

was done before the Washburn corrections were available, and with different conversion units, etc., quantitative comparison is difficult. The value reported by Swietoslawski to the Bureau of Standards is different from that in his published work.

TABLE III  
COMPARISON OF DATA ON *trans*-AZOBENZENE

| Investigator           | $-\Delta U_B$ | $-\Delta H_B^a$<br>kcal. mole <sup>-1</sup> | $-\Delta H_R$ |
|------------------------|---------------|---|---------------|
| Petit <sup>a</sup>     |               | 1555.2                                      |               |
| Lemoult <sup>b</sup>   |               | 1552.6                                      |               |
| S. and B. <sup>c</sup> | 1543.7        | 1544.6                                      |               |
| S. <sup>d</sup>        |               | 1545.9                                      |               |
| This paper             | 1545.7        | 1546.6                                      | 1545.6        |

<sup>a</sup> Petit, *Ann. chim. phys.*, [6] 18, 145 (1889). <sup>b</sup> Lemoult, *ibid.*, [8] 13, 562 (1908). <sup>c</sup> Swietoslawski and Bobinska, ref. 7. <sup>d</sup> Swietoslawski, private communication to U. S. Bur. Stds.; see Kharasch, *Bur. Standards J. Research*, 2, 425 (1929). <sup>e</sup> Heat evolved at constant pressure without Washburn correction to standard reference state.

The comparative results for the two pure forms from the present work are shown in Table IV. From them may be obtained  $-\Delta H$  for the transition *cis*  $\rightarrow$  *trans* at 25°. This amounts to 9.9 kcal. mole<sup>-1</sup> or  $54 \pm 4$  cal. g.<sup>-1</sup>. Hartley<sup>3b</sup> has found by another method  $65 \pm 4$  cal. as the

mean of three determinations. Finally, also,  $-\Delta H^\circ_{298.16}$ , the heat of formation of the compound, may be calculated using 68,318.1 cal. mole<sup>-1</sup> as  $-\Delta H^\circ_{298.16}$  for water and 94,030 cal. mole<sup>-1</sup> for carbon dioxide.<sup>8</sup> These results are shown in Table IV.

TABLE IV  
SUMMARY OF DERIVED DATA ON *cis*- AND *trans*-AZOBENZENE AT 25°

| Substance                              | <i>trans</i> -Azobenzene | <i>cis</i> -Azobenzene |
|--|--------------------------|------------------------|
| Mol. wt.                               | 182.21                   | 182.21                 |
| $-\Delta U_B$ kcal. mole <sup>-1</sup> | $1545.7 \pm 0.3^a$       | $1555.6 \pm 0.2^a$     |
| $-\Delta U_R$                          | $1544.7 \pm .4^b$        | $1554.6 \pm .6^b$      |
| $-\Delta H_R$                          | $1545.6 \pm .4^b$        | $1555.5 \pm .6^b$      |
| $-\Delta H^\circ_{298.16}$             | -75.65                   | -85.55                 |

<sup>a</sup> Precision uncertainty. <sup>b</sup> Accuracy uncertainty.

### Summary

1. The isothermal heat of combustion of *cis*- and of *trans*-azobenzene has been determined for 25° and constant pressure.
2. The heat of formation for each has been calculated.
3. The heat of the transition *cis*  $\rightarrow$  *trans* has been calculated.

(8) Rossini, *Bur. Standards J. Research*, 22, 407 (1939).

CORVALLIS, OREGON

RECEIVED JULY 31, 1939

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

## Fluorination of Phosphorus Trichloride<sup>1</sup>

BY HAROLD SIMMONS BOOTH AND ABE ROSCOE BOZARTH<sup>2</sup>

This investigation is a continuation of the studies by this Laboratory on the fluorination of non-polar inorganic halides.<sup>3-8</sup> Booth and Swinehart<sup>3</sup> reported the action of antimony trifluoride in the presence of a catalyst on phosphorus trichloride to give a smooth evolution of gases of unknown composition. The only chlorofluoride of phosphorus reported in the literature is PF<sub>3</sub>Cl<sub>2</sub> prepared by Moissan.<sup>9</sup>

The generator used in the preliminary study was similar to that shown in Fig. 1A except that the generator head

was attached directly to the flask, without a fractionating column. About 200 g. of reagent grade phosphorus trichloride was placed in the flask, the catalyst was added and powdered sublimed antimony fluoride was fed in, as needed for a smooth reaction, by means of the screw solid feed C, at room temperature. (Approximately two cubic centimeters of the catalyst, SbCl<sub>5</sub>, per 100 g. of PCl<sub>3</sub> was found to be an optimum amount.) With tap water in the generator head, (H), (+15°) the product was largely PF<sub>3</sub>, a small amount of PF<sub>3</sub>Cl and very little or no PFCl<sub>2</sub>.

On the assumption that the fluorination of phosphorus trichloride is stepwise, the application of precise control to the operating variables ought to lead to improvements in the yields of chlorofluorides. In a stepwise reaction probability of excessive fluorination should be a minimum when the reaction zone (generator flask A, Fig. 1A), is maintained at such a temperature that the unfluorinated liquid will be gently boiling and refluxing at the pressure maintained in the system, since then a fluorinated product would immediately distil out of the reaction zone as soon as it was formed, due to its lower boiling point.

