

	M. p., °C.	B. p., °C.
PFCl <sub>2</sub>	-144.0 ± 0.2	13.85 ± 0.05
PF <sub>2</sub> Cl	-164.8 ± .2	-47.3 ± .05
PF <sub>3</sub> (ours)	-151.5 ± .2	-101.15 ± .05
Moissan	-160	-95

PFCl<sub>2</sub>, PF<sub>2</sub>Cl and PF<sub>3</sub> react with chlorine to produce pentavalent chlorofluorides. PFCl<sub>2</sub> and PF<sub>2</sub>Cl yield liquid products which are unstable,

decomposing at room temperature into PCl<sub>5</sub> and PF<sub>5</sub>.

Phosphorus trifluoride when pure is odorless in toxic concentration and therefore care must be exercised in its manipulation.

The critical temperatures and pressures for PF<sub>3</sub>, PF<sub>2</sub>Cl and PFCl<sub>2</sub> have been determined.

CLEVELAND, OHIO

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[A CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

## The Fluorination of Phosphorus Tribromide<sup>1</sup>

BY HAROLD SIMMONS BOOTH AND SPENCER G. FRARY

The successful controlled partial fluorination of phosphorus trichloride<sup>2</sup> led us to study the fluorination of phosphorus tribromide by similar methods.

A preliminary generation was made using 36 cc. of c. p. phosphorus tribromide with 3 cc. of bromine as a catalyst. The fluorinator was immersed in a Dewar of water heated to +80°. Sublimed antimony trifluoride<sup>3</sup> was added gradually by a screw feed while the pressure was maintained at 20 mm. of mercury by the pressure regulator. Under these conditions the tribromide refluxed in the column with no refrigerant needed in the still-head. Fractional distillation<sup>4</sup> of the products obtained by generation at -20° and under 220 mm. pressure yielded PF<sub>3</sub>, HCl and HBr in small amounts, PF<sub>2</sub>Br, and small amounts of HF. The still residue contained PBr<sub>2</sub> and PBr<sub>3</sub>. Since these conditions favored the production of PBr<sub>2</sub>, the pressure was raised to about 250 mm. With the same temperature in the fluorinator and ice in the head there was no refluxing of either PBr<sub>3</sub> or PBr<sub>2</sub>. The products of this fluorination were 10 cc. of PBr<sub>2</sub>, an equal amount of liquid PF<sub>2</sub>Br and approximately 30 cc. of liquid PF<sub>3</sub>, along with a little HBr and HF due to hydrolysis.

Later, when larger amounts of PF<sub>2</sub>Br were needed in order to obtain a good fractional separation and purification, it was found that the yields obtained at 80 and 90° were poorer than

those at higher temperatures. With the temperature of the fluorinator at 170°, the yield of partially fluorinated products was doubled.

**The Fluorination of Monofluorodibromophosphine by Antimony Trifluoride and Bromine.**—Booth and Bozarth<sup>2</sup> have shown that the fluorination of phosphorus trichloride with antimony trifluoride and antimony pentachloride as catalyst is a stepwise reaction and that the intermediate PFCl<sub>2</sub> can be fluorinated readily under proper control to PF<sub>2</sub>Cl, but that the fluorination threshold temperature lowers with each fluorine atom introduced.

Fluorination of monofluorodibromophosphine was tried first at room temperature and at about 200 mm. absolute pressure. The heat of reaction raised the temperature to such an extent that PF<sub>3</sub> was the only product obtained.

The reaction was slowed by cooling the fluorinator to 0° and by reducing the pressure to 20–30 mm. While the product was chiefly PF<sub>2</sub>Br, only about 25% of the material was converted. Warming the fluorinator increased the yield but increased the percentage of the trifluoride at the same time.

Hence the fluorination of phosphorus tribromide by antimony trifluoride and antimony pentachloride is likewise stepwise and closely resembles that of phosphorus trichloride.

