmoles: PD_3, 1.817; B_2H_6, 0.905; mol. wt. exptl., 34.07; calcd., 33.96. Evidently aliquot no. 2 represented $B_2H_6 \cdot 2PD_3$,[6] which was retained at −127° but which dissociated into its components on warming. A calculation shows that the solid residue contained boron ($P_{1.00}B_{0.32}H_{1.09}$).

4. **Reaction of Biophosphine with Diborane at Room Temperature.**—In this experiment 2.05 mmoles of P_2H_4 and 5.03 of mmoles of B_2H_6 were sealed in a tube under an initial pressure of eight atmospheres. A yellow solid formed rapidly. After 96 hr. at 27° the tube was cooled with liquid air, opened and 0.657 mmole of hydrogen was recovered. On warming to −118° a mixture consisting of 0.16 mmole of phosphine and 3.33 mmoles of diborane was removed. Based on the amount of diborane consumed, the combining ratio of B_2H_6/P_2H_4 was 0.96, suggesting the initial formation of the compound $P_2H_4 \cdot B_2H_6$. More diborane, phosphine and hydrogen were evolved on further standing at room temperature. The boron to phosphorus ratio in the residual solid remained constant but the hydrogen content diminished with time. After 22 days the evolution of volatiles had virtually ceased and the composition of the residue was $B_{1.00}P_{0.98}H_{3.49}$. In contrast, when the compound was warmed directly, in the absence of excess diborane, the result was largely a disproportionation with elimination of diborane and decomposition of biphosphine.

5. **Reaction of $B_2H_6 \cdot P_2H_4$ with HCl.**—The product obtained in expt. no. 4, Table I, was maintained at −78° for 72 hr. without noticeable change in composition. Since decomposition of P_2H_4 is brought about by HCl at −125°[4] and $B_2H_6 \cdot 2PH_3$ reacts rapidly with HCl,[6] it was of interest to test the stability of $B_2H_6 \cdot P_2H_4$ toward HCl. The latter was condensed on the compound at liquid air temperature, and the quantity of hydrogen which evolved on warming was recorded as a function of time and temperature. When the evolution of hydrogen had ceased and it was evident that the HCl had been consumed, a second quantity of HCl was condensed on the product. The results are recorded in Table II.

TABLE II

REACTION OF HCl WITH $B_2H_6 \cdot P_2H_4$ FROM EXPERIMENT 4, TABLE I

Composition of compound: 2.21 mmoles B_2H_6, 2.25 mmoles P_2H_4

Total mmoles added HCl	Temp., °C.	Total reaction time, hr.	Total mmoles H_2 evolved
2.216	−118	3	0.00
	− 78	17	.07
	− 40	21	.32
	− 40	39	.72
	− 40	61	1.00
	− 40	71	1.06
Added 2.754 mmoles HCl			
4.970	− 40	83	1.59
	− 40	155	2.22
	− 40	303	4.08
	− 40	519	4.21
	− 78	567	4.23
	− 78	639	4.27
	− 25	644	4.27

Reaction with HCl is not evident below −78° and only becomes appreciable at −40°; the solid then acquires a yellow color. At −40° it was established that the compound itself undergoes a slow irreversible decomposition, yielding phosphine and diborane, but no hydrogen. A question then arises as to the source of hydrogen in these experiments. This could come from two sources: (1) direct action of HCl on the compound or, (2) reaction between HCl and $B_2H_6 \cdot 2PH_3$, which could form if the biphosphine adduct underwent an irreversible decomposition. While Gamble and Gilmont[6] report a much more rapid reaction between $B_2H_6 \cdot 2PH_3$ and HCl than we observe here, the rate-controlling step might well be the primary decomposition of $P_2H_4 \cdot B_2H_6$. Therefore our results must be interpreted with reservations.

6. **Biphosphine and Boron Trifluoride.**—At −118°, 7.98 mmoles of P_2H_4 was treated with 25.55 mmoles of BF_3. After 1 hr. 10.00 mmoles of BF_3 was recovered; the residue composition was then calculated to be $P_2H_4(BF_3)_{1.95}$. The gas was returned to the reaction vessel and after 1 additional hr., 10.34 mmoles of gas was recovered. The residue acquired a light yellow color during reaction—evidently some decomposition had occurred.

Considerable decomposition occurs at higher temperatures. For example: 1.79 mmoles of P_2H_4 and 4.01 mmoles of BF_3 were stored at −78° for 16 hr.; 4.64 mmoles of a mixture of BF_3 and PH_3 were recovered. The residue was of a deep orange color. In a second experiment 4.79 mmoles of P_2H_4 was stored with 11.05 mmoles of BF_3 for 2 hr.; 5.45 mmoles of gas was recovered; again the residue was colored a deep yellow.

These observations point to the formation of $P_2H_4 \cdot 2BF_3$, fairly stable below −118°, but undergoing rapid decomposition to eliminate phosphine at higher temperatures.

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