The apparatus shown as Fig. 1A was constructed so as to attain this end. The reaction flask A was a two-liter,

(1) Original manuscript received August 24, 1938.

(2) From a thesis presented by A. R. Bozarth, May, 1935, to the Graduate School of Western Reserve University in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry.

(3) Booth and Swinehart, *THIS JOURNAL*, 54, 4750, 4751 (1932).

(4) Booth and Bozarth, *ibid.*, 55, 3890 (1933).

(5) Booth and Stillwell, *ibid.*, 56, 1531 (1934).

(6) Booth and Swinehart, *ibid.*, 57, 1333 (1935).

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

(8) Booth and Morris, *ibid.*, 58, 90 (1936).

(9) H. M. Moissan, "Le Fluor et Ses Composés," 1900, p. 167.

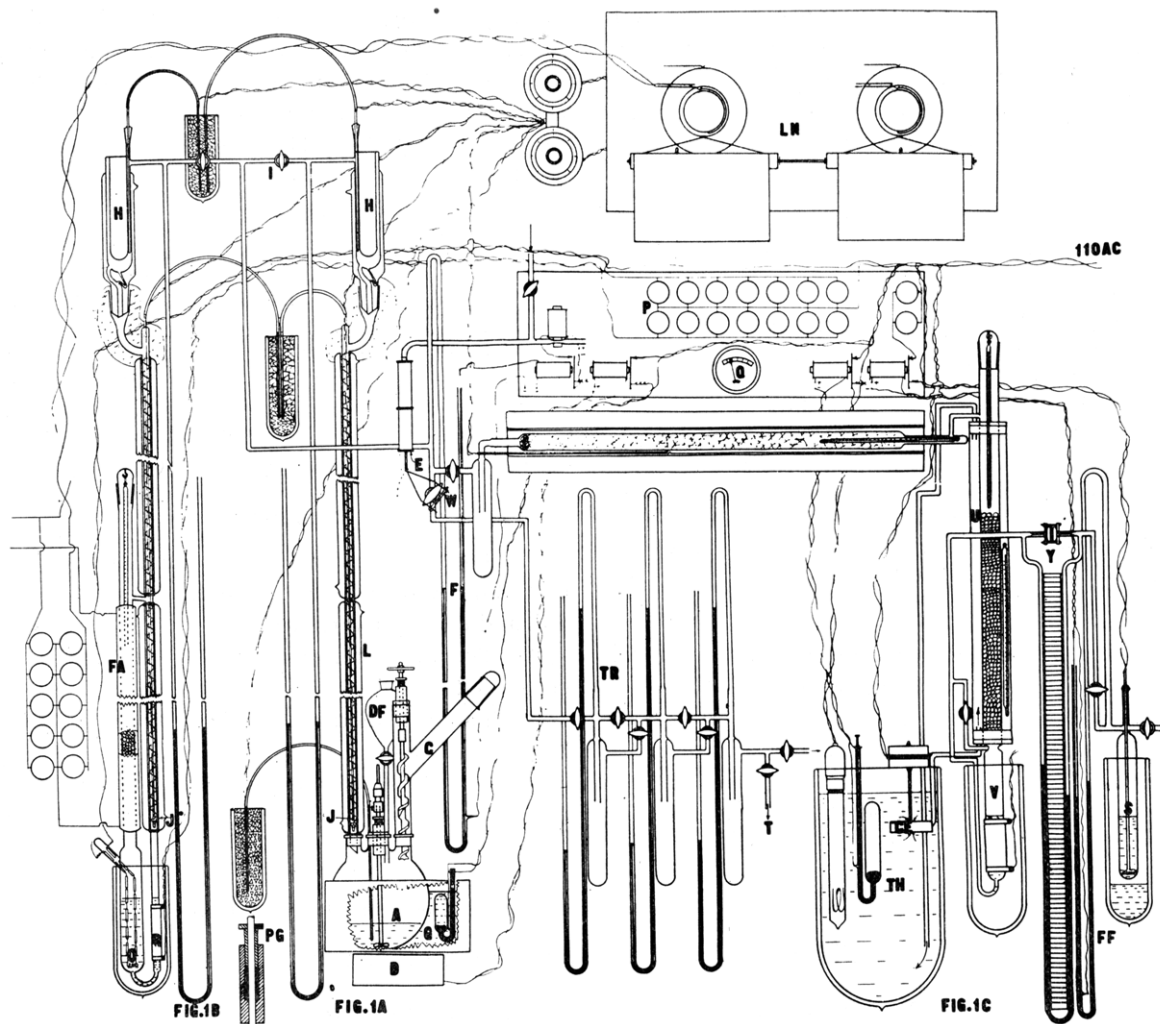


Fig. 1.