**Fluorination of Phosphorus Tribromide Using Calcium Fluoride.**—On account of the successful fluorination of phosphorus trichloride with calcium fluoride by Booth and Bozarth,<sup>2</sup> it was decided to try fluorinating the tribromide with calcium fluoride pellets. The apparatus was similar to that used in the fluorination of phosphorus chloride except that a vertical condenser cooled with

(1) From a portion of a thesis submitted by Spencer G. Frary in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, to the Graduate School of Western Reserve University, June, 1936. Original manuscript received August 24, 1938.

(2) Booth and Bozarth, *This Journal*, **61**, 2927 (1939).

(3) Kindly supplied by the Harshaw Chemical Co., Cleveland, Ohio.

(4) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

tap water was used to condense the unreacted tribromide. The pressure was kept at about 2 cm. and the ampoule heated to 130–140° by an oil-bath to circulate tribromide vapor rapidly. The tube containing the pellets was heated to about 200°. The reaction proceeded very slowly, twenty-four to thirty-six hours of continuous operation being required to obtain 30 cc. of liquid product. This on distillation yielded 15 cc. of  $\text{PF}_3$ , 10 cc. of  $\text{PFBr}_2$  and 5 cc. of  $\text{PF}_2\text{Br}$ , showing that the products were the same as those obtained by the reaction with antimony trifluoride and bromine.

**Separation and Identification of the Products of Fluorination of Phosphorus Tribromide.**—Since the products of the fluorination ranged in boiling point from  $-101$  to  $+170^\circ$ , they easily were roughly separated preliminarily.

The liquid  $\text{PFBr}_2$  was redistilled several times in a small all-glass column at atmospheric pressure, and a small amount transferred to the isoteniscope for a vapor pressure<sup>5</sup> determination. Samples also were taken for analysis, vapor density, melting point and specific gravity determinations as described previously in publications from this Laboratory.

The fraction containing the  $\text{PF}_2\text{Br}$  was returned to the gas fractionating column and purified by repeated distillation at high reflux ratio at 200 mm. pressure.

**Analysis.**—Samples for analysis were condensed in weighed bulbs of 2-cc. capacity, attached to the apparatus by conical joints. The bulbs were sealed off at a constriction in the connecting tube and both portions again weighed. The sample, weighing about 2.5 g., was then frozen with liquid air, the tube broken, and dropped into an excess of sodium hydroxide solution in a stoppered 250-cc. Erlenmeyer flask and allowed to stand for twenty-four hours to ensure complete hydrolysis.

Phosphorus was determined by oxidizing the phosphite with an excess of standard iodine solution and back-titrating with sodium thiosulfate according to the method of Rosenheim and Pinsker.<sup>6</sup> Bromine was determined volumetrically by the Volhard method. Fluorides do not interfere with this determination if sufficient ferric nitrate is added to form the colorless complex ferric fluoride with all the fluorine. Since

we have no satisfactory method for the determination of fluorine in the presence of phosphites, it was obtained by difference, but its presence was established qualitatively.

TABLE I

## ANALYSES

	$\text{PFBr}_2$		$\text{PF}_2\text{Br}$	
	Found	Calcd.	Found	Calcd.
Phosphorus	14.99		20.5	
	14.95		21.2	
Av.	14.97	14.76	20.85	20.88
Bromine	76.17		53.8	
	76.20		53.2	
Av.	76.19	76.14	53.5	53.66
Fluorine (difference)	8.84	9.10	25.65	25.46

Boiling points were taken from vapor pressure curves drawn from the data in Table II. The latent heat of vaporization was calculated by the Clausius-Clapeyron equation.

