The P^{31} chemical shifts of triphenylphosphine oxide were obtained in 1:20 mole ratio (solute:solvent) solutions of the oxide in a variety of reagent grade or Eastman White Label solvents. A measuring frequency of 15.1 Mc./sec. and the absorption mode were employed. Shifts were measured in a concentric-sphere sample container,[14] to eliminate bulk susceptibility effects, with respect to an external reference of 85% phosphoric acid in the center sphere, using the side-band technique.

The observed shifts referred to the resonance line of 85% phosphoric acid are presented in Table I. These shifts are the average results of at least five field scans in both increasing and decreasing senses and can be considered uncertain by less than ±0.2 p.p.m. They cover a total range of 35 p.p.m. with the largest positive shift occurring with dioxane as solvent and the largest negative shift corresponding to a 96% sulfuric acid solvent, in which the triphenylphosphine oxide can be described as a cationic protonated species. The effect of dilution was qualitatively checked with methanol as the solvent, in which case the shifts obtained with mole ratios of 1:20, 1:30, and 1:40 were identical within experimental error. As in the related investigation of the carbonyl group,[2] the shifts obtained with aprotic solvents covered a narrow range (1.2 p.p.m.) at the high-field end of the scale, while in protic solvents capable of forming hydrogen bonds with, or completely transferring a proton to, the solute molecule a large range of about 20 p.p.m. was observed. Thus, qualitatively the solvent effects observed in these two cases appear strikingly similar, as is seen from a comparison of the corresponding P^{31} shifts (triphenylphosphine oxide) with the C^{13} (acetone) shifts[2] in the same solvents listed in Table I. While a strict linear relationship does not exist between these two sets of shifts, a definite monotonic trend is apparent, with 1,4-dioxane the only solvent out of order.

TABLE I

P^{31} CHEMICAL SHIFTS OF $(C_6H_5)_3PO$ IN 1:20 MOLE RATIO SOLUTIONS IN SEVERAL SOLVENTS

Solvent	P^{31} chemical shift, p.p.m. with respect to 85% H_3PO_4[a]	C^{13} chemical shift of acetone in 1:6 mole fraction solutions[b]
1,4-Dioxane	−24.8	0.0
Carbon tetrachloride	−24.9	+1.3
Benzene	−26.1	+0.8
2-Propanol	−29.8	−1.9
Methanol	−32.6	−3.7
Acetic acid	−33.3	−6.2
m-Cresol	−36.4	−8.2
Formic acid	−37.3	−9.1
Dichloroacetic acid	−41.7	−11.9
Trifluoroacetic acid	−48.1	−14.1
Sulfuric acid	−59.8	−37.4

[a] Shifts in the direction of increasing field are considered positive. [b] Taken from ref. 2.

The difference between the shifts obtained in a highly acidic solvent and a moderately acidic or nonacidic solvent can be interpreted most simply in terms of a large change in the position of the equilibrium

$$(C_6H_5)_3PO + HA \rightleftharpoons (C_6H_5)_3POHA \rightleftharpoons (C_6H_5)_3P\overset{+}{O}H + A^-$$

In solutions of triphenylphosphine oxide, a substance which is less basic than water,[15] in solvents which are not highly acidic, the concentrations of the cationic species resulting from proton transfer would be too low to influence significantly the weighted-average chemical shift of the solute involved in the rapid acid–base equilibrium. In such solvents the predominant effect responsible for the downfield trend with increasing solvent acidity appears to be that of an increase in the number and strength of solvent-to-solute hydrogen bonds as represented by the hydrogen-bonded complex in the above equilibrium. There is ample evidence in the literature that such interactions are important in systems containing triphenylphosphine oxide and alcohols, phenols, carboxylic acids, or chloroform,[15–17] the association constant for the phenol–triphenylphosphine oxide complex in carbon tetrachloride solvent at 20° being 1055.[16] Of course, if the acidity of the solvent is high enough, the hydrogen-bonding effect will blend into, or be obscured by, the influence of an appreciable equilibrium concentration of the cationic protonated triphenylphosphine oxide. A distinction between these two types of acid–base interactions with triphenylphosphine oxide was made by Hadzi,[15] whose infrared experiments on crystalline adducts showed that a hydrogen-bonded complex is formed with trichloroacetic acid, while proton transfer may occur with the much stronger acid hydrogen bromide.

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[14] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

[15] D. Hadzi, *J. Chem. Soc.*, 5128 (1962).

[16] G. Aksnes and T. Gramstad, *Acta Chem. Scand.*, **14**, 1485 (1960).

