Contribution from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS,
Institut de Mathématiques et Sciences Physiques, Parc Valrose, 06034 Nice Cedex, France

Smooth Oxidation of Phosphorus Closo-Type Compounds. Preparation and Characterization of the *closo*-Hexa-*N*-methyloxythiophosphorimides $P_4(NMe)_6S_nO_{4-n}$ (n = 0–3) and an Improved Synthesis for the *closo*-Hexa-*N*-methylthiophosphorimides

FRANCIS CASABIANCA, A. ALAN PINKERTON, and JEAN G. RIESS*

Received July 14, 1976 AIC60518L

The *closo*-hexa-*N*-methylphosphorimides $P_4(NMe)_6S_n$ (n = 0–3) react with stoichiometric amounts of Me_3NO in benzene solution to form the corresponding oxides $P_4(NMe)_6S_nO_{4-n}$. The closo structure is demonstrated by ^{1}H NMR spectra and the presence of the P═S and P═O groups by ^{31}P NMR and IR spectra. Their mass spectra are discussed. The compound $P_4(NMe)_6$ reacts with stoichiometric quantities of elemental sulfur in CS_2 solution below room temperature to form the *closo*-thiophosphorimides $P_4(NMe)_6S_n$ (n = 1–4) in good yields.

Introduction

Phosphorus is known for its tendency to form closo-type structures in many of its simplest molecular compounds such as, for example, in its oxides, sulfides, imides, and so on.[1] We have been interested for some time in the class of compounds known as the *closo*-phosphorimides which have a structure based on the P_4N_6 "birdcage" of T_d symmetry. Our interest stems from the possibility of extensive p_π–d_π interactions in these molecules and the transmission of substituent effects by this mechanism. As the basic unit we have chosen the $P_4(NMe)_6$ molecule (Me = CH_3) which was first synthesized by Holmes.[2] Our first studies were concerned with some of their coordination compounds such as $P_4(NMe)_6[Ni(CO)_3]_n$[3] and $P_4(NMe)_6(BH_3)_n$[4] and with the synthesis of their sulfides $P_4(NMe)_6S_n$ (n = 1–4)[5] which led to a study of their relative thermodynamic stabilities.[6] More recently we have begun to carry out accurate structure determinations on these molecules and to try to relate the structural parameters with their photoelectron spectra.[7] We have also established that some of these cage compounds exhibit a plastic crystalline phase whereas others do not[8] and we are presently examining the possible determining criteria for this behavior.

With a view to extending our present knowledge we have introduced the electronegative oxygen substituent into these molecules and wish to report the synthesis and characterization of the *closo*-oxyphosphorimides $P_4(NMe)_6S_nO_{4-n}$ (n = 0–3). It should be noted that only two oxysulfides, $P_4O_6S_4$ and $P_4S_6O_4$, are known[1] and that no "mixed" compound having the P_4O_6, the P_4S_6, or the P_4N_6 core but with two different kinds of substituents on its periphery has been reported so far. It is also noteworthy that most of the common oxidizing agents, acting upon $P_4(NMe)_6$, have so far failed to give definite molecular structures.[9] New, improved syntheses of the thiophosphorimides are also given.

Experimental Section

All reactions were carried out under dry nitrogen. Benzene and *n*-pentane were distilled from sodium. Carbon disulfide was distilled from P_4O_{10} after treatment with mercury. Me_3NO was sublimed in vacuo before use. *closo*-Hexa-*N*-methylphosphorimide was prepared according to the literature.[2] Elemental sulfur was used as supplied. IR spectra were recorded as Nujol mulls or in ether solution with a Perkin-Elmer PE 577 spectrometer. The ^{1}H NMR spectra were obtained at 60.0 MHz in benzene solution on a JEOL C-60 HL instrument. The ^{1}H-decoupled ^{31}P NMR spectra were recorded on $CDCl_3$ solutions with a Bruker HX-90 spectrometer operating in the Fourier-transform mode. ^{1}H and ^{31}P chemical shifts are reported relative to TMS and 85% H_3PO_4, respectively. Mass spectra were obtained with an AEI-MS 30 instrument operating at 70 eV. Melting points were carried out in sealed capillaries under nitrogen and are uncorrected. The analyses were performed by the Service Central de Microanalyse of the Centre National de la Recherche Scientifique.