TABLE II

VAPOR PRESSURE OF  $\text{PFBr}_2$ 

$$\text{Log } p = 7.866 - (1646.2/T)$$

Temp., °C.	Press. obsd.	Press. calcd.	Deviation, mm.
23.5	96	101	5
38.0	186	185	-1
47.0	269	267	-2
54.9	353	351	-2
60.2	426	424	-2
65.3	505	502	-3
77.3	739	738	-1
77.7	746	746	0
78.2	758	757	-1
78.5	762	764	2

VAPOR PRESSURE OF  $\text{PF}_2\text{Br}$ 

$$\text{Log } p = 7.620 - (1217.9/T)$$

Temp., °C.	Press. obsd.	Press. calcd.	Deviation, mm.
-51.0	130	134	4
-35.2	315	317	2
-30.9	391	391	0
-23.0	561	564	3
-20.4	630	632	2
-18.2	691	695	4
-16.3	754	753	1
-15.3	779	787	8

The liquid density of  $\text{PFBr}_2$  was determined in a special pycnometer by the method used by Booth and Herrmann for  $\text{SO}_2\text{ClF}$ .<sup>7</sup>

The vapor density of the  $\text{PF}_2\text{Br}$  was determined by a gas density balance as usual. The  $\text{PFBr}_2$  was condensed in small bulbs and its vapor density determined in a regular Victor Meyer apparatus, using mercury in a gas buret to measure the volume.

Since these compounds are unstable and react

(5) Booth, Elsey and Burchfield, *THIS JOURNAL*, **57**, 2064 (1935).

(6) Rosenheim and Pinsker, *Z. anorg. Chem.*, **64**, 333 (1909).

(7) Booth and Herrmann, *THIS JOURNAL*, **58**, 63 (1936).

with mercury particularly under pressure and at higher temperatures, the critical constants were not determined, but were calculated by the "three-halves" rule.

TABLE III  
PHYSICAL CONSTANTS OF THE PHOSPHORUS BROMO-FLUORIDES

Subs.		PFBr <sub>2</sub>	PF <sub>2</sub> Br
Mol. wt.	Obsd.	218	149
	Calcd.	209.8	148.9
M. p., °C.		-115.0	-133.8
B. p., °C.		78.4 ± 0.1	-16.1 ± 0.1
Latent heat of vapn.		7624	5721
Crit. temp. calcd.		254	113
Trouton constant		21.7	22.3
Liquid density		2.1810 at 0°	

**The Chemical Properties of the Phosphorus Bromofluorides.**—The two bromofluorides condense to clear colorless liquids freezing to white

apparatus was necessary in order to obtain samples that gave the results shown in Table III.

If it is allowed to stand at low temperatures as a liquid, part of it decomposes to the fluoride and bromide:  $3\text{PF}_2\text{Br} \rightarrow 2\text{PF}_3 + \text{PBr}_3$ . When the mixture is transferred from the ampoule the fluoride distills over with the unchanged bromofluoride while the bromide remains behind, causing analyses to be low in bromine and high in phosphorus.

The following experiences suffice to reveal the instability of  $\text{PF}_2\text{Br}$ :

(1) A sample that froze at  $-133.8^\circ$  was allowed to stand in the melting point apparatus for several days. It then froze at  $-144^\circ$ .

(2) Fifteen cc. of the liquid  $\text{PF}_2\text{Br}$  was held in the column still-pot for ten days at dry-ice tem-

TABLE IV

Sample	(1)	(2)	(3)	(4)	(5)	(6)	Calcd.
Phosphorus	30.06	23.0	21.60	21.33	20.5	21.20	20.88
Bromine	29.20	51.33	52.10	53.10	53.8	53.2	53.66
Fluorine	40.74	25.67	26.30	25.57	25.7	25.60	25.46
%PF <sub>2</sub> Br from Br content	54.4	95.6	97.1	99.0	100	99.2	

(1) Sample that had stood in the melting point cell for several days before being transferred to the sample bulb. A portion of sample was discarded before transferring to the analysis bulb as well as part of that transferred, to remove some of the  $\text{PF}_3$ .

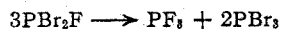
(2) Sample that had stood in an ampoule for a short time. Sample taken after about one-third the contents of an ampoule had been removed.