Pyrex, three-necked flask. Stirring was accomplished by a brass double-blade propeller which was rendered vacuum-tight at the point of entrance by a gland packed with commercial graphited string packing and lubricated with vacuum pump oil (shown in detail as PG). The temperature of the reaction flask above room temperature was maintained by a thermostatically controlled water-bath heated by an electric heater D, and below room temperature by a thermostatically controlled acetone-bath similar to that used for vapor pressure measurements and controlled either by liquid air or carbon dioxide snow cooling, as described by Booth and Bozarth.<sup>10</sup>

The fractionating column L was identical with that used and already described by the authors<sup>10</sup> except that it was made twice as high to improve the separation. A two-junction thermocouple inserted from the column top through the hollow center tube of the column indicated the temperature of the column bottom at J. A constant temperature was maintained in the still head H either by

suitable fixed temperature refrigerants such as tap water, liquid ammonia, carbon dioxide snow wet with acetone, or by automatic thermostatic control with either liquid air or carbon dioxide cooling.<sup>10</sup>

The gaseous product was removed automatically at a constant system pressure by the compressed air operated automatic stopcock W (Fig. 1A) which opened whenever the mercury thread in manometer F completed the relay circuit.

The general method of adjusting the operating variables of the improved generator was as follows.

The bath G (Fig. 1A) was adjusted to the temperature at which fluorination took place. The manometer contact in F (with stopcock I open) was adjusted so as to contact the mercury and thus to open the automatic stopcock to the traps TR, at a pressure equal to the vapor pressure of the unfluorinated halide at the temperature of the reaction flask. A suitable refrigerant was placed in the head (H) or it was thermostatically controlled so as to maintain the head at the temperature at which the desired chlorofluoride had a vapor pressure equal to the op-

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

TABLE I  
 CONTROLLED FLUORINATION—SWARTS REACTION

| Run number                       | II                           | III              | IV <sup>a</sup>           | V                 | VI                 |
|----------------------------------|------------------------------|------------------|---------------------------|-------------------|--------------------|
| Substance fluorinated            | PCl <sub>3</sub>             | PCl <sub>3</sub> | PFCI <sub>2</sub>         | PFCI <sub>2</sub> | PF <sub>2</sub> Cl |
| Substance, cc.                   | 130                          | 130              | 31                        | 53                | 15                 |
| SbCl <sub>3</sub> catalyst, cc.  | 2-3                          | 2-3              | 2                         | 2                 | 2                  |
| SbF <sub>3</sub> , g.            | 175                          | 175              | 150                       | 150               | .....              |
| Hours to complete                | 3.5                          | 3.5              | ...                       | 2.5               | 3.0                |
| Absolute generator pressure, mm. | 234                          | 250              | 270                       | 247               | 720                |
| Temp. of reaction zone, °C.      | 40                           | 39               | - 15                      | - 15              | - 50-55            |
| Col-umn                          | Bottom-J                     | 37               | - 13                      | - 15              | - 50-55            |
| temp., °C.                       | Bath-G                       | 39               | - 13                      | - 15              | - 50-55            |
|                                  | Still head                   | 14.2             | - 55                      | - 60-62           | - 100-150          |
|                                  | Bath in head                 | Tap water, 12    | CO <sub>2</sub> snow-EtOH |                   | Thermostat         |
| Distillation                     | PFCI <sub>2</sub> , cc. liq. | 30.5             | 2.2 <sup>a</sup>          | 14.0              | .....              |
| analysis of                      | PF <sub>2</sub> Cl, cc. liq. | 10.9             | 11.8                      | 20.0              | 4                  |
| product                          | PF <sub>3</sub> , cc. liq.   | 12.8             | 7.2                       | 11.5              | 10                 |
| Desired product, %               | 63                           | 58               | 62                        | 64                | 100                |

<sup>a</sup> The generator flask was not heated at the end of the fluorination to break up the loose addition compound probably formed between SbF<sub>3</sub> and PFCI<sub>2</sub>, which probably accounts for the loss of some of the PFCI<sub>2</sub>.

erating pressure. In the first studies upon an unknown gas this latter value must be approximated by means of the Swarts<sup>11</sup> rule and the Clapeyron equation.

The system was evacuated thoroughly and the halide added through the dropping funnel DF without breaking the vacuum. If the halide did not reflux after equilibrium was attained, the temperature of the bath G was increased until it did. The catalyst was then added through DF and allowed to mix well with the halide.

The reaction between phosphorus trichloride and antimony pentachloride is exothermic and the mixture had to be cooled to operating temperature before adding the antimony trifluoride. The contact in manometer F was adjusted until it was about 4 mm. above the mercury. A small amount of antimony trifluoride was fed in. As soon as the fluorination began the lower boiling fluorination product which is fractionated out formed a "gas block" in the still head H and raised the pressure and so caused the automatic stopcock W to open momentarily to remove the accumulated gaseous product. The stopcock I was opened until it allowed the gas to pass each time the automatic stopcock opened with a minimum fluctuation in generator pressure. As soon as the system settled down to equilibrium the temperature of the reaction zone, column bottom and still head, was determined. If the column bottom temperature (at J) was lower than the reaction zone temperature, the temperature of the bath about the flask had to be increased until the column bottom temperature reached a maximum which corresponded closely to the reaction zone temperature at the beginning of the fluorination. Under these conditions only pure unfluorinated halide returned to the reaction zone.