$P_4(NMe)_6O_4$. $P_4(NMe)_6$ (1.54 g, 5.17 mmol) and Me_3NO (1.55 g, 20.6 mmol) were stirred in benzene (20 mL) at room temperature. The reaction was considered to be complete when all of the solid Me_3NO (insoluble in benzene) had disappeared (~12 h). The solvent and Me_3N formed were pumped away. The residue was sublimed (100 °C, 5 × 10^{-3} mmHg) to give a white product; yield 1.79 g, 96%; mp 179 °C dec. Anal. Calcd for $C_6H_{18}N_6O_4P_4$: C, 19.90; H, 5.01; N, 23.20; P, 34.21. Found: C, 20.03; H, 4.98; N, 23.08; P, 33.99.

A similar reaction carried out in a sealed tube (24 h) gave Me_3N in 89% yield (separated in vacuo, weighed, identified by IR).

$P_4(NMe)_6SO_3$. $P_4(NMe)_6S$ (0.288 g, 0.87 mmol) and Me_3NO (0.228 g, 3.04 mmol) were allowed to react as indicated above. The excess Me_3NO was filtered off before evaporation, and the residue was sublimed; yield 0.308 g, 94%; mp 157 °C dec. Anal. Calcd for $C_6H_{18}N_6O_3P_4S$: C, 19.06; H, 4.79; N, 23.23; P, 32.79; S, 8.48. Found: C, 19.18; H, 4.72; N, 22.07; P, 32.80; S, 8.42.

$P_4(NMe)_6S_2O_2$. $P_4(NMe)_6S_2$ (0.420 g, 1.16 mmol) and Me_3NO (0.190 g, 2.54 mmol) were treated as above to give, after sublimation, a yield of 0.420 g, 90%; mp 185 °C dec. Anal. Calcd for $C_6H_{18}N_6O_2P_4S_2$: C, 18.28; H, 4.60; N, 21.32; P, 31.42. Found: C, 18.42; H, 4.56; N, 21.33; P, 31.72.

$P_4(NMe)_6S_3O$. $P_4(NMe)_6S_3$ (0.60 g, 1.52 mmol) and Me_3NO (0.114 g, 1.52 mmol) were allowed to react in the above manner to yield, after sublimation, 0.51 g, 82%; mp 215 °C dec. Anal. Calcd for $C_6H_{18}N_6OP_4S_3$: C, 17.56; H, 4.42; N, 20.48; P, 30.19; S, 23.44. Found: C, 17.59; H, 4.55; N, 20.28; P, 29.90; S, 23.17.

Improved Synthesis of the Hexa-*N*-methylthiophosphorimides. Identification[5] and purity were monitored by NMR.

$P_4(NMe)_6S$. $P_4(NMe)_6$ (1.12 g, 3.74 mmol) was dissolved in CS_2 (~20 mL) and cooled to −20 °C. Elemental sulfur (0.124 g, 3.8 mmol) in CS_2 (~10 mL) was added slowly and the solution stirred for 12 h. The solvent was pumped away and the residue crystallized from pentane (−30 °C); yield 0.725 g, 58%; mp 94 °C.

$P_4(NMe)_6S_2$. $P_4(NMe)_6$ (1.05 g, 3.52 mmol) and elemental sulfur (0.225 g, 7.05 mmol) were treated as above to give a yield of 0.750 g, 60%, after recrystallization in *n*-pentane; mp 125 °C.

$P_4(NMe)_6S_3$. The same reaction conditions as above, but with $P_4(NMe)_6$ (1.59 g, 5.33 mmol) dissolved in EtOH (20 mL) and sulfur (0.514 g, 16.1 mmol) in CS_2, gave a yield of 1.37 g, 65%, after recrystallization from *n*-pentane; mp 174 °C.

$P_4(NMe)_6S_4$. $P_4(NMe)_6$ (1.52 g, 5.11 mmol) and sulfur (0.656 g, 20.5 mmol) were allowed to react similarly in ethanol to yield 1.57 g, 72%, after recrystallization in a pentane/$CHCl_3$ mixture (5:1); mp 246 °C.