[17] T. Gramstad, *ibid.*, **15**, 1337 (1961).

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B-Tribromoborazines from the Bromination of Borazine and N-Trimethylborazine

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Wiberg[2] has reported that bromination of borazine using excess bromine in the absence of solvent yields a yellow, unsymmetrical "adduct" which he formulated as B,B′-dibromo-N,N′-dibromocyclotriborazane. He further reported that pyrolysis of the "adduct" gives B,B′-dibromoborazine by splitting out two molecules of hydrogen bromide.

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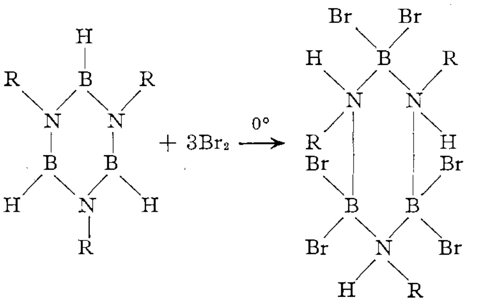
[1] Taken in part from a thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1964.

[2] E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940).

This result appeared to be unusual; first, because it was the first example of a N-halocyclotriborazane and second, because all reported additions of RX agents to borazines involve three moles of RX. On reinvestigation of this addition we have found the "adduct" to be B-hexabromocyclotriborazane. We have further found that the same reaction when applied to N-trimethylborazine yields B-hexabromo-N-trimethylcyclotriborazane in high yield.

As expected, the infrared spectrum of the compound secured in the borazine reaction shows no B–H stretching frequency but has a strong NH_2 deformation band[3] at 1540 cm.$^{-1}$. A spectrum of the product from the N-trimethylborazine reaction shows an N–H stretch at 3180 cm.$^{-1}$ and again no B–H stretch. The thermal decomposition of these "adducts" produces the respective B-tribromoborazine and hydrogen bromide in a roughly 1:3 mole ratio as shown in Table II. The reaction sequence outlined above is shown below.



R = H, CH$_3$ (1)

$$B_3N_3Br_6H_3R_3 \xrightarrow{\text{heat}} B_3N_3Br_3R_3 + 3HBr \qquad (2)$$

The "adduct" structures are further supported by the fact that the N–H stretching frequency for both compounds is in the region observed in cyclotriborazanes[4,5] (3300–3160 cm.$^{-1}$) and expected for the NH_2^+ group[3,6] (3200 cm.$^{-1}$). Further, the band is sharp, indicating the equivalence of all NH bonds, and the relative intensity of the N–H stretch and NH_2 deformation bands is in agreement with that observed in other cyclotriborazanes[7] in which all nitrogen present is in NH_2 groups. Also, the infrared spectrum (Nujol mull) of the borazine "adduct" is virtually identical with that of B-hexachlorocyclotriborazane (prepared by Schaeffer[8] and also in this laboratory) for absorption bands not due to B–X bonds. Differences in the spectra occur only below 1000 cm.$^{-1}$ where it might be suspected that the normal modes in the two compounds would differ because of a large involvement of B–X out-of-plane and/or in-plane deformations.

It has been reported[8] that the addition of hydrogen chloride to B-trichloroborazine is reversible. Similar reversibility has been observed by the authors for the hydrogen chloride adducts of methylborazines under the same vacuum pyrolysis conditions as employed for the pyrolysis of the bromine adducts. Therefore the pyrolysis results in Table II are in good accord with the proposed structure for the intermediates. That the hydrogen bromide to B-tribromoborazine ratios are not closer to the theoretical 3:1 is due partially to the difficulty of collecting and weighing the small amounts of solid borazine in the glove box necessary for work with this hydrolyzable compound.

TABLE I

INFRARED ABSORPTION FREQUENCIES

$(Cl_2BNH_2)_3$		"Adduct"	
Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity
3250	m	3240	m
1550	m	1540	m
1450	s	1430	s
1260	s	1250	s
1150	w	1145	w
990	s	955	s
820	m	795	m
790	m	720	w
725	w		

TABLE II

BROMINE ADDUCT PYROLYSES

	HBr, mmoles	$(BrBNR)_3$,[a] mmoles	Ratio HBr/ borazine	Borazine yield, %
$B_3N_3H_6 \cdot 3Br_2$	1.97	0.60	3.3	83
	0.78	0.30	2.6	58
$B_3H_3N_3(CH_3)_3 \cdot 3Br_2$	2.47	0.86	2.9	76
	0.82	0.27	3.0	74

[a] R = H or CH$_3$.