(3) and (4) Samples that were distilled into an ampoule and then immediately transferred to the sample bulbs. About one-sixth of product discarded first.

(5) and (6) Samples distilled directly into analysis bulbs by distillation of middle fraction from column.

crystalline solids. They fume in air to a greater extent than do either the tribromide or the trifluoride and have a sharp odor. They hydrolyze readily to form phosphorus, hydrobromic and hydrofluoric acids. They react with excess bromine to produce reddish-brown solids which presumably are  $\text{PBr}_4\text{F}$  and  $\text{PBr}_3\text{F}_2$ . These latter are quite unstable and on warming liberate bromine; they were not studied further.

$\text{PBr}_2\text{F}$  is relatively stable and can be distilled at atmospheric pressure. However, on standing, it very slowly decomposes into  $\text{PF}_3$  and  $\text{PBr}_3$ .



It reacts with mercury forming halides of mercury and free phosphorus.

$\text{PF}_2\text{Br}$  is somewhat less stable than  $\text{PFBr}_2$  and difficulty was encountered in obtaining it pure. The chemical analysis showed high phosphorus and low bromine, indicating contamination with  $\text{PF}_3$ . Distillation at low pressure from the column directly into the analysis bulbs and vapor pressure

perature ( $-78^\circ$ ). The pressure rose steadily to almost atmospheric at the end of that time. The sample was then distilled and about 1 cc. of liquid  $\text{PF}_3$  and 0.5 cc. of  $\text{PBr}_3$  were obtained. This agrees with the equation for the decomposition given above, and indicates a conversion of about 1.5 cc. or 10% in ten days or about 1% per day.

(3) A series of analyses to show how the composition changes is given in Table IV.

### Summary

Fluorination of phosphorus tribromide both by the action of antimony trifluoride at 70 and  $170^\circ$  using bromine as a catalyst, and also in the vapor state by reaction with calcium fluoride at  $140^\circ$  yields two new compounds, dibromomonofluorophosphine and monobromodifluorophosphine, as well as phosphorus trifluoride.

Dibromomonofluorophosphine is a clear colorless liquid which boils at  $+78.4^\circ$  and freezes at  $-115.0^\circ$  to a white solid.

Monobromodifluorophosphine is a gas at ordi-

nary temperatures. It condenses to a colorless liquid boiling at  $-16.1^{\circ}$  and freezes to a white solid at  $-135.8^{\circ}$ .

Both of these compounds hydrolyze on contact with the moisture in the air, react with mercury,

liberating phosphorus, combine with bromine to form unstable compounds, probably  $\text{PFBr}_4$  and  $\text{PF}_2\text{Br}_3$ , and decompose slowly forming  $\text{PF}_3$  and  $\text{PBr}_3$  at dry-ice temperatures ( $-78^{\circ}$ ).

CLEVELAND, OHIO

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

## The Fluorination of Phosphoryl Trichloride

BY HAROLD SIMMONS BOOTH AND FREDERIC B. DUTTON<sup>1</sup>

Booth and Swinehart<sup>2</sup> have shown that antimony trifluoride in the presence of a catalyst such as antimony pentachloride causes the progressive fluorination of inorganic non-polar halides. The present investigation is a study of the fluorination of phosphoryl chloride. Phosphoryl trifluoride had been prepared, and its properties first described by Moissan<sup>3</sup> by sparking a mixture of phosphorus trifluoride and oxygen. It has been prepared since by a number of workers using different methods.<sup>4</sup> The intermediate chlorofluorides have not been described previously.