Results and Discussion

Trimethylamine oxide reacts smoothly with the *closo*-hexa-*N*-methylphosphorimides and -thiophosphorimides of the series $P_4(NMe)_6S_n$ (n = 0–3) in benzene solution at room temperature to give the oxidized phosphorus analogues $P_4(NMe)_6S_nO_{4-n}$ and trimethylamine, according to

$$P_4(NMe)_6S_n + (4-n)Me_3NO \rightarrow P_4(NMe)_6S_nO_{4-n} + (4-n)Me_3N \quad (n = 0\text{–}3)$$

Because Me_3NO is sparingly soluble in benzene, any excess

Table I. NMR Parameters for the Oxythiophosphorimides $P_4(NMe)_6S_nO_{4-n}$

Compd	Type of proton	δ_H[a]	J'_{HP}, Hz	δ_P[b]	J_{PP}, Hz
$P_4(NMe)_6O_4$	All	3.10 (t)[c]	9.6 (PO)[d]	−2.7 (PO)[d]	
$P_4(NMe)_6SO_3$	a	2.92 (t)	9.9 (PO)	−5.3 (PO)	<1
	b	3.04 (d-d)	8.7 (PO), 13.2 (PS)	−53.6 (PS)	
$P_4(NMe)_6S_2O_2$	a	3.14 (t)	13.1 (PS)	−7.0 (PO)	2
	b	2.91 (t)	10.1 (PO)	−63.5 (PS)	
	c	3.02 (d-d)	13.8 (PS), 9.5 (PO)		
$P_4(NMe)_6S_3O$	a	3.16 (t)	12.9 (PS)	−7.5 (PO)	4.5
	b	3.03 (d-d)	9.3 (PO), 13.2 (PS)	−66.1 (PS)	

[a] Ppm downfield from TMS. [b] Ppm upfield from 85% H_3PO_4. [c] t = triplet, d-d = doublet of doublets. [d] PO and PS indicate the phosphorus atom referred to.

Table II. Characteristic Infrared Absorptions for $P_4(NMe)_6S_nO_{4-n}$ and Tentative Assignments

$P_4(NMe)_6$	$P_4(NMe)_6S_4$	$P_4(NMe)_6S_3O$	$P_4(NMe)_6S_2O_2$	$P_4(NMe)_6SO_3$	$P_4(NMe)_6O_4$	Assignments[5]
		1280 m	1280 m	1280 m	1280 m	ν(P=O)
		1260 m				
1165 m	1170 m	1170 m	1170 m	1170 m	1190 w	Def of CH_3-N
1070 s	1070 w	1030 m	1040 m	1040 m	1010 w	
825 s	880 s	905 s	910 s	920 s	925 m	ν(P-N)
780 w		800 m	810 w	810 w	830 w	Def of PNP, HCN, CNP angles
					790 w	and of the P_4N_6 skeleton
675 w		690 w	710 m	730 w	690 m	
580 s	655 m	640 m	660 m	670 m		
			650 m	660 m		
	590 s	615 m	630 m	645 m		ν(P=S)

may be removed by filtration. If, at any stage, some hydrolysis has occurred, the products are left behind on sublimation. In this manner a pure product is obtained if the reaction is allowed to go on to completion.

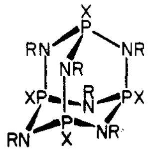
This smooth reaction obtained with Me_3NO is in contrast to previous attempts to oxidize the cage compounds which have either given no reaction or destroyed the cage. Thus by treating $P_4(NMe)_6$ with molecular oxygen at 170 °C Holmes and Forstner obtained a compound of $P_2O_2(NME)_3$ stoichiometry to which they attributed a polymeric structure on the basis of its insolubility in all the common solvents, the absence of detectable vapor pressure at 300 °C, and lack of melting on heating to 650 °C (which converted the material toward a PNO composition).[10]

On the other hand, we have tried various metal oxides, such as CuO and HgO (reflux in benzene), with no reaction. The substitution of pyridine-*N*-oxide for Me_3NO was also ineffective. The use of nitric acid oxidation is excluded due to the facile rupture of the P–N bond by acids.