In further experiments we have attempted to add bromine to B-trichloroborazine and hexamethylborazine but reaction does not occur under these conditions and the borazines are recovered unchanged. These results are unexpected if the first step in the reaction is addition across the B–N bond, and simple addition of bromine across the B–N bond as proposed by Wiberg for the first step is unlikely. The most probable reaction route involves the nucleophilic attack of bromine at a ring boron atom with subsequent elimination of hydrogen bromide. The hydrogen bromide then adds to the B-tribromo compound in the manner normal for such HX additions to borazines. Such a reaction sequence is chemically reasonable and would give the intermediate "adducts" which were found in this study.

Experimental

Addition to Borazine.—A 0.13-g. sample of borazine (1.6 mmoles) was placed in a dry tube, surmounted by a $CaCl_2$ drying tube which contained a stirring bar, and was maintained at 0°. A large excess of liquid bromine (2 ml., 36 mmoles) was slowly added to the liquid borazine sample. Immediate reaction occurred and an orange solid was deposited. Stirring was continued for several minutes after the bromine had been added, and then the excess Br_2 and any unreacted borazine were removed by pumping. The solid was dried by further pumping at 30–40° for several hours before collecting and weighing in a nitrogen-filled glove box. The yield of solid, 0.76 g., is 84% based on the addition of 3 moles of Br_2 to 1 of borazine. The adduct did not melt to 350° but

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(3) L. J. Bellamy, "The Infrared-red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., London, 1958, pp. 259, 260.

(4) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).

(5) Comparison made with many other cyclotriborazanes prepared in this laboratory.

(6) The NH stretch in borazines is at 3500–3430 cm.$^{-1}$.

(7) B-Trichloro,B-tris(trifluoroacetato)cyclotriborazane and B-hexachlorocyclotriborazane prepared in this laboratory, unpublished work.

(8) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3592 (1963).

decomposed over a wide range. Attempts to prepare an analytically pure sample have failed.

Addition to N-Trimethylborazine.—On attempting the reaction of N-trimethylborazine and bromine under vacuum, by condensing them together as solids and then warming to their melting point, an explosion resulted. However, if the reaction was carried out at atmospheric pressure as described for borazine, the N-trimethylborazine also reacted smoothly. For 0.90 g. of N-trimethylborazine (7.4 mmoles) plus 3 ml. of Br_2 (54 mmoles) at 0°, the yield of dried solid adduct was 4.04 g. or 91% of the theoretical based on three molecules of Br_2 adding to one of N-trimethylborazine. The adduct softened at 125°, m.p. 145° dec.

Purification of this intermediate was precluded by its ready hydrolysis, particularly in solution. Similar behavior has been noted[8] for other halocyclotriborazanes and they are normally allowed to react as soon as they are formed. Thus, B-hexachlorocyclotriborazane[7] prepared directly from HCl and B-trichloroborazine under vacuum conditions has been found to be hydrolyzed a few per cent.

Treatment, similar to the above, of B-trichloroborazine and hexamethylborazine with Br_2 produced no reaction as evidenced by the 95% recovery of the respective unreacted borazines.

Bromine Adduct Pyrolyses.—The orange-yellow solid adducts were pyrolyzed for several hours under vacuum at 80–140°. A white crystalline solid collected on a cold water condenser immediately above the hot zone and the more volatile materials traveled into a succeeding −196° trap. The volume of gas trapped at −196° (but volatile at −80°) was measured in calibrated bulbs on a vacuum system. The gas was identified as HBr by its infrared spectrum.[9] The solids were identified by their melting points and infrared spectra[10] as B-tribromoborazine (m.p. 126–128°; lit.[11] 128°) for the borazine adduct and B-tribromo-N-trimethylborazine (m.p. 143–146°; lit.[10] 143°) for the N-trimethylborazine adduct. The pyrolysis data are summarized in Table II.

Infrared Spectra.—Nujol mulls of all solids were prepared in a glove box and the spectra determined on a Perkin-Elmer Infracord spectrophotometer.

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[9] R. H. Pierson, A. N. Fletcher, and E. S. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

[10] I. M. Butcher, W. Gerrard, E. F. Mooney, R. A. Rothenbury, and H. A. Willis, *Spectrochim. Acta*, **18**, 1487 (1962).

[11] R. Schaeffer, M. Steindler, L. Hohnstedt, H. Smith, L. Eddy, and H. Schlesinger, *J. Am. Chem. Soc.*, **76**, 3033 (1954).