Fluorinations which are comparatively rapid such as fluorination of phosphorus trichloride do not lend themselves to the preparation of the difluoro compound exclusively directly from the unfluorinated halide. Any accumulation of the monofluoro is rapidly fluorinated so that the product is a mixture of the difluoro derivative and the completely fluorinated product. This is

due to the fact that the threshold fluorinating temperature lowers with the replacement of each chlorine atom by fluorine in covalently unsaturated non-polar halides.

Table I shows the average data obtained for two runs fluorinating phosphorus trichloride with the conditions controlled to favor PFCI<sub>2</sub>, two runs fluorinating PFCI<sub>2</sub> under conditions favoring PF<sub>2</sub>Cl and one run fluorinating PF<sub>2</sub>Cl to PF<sub>3</sub>. The product condensed in each case was 50 to 75% the product desired, which was the opposite of the yields obtained without precise control, in which the product was 75-90% PF<sub>3</sub> (Table II).

 TABLE II  
 FLUORINATION OF PHOSPHORUS TRICHLORIDE WITHOUT PRECISE CONTROL

Reaction zone at room temp.; press. 760 ± 20 mm.; PCl<sub>3</sub> used, 450 g.

| Run  | Vol. of catalyst, cc.    | Distillation analysis of product, % | PF <sub>2</sub> Cl | PF <sub>3</sub> |
|------|--------------------------|-------------------------------------|--------------------|-----------------|
| VIII | 5                        | 16.7                                | 32.0               | 51.5            |
| IX   | 10 dropped in            | 19.8                                | 6.2                | 74.0            |
| X    | 20 added at start        | 0                                   | 25.0               | 75.0            |
| XI   | 20 at start, total of 60 | 0                                   | 16.7               | 83.3            |
| XII  | 1 at start               | 0                                   | 5.88               | 94.0            |
| XIII | 10 at start              | 8.33                                | 25.0               | 66.7            |

Whereas phosphorus trichloride fluorinated smoothly at a temperature of +40° and 250 mm. pressure, PFCI<sub>2</sub> can be fluorinated at an equal rate at -13° and 250 mm. pressure; furthermore, it is even possible to fluorinate PF<sub>2</sub>Cl to PF<sub>3</sub> at the low temperature of -50 to -55° and 720 mm. pressure. At +40° the rate of fluorination of PFCI<sub>2</sub> was quite rapid and that of PF<sub>2</sub>Cl was very rapid, while the rate of fluorination of phosphorus trichloride was relatively slow. These facts explain both the difficulty of avoiding fluorination

(11) F. Swarts, *Bull. soc. chim.*, **85**, 1556 (1924).

beyond the first step even under controlled conditions, and the completeness of fluorination under uncontrolled conditions, due to increasing rate with increased fluorination.

Antimony trifluoride does not react with phosphorus trichloride to any appreciable extent in the absence of the catalyst ( $\text{SbCl}_5$ ) at the temperatures maintained during this study.

### Fluorination of Phosphorus Trichloride in the Vapor Phase by Solid Heated Calcium Fluoride

E. I. du Pont de Nemours and Company<sup>12</sup> have indicated that heated calcium fluoride may act as a fluorinating agent for organic halides in the vapor phase, producing chlorofluoro compounds from aliphatic chlorides.

An apparatus for the vapor phase fluorination of phosphorus trichloride by calcium fluoride was constructed of soda-lime glass as shown in Fig. 1B. The calcium fluoride furnace FA was a glass tube 1.6 cm. in diameter by 60 cm. long, wound with a thin layer of asbestos tape followed by no. 18 nichrome wire, three turns per inch, and then wrapped with heavy asbestos paper. The temperature was controlled by a split lampbank, one-half of which was controlled by the contacts of a recording controlling potentiometer.

C. p. precipitated calcium fluoride was formed into pellets about 0.5 cm. in diameter by a pharmaceutical pellet machine, and then dried at 125–150° before use.

The fluorination of a halide by this reaction was carried out as follows. The temperature of the furnace was indicated by a thermometer, at the exit end of the furnace. The halide was boiled at a constant rate by an internal coil heater O (fed by a constant current). The exit furnace gases passed into the middle of the fractionating column where the fluorinated product was separated from the unfluorinated. The still-head temperature in H was adjusted so as to correspond to the boiling point of the product desired at the pressure maintained in the system. The contact in the manometer F was adjusted so as to make contact and so to open the automatic stopcock W, whenever the pressure rose slightly due to accumulation of fluorinated product in the still head. A thermocouple at J at the column bottom indicated the temperature of the liquid returned to the boiling ampoule O. By controlling the heat input to the auxiliary heating coil, R, the column bottom temperature could be maintained identical with the temperature of the pure halide at the pressure maintained in the system. Under these conditions no fluorinated substance was being returned to the reaction zone and consequently recirculated through the furnace to be further fluorinated.

Although it was not tried, it seems perfectly feasible, by this method, to convert  $\text{PFCl}_2$  over mainly to  $\text{PF}_2\text{Cl}$  by proper adjustment of operating variables.