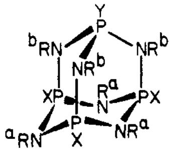
Noteworthy is the fact that, although sulfur may be added stepwise to the $P_4(NMe)_6$ moiety, leading to the formation of all four possible sulfides, this has not proved possible with the oxides. Reaction of less than 4 equiv of Me_3NO has always led to mixtures of starting material and $P_4(NMe)_6O_4$, the completely oxidized product, with no detectable amounts of the intermediate oxyimides. Again, in contrast to the sulfides,[6] the intermediate oxides $P_4(NMe)_6O_n$, where n = 1–3, were not observed to form by redistribution reactions on heating the above mixture for 8 days at 120 °C. Attempts to prepare them by desulfurizing the oxidized thiophosphorimides have also been unsuccessful so far.

The closo structure of the compounds $P_4(NMe)_6S_nO_{4-n}$ has been confirmed by their ^1H NMR spectra. Due to magnetic nonequivalence of the methyl groups the spectra are inherently complex, as was found for the analogous sulfides.[5] As the spectra are not well resolved, we have not attempted complete analyses. However, the major features of the spectra may be explained by a pseudo-first-order approximation, by assuming that $J_{HH} = 0$ and that $^3J_{PH} >> {}^5J_{PH}$. This means that the most important features of the spectra are determined by the chemical shifts of the methyl protons and their short-range coupling to two phosphorus atoms.

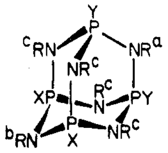
All of the molecules discussed here, including the previously reported sulfides, may be divided into three types, i.e.



I_1, X = O
I_2, X = S
I_3, X = lone pair



II_1, X = O, Y = S
II_2, X = S, Y = O
II_3, X = S, Y = lone pair
II_4, X = lone pair, Y = S



III_1, X = O, Y = S
III_2, X = S, Y = lone pair

The first (I) is the completely symmetric case where all of the phosphorus atoms and consequently all the methyl protons are *chemically* equivalent. Each methyl group is thus strongly coupled to two chemically equivalent phosphorus atoms and the ^1H spectrum tends toward a triplet structure. This system is exemplified by the molecules $P_4(NMe)_6$, $P_4(NMe)_6S_4$, and $P_4(NMe)_6O_4$. In the second case (II) three phosphorus atoms are chemically equivalent, and the fourth is unique. This generates two types of methyl groups (a, b), characterized by two distinct chemical shift values. The first type (a) are strongly coupled to two chemically equivalent phosphorus atoms and tend toward a triplet as above. The others (b) are strongly coupled to two chemically different phosphorus atoms and tend toward a doublet of doublets. The relative intensities of the triplet and the doublet of doublets are 1:1. The molecules $P_4(NMe)_6S$, $P_4(NMe)_6S_3$, $P_4(NMe)_6SO_3$, and $P_4(NMe)_6S_3O$ belong to this system. In the final case (III), there are two phosphorus atoms of one chemical type and two

Table III. Mass Spectra of Compounds $P_4(NMe)_6S_nO_{4-n}$ (n = 0-3)

	Relative intensity			
m/e	$P_4(NCH_3)_6O_4$	$P_4(NCH_3)S_3O$	$P_4(NCH_3)_6S_2O_2$	$P_4(NCH_3)_6SO_3$
410		21 M^+		
394			38 M^+	
378		5 $(M - S)^+$		25 M^+
377		26 $(M - SH)^+$		
362	90 M^+		10 $(M - S)^+$	
361			60 $(M - SH)^+$	
347	20 $(M - CH_3)^+$			
346				6 $(M - S)^+$
345				50 $(M - SH)^+$
334	28 $(M - NCH_2)^+$	19	8	
333	22 $(M - NCH_3)^+$			
332			10	
329			18	
318	$10 \begin{cases}(M - CH_2NO)^+ \\ (333 - CH_3)^+\end{cases}$	8	20	5
315	12 $(M - PO)^+$			
305	18 $(M - NCH_2 - NCH_3)^+$			
302		17		18
289		10		
286			12	10
273		10	12	
257	6		10	15
60	100 $(P - NCH_3)^+$	100	100	100

of another. This generated three types of methyl groups (a, b, c). Two of these (a, b) are coupled symmetrically and give two first-order triplets of relative intensity 1:1. The third type (c) are distinguished by two different strong couplings and tend to a doublet of doublets of relative intensity 4. As examples of this situation we may cite compounds $P_4(NMe)_6S_2$ and $P_4(NMe)_6S_2O_2$.