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Reaction between Sulfur Hexafluoride and Hydrogen Iodide

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Sulfur hexafluoride is well known for its inert character. It is reported that this gas is not reactive under ordinary laboratory conditions.[1]

A variety of sulfur compounds are reduced by anhydrous hydrogen iodide, liberating hydrogen sulfide and iodine in quantitative yields.[2–4] It was of interest therefore to investigate the reaction between hydrogen iodide and sulfur hexafluoride. Preliminary studies indicated that this seemingly inert gas could be reduced easily at room temperature (30 ± 2°). The results of such an investigation are reported in this communication.

Experimental

Preparation of Sulfur Hexafluoride.—In the absence of a source for elemental fluorine, sulfur hexafluoride was prepared in the present investigation by the reaction between elemental sulfur and a metallic fluoride like cobalt(II) fluoride or antimony(III) fluoride, at elevated temperature under vacuum, although the yield of sulfur hexafluoride was very small under these conditions. The products of such a reaction are known to contain lower fluorides of sulfur (S_2F_2, SF_4, and traces of S_2F_{10}) and fluorides of silicon as well as a small quantity of sulfur hexafluoride.[1] The hexafluoride could be freed from these impurities in the following way. The gaseous products evolved from the reaction vessel were condensed in a trap cooled by liquid air. The condensate was later allowed to thaw in a current of nitrogen, and the issuing gases were passed through an aqueous solution of potassium hydroxide and then through an alcoholic solution of potassium hydroxide.[5] The unabsorbed gas was dried through a sulfuric acid bubbler and over phosphorus pentoxide and then frozen in a trap cooled by liquid air. The noncondensable gaseous impurity was removed by evacuation. The condensate was allowed to sublime into a gas measuring buret over mercury from which known volumes of the gas could easily be dispensed into the reaction vessel connected to a vacuum manifold. In this way it was possible to obtain 5–10 ml. of pure sulfur hexafluoride at a time.

Preparation of Anhydrous Hydrogen Iodide.—Hydrogen iodide was prepared by the hydrolysis of phosphorus triiodide formed by the action of iodine and red phosphorus.[6] The hydrogen iodide liberated was swept off by a stream of dry hydrogen or nitrogen and passed through U tubes cooled to −16 and −60° to remove moisture and iodine.[7] The gas was then solidified in a trap cooled by liquid air. The carrier gas was pumped off, and pure anhydrous hydrogen iodide was sublimed into the reaction vessel. The hydrogen iodide taken for the reaction was in 50- to 100-fold excess over the amount of sulfur hexafluoride.

The reaction between sulfur hexafluoride and hydrogen iodide started immediately when the two gases were allowed to mix with each other in the reaction vessel. This was indicated by the color of the liberated iodine, the intensity of which increased gradually with time. After 4–6 hr., the products of the reaction were analyzed in the following way. A stream of nitrogen was passed (for 1 hr.) through the vessel to sweep off the products through traps containing chilled carbon tetrachloride (−16°) followed by sodium hydroxide (4 *N*) holding a cadmium hydroxide suspension. The carbon tetrachloride dissolved and retained iodine vapors present in the gaseous stream while hydrogen sulfide and hydrogen fluoride were absorbed by the alkali. Cadmium sulfide was separated by filtration and estimated iodometrically.

Fluorine was estimated in the filtrate by a modified method of Willard and Winter.[8] Iodine retained in carbon tetrachloride and in the reaction vessel was extracted with an aqueous solution of potassium iodide (10%) and titrated against a standard solution of thiosulfate to determine the iodine content.

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[1] J. H. Simons, "Fluorine Chemistry," Volume I, Academic Press, Inc., New York, N. Y., 1950, p. 90.

[2] A. R. V. Murthy, *Proc. Indian Acad. Sci.*, **36**, 425, 537 (1952).

[3] A. R. V. Murthy, *ibid.*, **37**, 11, 17, 23 (1953).

[4] K. Sharada and A. R. V. Murthy, *Chem. Ind.* (London), 288 (1960).

[5] J. W. Mellor, "Supplement to the Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Supplement I, Longmans, Green and Co., London, 1956, p. 57.

[6] J. N. Friend, "A Text Book of Inorganic Chemistry," Vol. VIII, Charles Griffin and Co., Ltd., London, 1915, p. 210.

[7] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, 1922, p. 172.

[8] D. S. Reynolds and W. L. Hill, *Ind. Eng. Chem., Anal. Ed.*, **11**, 21 (1939); H. H. Willard and O. B. Winter, *ibid.*, **5**, 7 (1933).