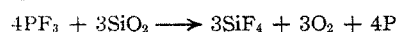
### Reaction between Phosphorus Trichloride and Phosphorus Trifluoride at High Temperature

It was thought that perhaps at higher temperatures phosphorus trichloride and phosphorus trifluoride might react to give the equilibrium,  $\text{PF}_3 + \text{PCl}_3 \rightleftharpoons \text{PF}_2\text{Cl} + \text{PFCl}_2$ . Since we started our experiments, T. Mitobedzki<sup>13</sup> has described a similar reaction for the preparation of the bromochlorides of phosphorus.

The apparatus finally developed is shown as Fig. 1C. The  $\text{PF}_3$  was condensed into ampoule S. It was then melted and a Dewar one-third full of liquid air was placed around the ampoule (but not in contact with it). A small heating coil in the liquid phosphorus trifluoride (boiling point  $-101^\circ$ ) heated it much faster than it cooled, so that the pressure was raised rapidly to 720 mm. When the pressure reached 720 mm. the mercury in manometer FF made contact, closing a relay circuit which interrupted the heating current. The net result was that phosphorus trifluoride was fed at constant pressure ( $\pm 2$  mm.). The rate of flow of the phosphorus trifluoride was indicated by a sharp-edged orifice flow meter Y. The orifice was a thin platinum sheet with a perfect hole 0.013 mm. in diameter drilled in the center. The platinum plate was clamped between two glass flat joints as indicated. A constant flow was obtained by maintaining a constant pressure drop across the orifice. Since the ampoule S was automatically kept at constant pressure and the pressure on the other side of the orifice was kept constant by the contacting manometer F which operated the automatic stopcock W, a constant pressure drop and therefore a constant flow was maintained through the system.

The phosphorus trifluoride was saturated with phosphorus trichloride by being bubbled through the phosphorus trichloride in ampoule V, heated by a coil of nichrome wire fed by a constant current. The temperature of the jacket U was adjusted to that temperature at which phosphorus trichloride has a vapor pressure equal to one-half the total pressure in the system. The mixture leaving the saturator under these conditions contained a one to one molal ratio of phosphorus trifluoride to phosphorus trichloride. A centrifugal pump, CE, pumped water, maintained at constant temperature, from the bath TH through the jacket U. The reaction tube was made of glass, and the furnace temperature was controlled by a recording, controlling potentiometer, LN.

Preliminary runs in a smaller and less refined apparatus showed that at around 230–250° no appreciable reaction occurs; at 500° reaction takes place but phosphorus deposits and probably silicon fluoride is produced by a reaction analogous to that indicated by A. Simon<sup>14,15</sup> between silica and phosphorus trifluoride,



When the furnace temperature approximated 400° no phosphorus deposited, indicating little or no reaction with the glass tube. Under these con-

(12) French Patent 730,874, May 23, 1932, "Perfectionnements a la Fabrication des Hydrocarbures Acycliques Fluores."

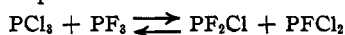
(13) T. Mitobedzki, C. A., **27**, 475 (1933).

(14) Mellor, "Treatise on Inorganic Chemistry," Vol. VIII, p. 995.

(15) Simon, German Patent 131,414 (1900).

ditions approximately 30% conversion of phosphorus trifluoride was obtained per pass.

Two runs at 500° in the apparatus just described gave considerable phosphorus and etching. The product, moreover, upon distillation, yielded a constant boiling fraction, probably consisting of SiF<sub>4</sub> and PF<sub>2</sub>Cl, as analysis showed a mean value of 14.1% chlorine (calcd. for PF<sub>2</sub>Cl, 34%). We were able to purify the PFCl<sub>2</sub> fraction and the molecular weight of the product coming from the still gave a mean value of 122, which is in accord with 121.8 found for the calcium fluoride reaction product and the theoretical molecular weight, 121.5. Between 350 and 400° it is possible to get mainly the equilibrium



At the temperature at which the equilibrium shifts appreciably to the right (400°), other products such as POF<sub>3</sub> and SiF<sub>4</sub> are formed. It was soon found that PF<sub>2</sub>Cl readily forms constant boiling point mixtures with POF<sub>3</sub>, etc., which are difficult to separate and identify, as their molecular weights are close. Considerable time also is required to attain equilibrium in this reaction. Hence, as a method of preparation this method is of little value.

The possibilities of using a Pyrex or metal tube and a catalyst suggested themselves but they were not tried since the Swarts reaction and the calcium fluoride reaction had been simultaneously modified and improved by precise control so as to produce mainly PFCl<sub>2</sub> and PF<sub>2</sub>Cl.

#### Purification

The gases were purified by fractional distillation in an automatic column and their physical properties determined as described by Booth and Bozarth.<sup>10</sup>

#### Analysis

One hundred-cc. sample bulbs, filled to not over 700 mm. pressure, were weighed against counterpoises. The samples were absorbed at once (to minimize reaction with the stopcock grease) into a sodium hydroxide solution containing 100% excess sodium hydroxide, by placing the lower stopcock tube under the caustic and opening the cock. The gas is absorbed rapidly, the caustic rushing into the bulb with the evolution of heat. The solution was allowed to stand in the bulbs for two to three hours to ensure complete reaction.