In Table I we have reported the NMR parameters analyzed on the above basis. The coupling constants, J', quoted are of course sums of couplings, except for the first-order case; however, the most important contribution to the sum must be $^3J_{PH}$.[5] We note that the couplings to phosphoryl phosphorus are, as expected,[11] smaller than those to thiophosphoryl, with an average of 9.5 and 13.2 Hz, respectively. Likewise $^2J_{PP}$ decreases with increasing substitution of sulfur by oxygen.

The ^{31}P chemical shifts are typical of phosphoryl and thiophosphoryl groups and confirm their presence in the molecules.[12] This is also demonstrated by the observation of typical stretching vibrations in the IR spectra (1280 and 645–615 cm^{-1}, respectively) as reported in Table II, where additional tentative assignments are given.

In the mass spectra of the previously reported sulfides, one of the most striking features in the fragmentation patterns was the loss of sulfur without rupture of the cage structure.[13] One must be cautious in the interpretation of the low-resolution mass spectra of the mixed oxysulfides (Table III), since a loss of 32 mass units can be accounted for by a loss of S, O_2, or PH (the latter being however very unlikely). Thus as an example, in the case of $P_4(NCH_3)_6S_2O_2$, the peak at *m/e* 286 (12%) can be assigned to $[M - OPNCH_3 - S]^+$, $[M - SPNCH_3 - O]^+$, [*m/e* $362 - OPNCH_3]^+$, [*m/e* $334 - O - S]^+$, [*m/e* $332 - 2CH_3 - O]^+$, [*m/e* $329 - CH_3 - NCH_2]^+$, [*m/e* $318 - S]^+$, or [*m/e* $318 - 2O]^+$, and there are no metastable ions detectable in the low-resolution spectra to allow a distinction among these various possibilities. One should note that the number of possible assignments increases with increasing substitution of oxygen by sulfur atoms.

Nevertheless the following features can be observed: the molecular ion is present for all of the compounds of the series; the base peak is in all cases *m/e* 60 $[(PNCH_3)^+]$ as for the thiophosphormides of the series $P_4(NMe)_6S_n$ (n = 0–4).[13] Contrary to $P_4(NMe)_6S_4$, for which the loss of S and SH was important, $P_4(NMe)_6O_4$ does not show the loss of oxygen in its higher mass fragments. Thus the PO bond appears to be much more stable than the PS bond under the electronic impact, and there is first a loss of CH_3 (*m/e* 347 (20%)), of NCH_2 (*m/e* 334 (28%)), and of NCH_3 (*m/e* 333 (22%)); when the molecule loses oxygen, it is in the form of a phosphoryl group (*m/e* 315 (12%)), which implies a rupture of the cage structure. On this basis one can suppose that the initial loss of two oxygen atoms is much less probable than the loss of one sulfur atom in $P_4(NMe)_6SO_3$ and $P_4(NMe)_6S_2O_2$, whose higher fragments can thus be assigned to $(M - S)^+$ and $(M - SH)^+$ with some certainty.

An improved synthesis of the thioimides of the series $P_4(NMe)_6S_n$ was achieved by treating *closo*-hexa-*N*-methylphosphorimide with stoichiometric amounts of elemental sulfur in dry carbon disulfide or ethanol *solutions* below room temperature (60–70% yields). This is a much cleaner reaction than the previously reported synthesis under vacuum in the absence of solvent, which led to mixtures of several members of the series which were hard to separate.