**Preparation of Phosphoryl Chlorofluorides.**—Phosphoryl trichloride was fluorinated by means of antimony trifluoride using antimony pentachloride as a catalyst, and by means of calcium fluoride pellets at elevated temperatures. The apparatus used in these experiments has been described by Booth and Bozarth.<sup>5</sup>

**Fluorination with Calcium Fluoride.**—Fluorination by means of calcium fluoride was effected by passing the vapor of boiling phosphoryl trichloride over calcium fluoride pellets contained in an electrically-heated glass tube. The gases on leaving the reactor were so separated in a fractionating column that any unreacted material was returned to the boiling chamber and the fluorinated products were removed continuously. A generation carried out at a pressure of 100 mm. and with the reactor column containing the calcium fluoride pellets held at a tempera-

ture of  $200^{\circ}$  yielded about 90% phosphoryl trifluoride and 10% of higher-boiling substances. A generation carried out at  $150^{\circ}$  yielded about 35% of the trifluoride, 25% difluoromonochloride, and 40% monofluorodichloride. A generation at  $120^{\circ}$  gave chiefly the trifluoride but soon stopped and could be continued only by raising the temperature.

**Fluorination with Antimony Trifluoride.**—Fluorination by means of antimony trifluoride was carried out by slowly adding resublimed, finely crystalline antimony trifluoride<sup>6</sup> to a mixture of 200 g. of phosphoryl trichloride and 50 g. of antimony pentachloride while the liquid mixture was stirred rapidly and maintained at a predetermined temperature. The volatile products of the reaction passed through a condenser which was cooled by running water at about  $10^{\circ}$ .

A generation carried out with the reaction flask at  $75^{\circ}$  and a pressure of 190–200 mm. yielded about 55% of phosphoryl trifluoride, 5% of difluoromonochloride and 40% of monofluorodichloride. Higher temperatures (up to the boiling point of phosphoryl trichloride) did not seem to alter the above ratio and lower temperatures increased the yield of the trifluoride at the expense of the other products. The fluorinated products were fractionally distilled in a column, rapidly at first, to effect rough separation of the components. Each component was then carefully refractionated two or more times until further fractionation produced no change in the melting point.

### Identification of the Phosphoryl Fluorochlorides

**Analysis.**—Samples for analysis were condensed in heavy walled bulbs connected to the apparatus by flat-joint connections. After filling, the bulbs were sealed off, weighed, frozen, the necks broken and all dropped into half-normal alkali. The gases dissolved completely on warming. Chlorine was determined either gravimetrically or by the Volhard method, and phosphorus by precipitation as the phosphomolybdate and twice as magnesium ammonium phosphate before ignition to the pyrophosphate.

No particular difficulty was encountered in the analysis of phosphoryl monofluorodichloride or the difluoromonochloride, but phosphoryl trifluoride gave results at first 2–4% low and it was found necessary to evaporate the acidified sample to dryness in a platinum dish to decompose fluophosphates before proceeding with the analysis.

(6) Kindly furnished by the Harshaw Chemical Company, Cleveland, Ohio.

(1) Submitted by Frederic B. Dutton to the Graduate School, Western Reserve University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, May, 1937. Reported at the Rochester Convention of the American Chemical Society, September 10, 1937. Original manuscript received August 24, 1938.

(2) H. S. Booth and C. F. Swinehart, *THIS JOURNAL*, **54**, 4751 (1932).

(3) H. Moissan, *Compt. rend.*, **99**, 655 (1884).

(4) H. Moissan, *ibid.*, **102**, 1245 (1886); H. Moissan, *Bull. soc. chim.*, [3] **4**, 260 (1890); *ibid.*, [3] **5**, 456 (1891); *ibid.*, [3] **5**, 458 (1891); H. Schulze, *J. prakt. Chem.*, [2] **21**, 443 (1880); Thorpe and Hambly, *J. Chem. Soc.*, **55**, 759 (1889); A. Guntz, *Compt. rend.*, **103**, 58 (1886); C. Poulenc and H. Moissan, *ibid.*, **113**, 75 (1891).

(5) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937); *THIS JOURNAL*, **61**, 2927 (1939). Additional illustrations and descriptions of this type of apparatus have been given by H. S. Booth and C. V. Herrmann, *ibid.*, **58**, 63 (1936); H. S. Booth and W. C. Morris, *ibid.*, **58**, 90 (1936).