The chlorine was determined gravimetrically with the following precautions. The samples were diluted to 200 cc. and acidified with nitric acid and then 30 cc. of concentrated nitric acid was added. It was found that in the presence of this amount of nitric acid the phosphite did not reduce the silver in the cold. If the concentration of nitric acid was too low, boiling immediately threw down metallic silver.

The phosphorus content was determined by oxidation with excess standard iodine solution and back titration of the excess with sodium thiosulfate, according to the method of Rosenheim and Pinsker.<sup>16</sup> The presence of fluorine was established qualitatively. The analytical results are recorded in Table III.

TABLE III

| ANALYSIS OF PCl <sub>3</sub>   |  |  |                             |
|--------------------------------|--|--|-----------------------------|
|                                | Chlorine   | Phosphorus   |                             |
| Found                          | 77.20  | 22.70  |                             |
|                                |  | 22.38  |                             |
|                                |  | 22.74  |                             |
| Mean                           | 77.20  | 22.61  |                             |
| Calcd.                         | 77.42  | 22.55  |                             |
| ANALYSIS OF PF <sub>2</sub> Cl |  |  |                             |
|                                | Chlorine<br>(sample made<br>by Swarts reaction)                    | Phosphorus<br>(sample made<br>by Swarts reaction)    | Fluorine<br>(by difference) |
| Found                          | 34.04  | 29.42  |                             |
|                                | 33.75  | 29.56  |                             |
|                                | 33.84  |  |                             |
|                                | 33.90  |  |                             |
| Mean                           | 33.88  | 29.49  | 36.63                       |
| Calcd.                         | 33.94  | 29.69  | 36.37                       |
| ANALYSIS OF PFCl <sub>2</sub>  |  |  |                             |
|                                | Chlorine<br>(sample made<br>from the calcium<br>fluoride reaction) | Phosphorus<br>(sample made<br>by Swarts<br>reaction) | Fluorine<br>(by difference) |
| Found                          | 58.59  | 25.75  |                             |
|                                | 58.70  | 25.61  |                             |
|                                | 58.78  |  |                             |
| Mean                           | 58.60  | 25.68  | 15.72                       |
| Theory                         | 58.63  | 25.63  | 15.74                       |
| ANALYSIS OF PF <sub>3</sub>    |  |  |                             |
|                                |  | Phosphorus<br>(sample made<br>by Swarts<br>reaction) | Fluorine<br>(by difference) |
| Found                          |  | 34.98  |                             |
|                                |  | 35.00  |                             |
| Mean                           |  | 34.99  | 65.0                        |
| Calcd.                         |  | 35.24  | 64.76                       |

#### Physical Constants and Properties

After preliminary separation of the generation product, each fraction was purified carefully by the distillation technique already described. Finally a middle portion of a fraction coming from the still at constant still-head temperature and constant molecular weight was collected separately. This sample was used for measurement of the physical constants.

PFCl<sub>2</sub>, Monofluorodichlorophosphine is a colorless gas which can be condensed to a colorless sparkling liquid and frozen to a clear white solid. This substance yields twig-like crystals upon freezing. Table IV gives the physical constants of PFCl<sub>2</sub>.

PFCl<sub>2</sub> hydrolyzes in moist air and is hydrolyzed by water, but does not fume. It is absorbed very rapidly by sodium hydroxide solution with the evolution of heat. The compound appears to be stable: approximately 50 cc. of liquid PFCl<sub>2</sub> was stored under pressure in a sealed

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

glass tube for ten months. At the end of this time the liquid was homogeneous and no excess pressure above that of the vapor pressure of  $\text{PFCl}_2$  had developed.

$\text{PF}_2\text{Cl}$ , **Difluoromonochlorophosphine** is a colorless gas which can be condensed to a colorless sparkling liquid and frozen to a white solid.

TABLE IV

PHYSICAL CONSTANTS OF  $\text{PFCl}_2$ Vapor pressure  $\text{PFCl}_2$ ,  $\log p_{\text{mm.}} = 7.439 - (1308/T)$ 

| Temp., °C. | Prepared by the Swarts reaction | Pressure, mm. at 0° obsd. by $\text{CaF}_2$ reaction | mean two methods of prepn. | Pressure Calcd. | Deviation, mm. |
|------------|---------------------------------|--|----------------------------|-----------------|----------------|
| -61.22     | 6.3                             | 6.6  | 6.5                        | ...             | ...            |
| -53.92     | 24.6                            | 27.9   | 26.2                       | 29.6            | +3.4           |
| -44.52     | 51.3                            | 50.5   | 50.9                       | 52.1            | +1.2           |
| -33.74     | 92.3                            | 91.2   | 91.8                       | 94.4            | +2.6           |
| -22.96     | 161.8                           | 161.5  | 161.7                      | 163.4           | +1.7           |
| -12.46     | 263.2                           | 262.9  | 263.0                      | 263.8           | +0.8           |
| - 8.16     | 319.7                           | 319.2  | 319.5                      | 318.1           | -1.4           |
| - 3.99     | 378.8                           | 378.9  | 378.9                      | 379.4           | +0.5           |
| + 2.28     | 489.6                           | 490.9  | 490.3                      | 489.6           | -0.7           |
| + 7.40     | 596.1                           | 598.7  | 597.4                      | 597.6           | +0.2           |
| +12.85     | 729.3                           | 734.2  | 731.8                      | 733.3           | +1.5           |
| +14.94     | 796.0                           | 799.2  | 797.6                      | 791.6           | -6.0           |
| +18.17     | 881.6                           | 884.0  | 883.3                      | 888.8           | +5.5           |