Acknowledgment. The authors thank Mr. R. Favez for measuring the ^{31}P spectra and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. $P_4(NMe)_6O_4$, 58979-11-6; $P_4(NMe)_6SO_3$, 61491-22-3; $P_4(NMe)_6S_2O_2$, 61491-23-4; $P_4(NMe)_6S_3O$, 61491-24-5; $P_4(NMe)_6$, 10369-17-2; $P_4(NMe)_6S$, 38448-57-6; $P_4(NMe)_6S_2$, 38448-56-5; $P_4(NMe)_6S_3$, 38448-55-4; $P_4(NMe)_6S_4$, 37747-07-2; Me_3NO, 1184-78-7; ^{31}P, 7723-14-0.

References and Notes

(1) J. R. Van Wazer, "Phosphorus and Its Compounds", Interscience, New York, N.Y., 1958; D. E. C. Corbridge, "The Structural Chemistry of Phosphorus", Elsevier, London, 1974; D. A. Armitage, "Inorganic Rings and Cages", Arnold, New York, N.Y., 1972.

(2) R. R. Holmes, *J. Am. Chem. Soc.*, **83**, 1334 (1961).

(3) J. G. Riess and J. R. Van Wazer, *Bull. Soc. Chim. Fr.*, 1846 (1966); *J. Organomet. Chem.*, **8**, 347 (1967).

(4) J. G. Riess and J. R. Van Wazer, *Bull. Soc. Chim. Fr.*, 1846 (1966); 3087 (1968).

(5) J. G. Riess and A. Wolff, *J. Chem. Soc., Chem. Commun.*, 1050 (1972); A. Wolff and J. G. Riess, *Bull. Soc. Chim. Fr.*, 1587 (1973).

(6) J.-C. Elkaim, A. Wolff, and J. G. Riess, *Phosphorus*, **2**, 249 (1973).

(7) F. A. Cotton, J. M. Troup, F. Casabianca, and J. G. Riess, *Inorg. Chim. Acta*, **11**, L33 (1974).

(8) M. Postel, F. Casabianca, and J. G. Riess, *Inorg. Chim. Acta*, **17**, L23 (1976).
(9) J. G. Riess, F. Casabianca, and A. A. Pinkerton, *Inorg. Chim. Acta*, **17**, L27 (1976).
(10) R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **1**, 89 (1962).
(11) G. Mavel, *Annu. Rep. NMR Spectrosc.*, **5B** 47 (1973).
(12) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5** (1967).
(13) A. Wolff, A. Cambon, and J. G. Riess, *Org. Mass Spectrom.*, **9**, 594 (1974).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14853

Thermodynamic and Kinetic Parameters for Borane Exchanges

K-R. CHIEN and S. H. BAUER*

Received August 13, 1976 AIC60603T

Equilibrium compositions and bimolecular exchange rates were measured at two temperatures for the following reactions: $H_3BCO + PF_3 \rightleftarrows H_3BPF_3 + CO$; $B_2H_6 + D_3BPF_3 \rightleftarrows H_3BPF_3 + H_3B \cdot BD_3$; $H_3BCO + D_3BPF_3 \rightleftarrows H_3BPF_3 + D_3BCO$. These homogeneous reactions are of unit order in each of the reagents, with activation energies 13–15 kcal mol^{-1}. We included in this summary six analogous reactions for which rate data have been published, to demonstrate the existence of a consistent pattern for the borane exchange steps.

Introduction

To facilitate the development of a mechanism for the laser augmented decomposition[1,2]

$$2H_3BPF_3 \xrightarrow[CO_2\ \text{laser}]{10.6\ \mu m} B_2H_6 + 2PF_3$$

we found it necessary to review the available thermochemical and kinetic data for reactions wherein BH_3 serves as a Lewis acid, interacting with very weak bases. The experimental procedures consisted of sample preparation and purification, measurement of the rate of exchange of the species BH_3, BD_3, PF_3, and CO between adducts (or dimers), and the determination of equilibrium compositions of their mixtures, utilizing the intensities of absorption of characteristic infrared bands.

We are concerned with three types of reactions, designated: association ⇄ dissociation, displacement, and exchange. For the radicals listed we considered all seven possible pairwise adducts [exclusive of $(PF_3)_2$, $(CO)_2$, and $PF_3 \cdot CO$]. Since H/D were the only isotopic labels readily available we did not investigate reactions of the types

$$H_3B^{13}CO + {}^{12}CO \rightleftarrows H_3B^{12}CO + {}^{13}CO \qquad \text{displacement} \qquad (\alpha)$$

$$H_3{}^{10}BPF_3 + H_3{}^{11}BCO \rightleftarrows H_3{}^{11}BPF_3 + H_3{}^{10}BCO \qquad \text{exchange} \qquad (\beta)$$

$${}^{10}B_2H_6 + {}^{11}B_2H_6 \rightleftarrows 2{}^{10}B^{11}BH_6 \qquad \text{exchange} \qquad (\gamma)$$

However, since our objective was to establish general trends for this class of reactions rather than to obtain precise rate constants for any specific step, we postulated that H/D isotope effects introduce only small perturbations as long as the B–H and B–D bonds remain intact.[3] Reactions β and γ are essentially equivalent to (8) and (9), respectively; the analogue of (α) is (4). In several cases we measured both the forward and the reverse rate constants; in most cases rate data in one direction were recorded and the reverse rate was deduced from the equilibrium constant.

Experimental Section

The samples were prepared according to standard methods, and their purities were checked via their infrared spectra (Perkin-Elmer No. 521). For the kinetic studies the reactants were separately introduced into two identical cells (constructed from a single Al block) to the desired pressures, at the reaction temperature. One of the reagents was mixed with a substantial excess of Ar. The Al block was wrapped with heating wire, thermally lagged, and fitted with several chrome–alumel thermocouples. With the reactants in separate cells at the desired temperature selected portions of their absorption spectra were quickly recorded. Then ($t = 0$) the metal valve connecting the two cells was rapidly opened. The Ar overpressured reactant jetted into the lower pressure cell, the components mixed, and the reaction was initiated. The extent of conversion was followed by recording the time dependent intensity of transmitted radiation at a present wavelength. The applicability of Beer's law was checked for the pressures and spectral resolution used in these experiments. The rate constants were calculated either on the basis of a second-order reversible mechanism or via a pseudo-first-order equation, depending on the combination of pressures used.

Table I. Thermodynamic Functions[h] ($T = 298$ K)

Compd	ΔH_f°, kcal/mol	Ref	S°, eu/mol	Ref
BH_3	23.87	*a*	44.88	*b*
B_2H_6	9.80	*b*	55.71	*b, c*
CO	−26.42	*b*	47.21	*b*
PF_3	−224.90	*b*	65.28	*b, d*
H_3BPF_3	−225.52	*e*	74.54	*b*
H_3BCO	−26.53	*f*	59.69	*b, g*

[a] Mean value: R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967), and references quoted therein. [b] "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). [c] S. Sundaram, *Z. Phys. Chem. (Frankfurt am Main)*, **36**, 376 (1963). [d] E. L. Pace and P. V. Petrella, *J. Chem. Phys.*, **36**, 2991 (1962). [e] Equilibrium for decomposition of H_3BPF_3: A. B. Burg and Y. C. Fu, *J. Am. Chem. Soc.*, **88**, 1147 (1966). [f] Equilibrium for displacement reaction $PF_3 + H_3BCO$, this investigation. [g] S. Sundaram and F. F. Cleveland, *J. Chem. Phys.*, **32**, 166 (1960). [h] See also, T. P. Fehlner, "Boron Hydride Chemistry", Academic Press, New York, N.Y., E. L. Muetterties, Ed., Chapter 4.

A collection of "best" standard molar enthalpies of formation and entropies at 298 K for the gases (at 1 atm) is presented in Table I; their sources are indicated. We emphasize that these constitute a mutually consistent set of values.

Association ⇄ Dissociation Reactions

None of the following unimolecular dissociation rates were measured directly; indeed, these would be very difficult experiments to perform, since the cross sections for the bimolecular steps are within 10^{-2} of gas kinetic. However, mutually consistent mechanisms for the decomposition of H_3BCO and H_3BPF_3[4] and the various flow experiments of Fehlner[5] lead to reasonable values for k_{diss} (s^{-1}) when equated to $K_{eq}{}^{(c)}k_{assoc} = (\tilde{R}T)^{-1}K_{eq}{}^{(p)}k_{assoc}$; units $\tilde{R}$ in cm^3 atm mol^{-1} deg^{-1}