|  |                    |
|--|--------------------|
| Normal boiling point.....              | +13.85 $\pm$ 0.05° |
| Latent heat of evaporation.....        | 5950 cal./g. mole  |
| Trouton's constant.....                | 20.7               |
| M. p., °C. { Swarts reaction 1934..... | -144.0 $\pm$ 0.2   |
| { Swarts reaction 1933.....            | -144.0 $\pm$ .2    |
| { Calcium fluoride reaction..          | -144.4 $\pm$ .2    |
| Mol. weight { Swarts reaction.....     | 122.0              |
| { Calcium fluoride reaction            | 122.0              |

This gas tends to form difficultly separable mixtures with  $\text{SiF}_4$  and  $\text{POF}_3$ . The molecular weights of  $\text{SiF}_4$  (104.06),  $\text{POF}_3$  (104.03) and  $\text{PF}_2\text{Cl}$  (104.48) are so near that indication of precise separation by means of the density balance becomes impossible. It was found that the  $\text{PF}_2\text{Cl}$  produced by high-temperature fluorination with calcium fluoride could not be rendered completely pure by repeated distillation, as evidenced by low analytical results and molecular weights.

TABLE V

PHYSICAL CONSTANTS OF  $\text{PF}_2\text{Cl}$ Vapor pressure  $\text{PF}_2\text{Cl}$ ,  $\log p_{\text{mm.}} = 7.043 - (939.7/T)$ 

| Temp., °C. | Press. obsd., mm. | Press. calcd. from equation | Deviation, mm. |
|------------|-------------------|-----------------------------|----------------|
| -83.22     | 125.4             | 124.4                       | -1.0           |
| -71.81     | 236.5             | 236.0                       | -0.5           |
| -64.34     | 346.3             | 348.3                       | 2.0            |
| -60.73     | 419.9             | 423.5                       | 3.6            |
| -55.14     | 535.8             | 539.9                       | 4.1            |
| -50.21     | 668.0             | 672.3                       | 4.3            |
| -49.23     | 702.4             | 701.6                       | -0.8           |
| -46.20     | 798.4             | 800.0                       | 1.6            |
| -42.22     | 934.4             | 940.6                       | 6.2            |

|   |                   |
|---|-------------------|
| Normal boiling point.....   | -47.3 $\pm$ 0.05° |
| Latent heat of evaporation.....   | 4200 cal./g. mole |
| Trouton's constant.....   | 19.1              |
| Melting point, prepared by fluorina-<br>tion of $\text{PFCl}_2$ by Swarts reaction..... | -164.8 $\pm$ 0.2° |
| Molecular weight.....   | 105.5             |

By avoiding leaks and by careful drying, the Swarts reaction yielded samples of  $\text{PF}_2\text{Cl}$  which could be purified to yield a pure fraction for melting point, vapor pressure, and analysis. The physical constants of  $\text{PF}_2\text{Cl}$  are given in Table V.

$\text{PF}_2\text{Cl}$  hydrolyzes in moist air and water less rapidly than  $\text{PFCl}_2$  but does not fume. It is absorbed very rapidly by sodium hydroxide solution with the evolution of heat. When stored as a liquid at  $-78^\circ$  over long periods it appears to be stable.

$\text{PF}_3$ , **Trifluorophosphine**.—This gas was prepared first by Moissan.<sup>9</sup> It is a colorless gas which can be condensed to a liquid, and frozen to a white solid. It is prepared best by dropping solid antimony fluoride into 200 g. of vigorously stirred phosphorus trichloride and slowly adding the catalyst. Every precaution must be taken to keep the partially fluorinated products in the reaction zone. The product is 80–90% trifluorophosphine (see Table II). A large sample was precisely distilled and the middle portion of the pure fraction used for measurement of the physical constants (Table VI).

TABLE VI

PHYSICAL CONSTANTS OF  $\text{PF}_3$ Vapor pressure  $\text{PF}_3$  (made by Swarts reaction)  $\log p_{\text{mm.}} = 7.310 - (761.4/T)$ 

| Temp., °C. | Sample | Press. obsd. at 0° | Press. calcd. from equation | Deviation, mm. |
|------------|--------|--------------------|-----------------------------|----------------|
| -116.8     | A      | 274.0              | 275.1                       | 1.1            |
| -113.48    | B      | 345.9              | 347.4                       | 1.5            |
| -110.02    | B      | 435.0              | 437.1                       | 2.1            |
| -103.51    | A      | 662.6              | 662.4                       | -0.2           |
| -102.61    | B      | 690.9              | 699.9                       | 8.5            |
| -101.07    | A      | 762.5              | 767.0                       | 4.5            |
| -100.04    | B      | 800.4              | 796.4                       | -4.0           |
| - 99.45    | A      | 844.7              | 843.5                       | -1.2           |
| - 97.50    | A      | 945.0              | 943.4                       | -1.2           |

Normal boiling point (Moissan found

|   |  |
|---|--|
| -95°).....                                  | -101.15 $\pm$ 0.05°                                    |
| Latent heat of evaporation.....             | 3489 cal./g. mole                                      |
| Trouton's constant.....                     | 20.3   |
| Melting point (Moissan, $-160^\circ$ )..... | -151.5 $\pm$ 0.2°                                      |
| Molecular weight.....                       | { 89.0 (this study)<br>87.2 (Moissan)<br>88.0 (theory) |

Trifluorophosphine hydrolyzes very slowly in air and when pure it is odorless in toxic concentrations. This property of trifluorophosphine makes it hazardous to handle since any leaks are not detected readily until the operator begins to feel the effects. Its symptoms are a sharp pain in the chest cavity upon inhalation of a deep breath. There is a pronounced rise in body temperature, vomiting is induced in some cases, and the victim feels very weak for several hours. (These are the authors' experiences.) Very small concentrations will cause the sharp chest pain. Trifluorophosphine is absorbed rapidly by sodium hydroxide with the evolution of heat.

### Critical Constants

These physical constants were measured by means of the apparatus and improved technique developed in this Laboratory.<sup>17</sup> The critical temperature was taken as that temperature at which the meniscus disappeared from the tube without rising or falling. The temperature above that of the room was maintained by resistance knife heaters; below room temperature by a new method using dry-ice as described by Booth and Bozarth.<sup>10</sup>

Considerable difficulty was encountered while measuring the critical constants of  $\text{PFCl}_2$ . Due to the high critical temperature the sample would liquefy in the upper part of the Cailletet tube exposed to the room. When the pressure was further increased so as to force the sample into the cell the liquid would wet the walls of the capillary and tend to come back past the mercury so that the sample could not be readily forced into the cell without mercury going into the cell also. In contact with mercury at the critical temperature this gas decomposed probably forming halides of mercury and leaving a deposit of yellow phosphorus. By careful manipulation of one sample mercury was kept out of the cell. In this case slight decomposition also was noted; a light brown film, probably elemental phosphorus, was formed. One sample was held at the critical temperature for five and one-half hours; a  $2.3^\circ$  rise in the critical temperature and a 0.94 atm. rise in the critical

pressure was noted, simultaneously with the formation of a brown film on the walls of the cell. Table VII lists the critical constants found for this series.

**Reaction of the Fluorination Products with Chlorine.**—Chlorine was mixed with one of the chlorofluorides of phosphorus at the entrance of an empty tube 2.0 cm. in diameter and 40 cm. long. The fluoride gas was fed into the reactor tube at constant rate by a gas feed identical with that described in Fig. 1C. It was found that the reaction would not start in a clean glass apparatus but the presence of a single crystal of iodine immediately catalyzed the reaction. The reaction of  $\text{PF}_2\text{Cl}$  and chlorine is evidently exothermic since the chlorination tube warmed to  $80\text{--}100^\circ$  whereas the reaction between  $\text{PFCl}_2$  and chlorine is not as exothermic since the reaction tube temperature remains unchanged.  $\text{PF}_3$  and chlorine do not combine readily in the presence of iodine. If, however, the reaction tube is radiated with a carbon arc, rapid reaction takes place to form  $\text{PF}_3\text{Cl}_2$ . Preliminary experiments indicate that Moissan's value for the boiling point of  $\text{PF}_3\text{Cl}_2$  given as  $-8.0^\circ$  is incorrect; the correct value probably lies in the range  $0$  to  $10^\circ$ .

The products obtained by chlorination of  $\text{PFCl}_2$  and  $\text{PF}_2\text{Cl}$ , probably  $\text{PFCl}_4$  and  $\text{PF}_2\text{Cl}_3$ , are unstable liquids having the respective vapor pressures 275 mm. at  $75\text{--}80^\circ$  and 387 millimeters at  $32^\circ$ .  $\text{PFCl}_4$ , which decomposes in about thirty hours at  $25^\circ$ , yields as decomposition products a white solid, probably  $\text{PCl}_5$ , and a colorless gas, probably  $\text{PF}_3$ .  $\text{PF}_2\text{Cl}_3$  does not decompose as rapidly; a white solid was apparent after standing for twenty-four hours and decomposition was complete in about six days. Moissan found that  $\text{PF}_3\text{Cl}_2$  decomposed at  $200^\circ$  to form a white solid,  $\text{PCl}_5$ , and a gas,  $\text{PF}_3$ .

### Summary

An apparatus and technique applicable to the controlled fluorination of inorganic halides is demonstrated.

The chlorofluorides of phosphorus have been prepared by three methods: (1) The Swarts reaction between  $\text{PCl}_3$  and  $\text{SbF}_3$  in the presence of  $\text{SbCl}_5$  as a catalyst. (2) The calcium fluoride reaction, a gas-solid reaction between  $\text{PCl}_3$  vapor and hot solid  $\text{CaF}_2$ . This is the first time to our knowledge that this reaction has been applied to the preparation of chlorofluorides from inorganic halides. (3) The reaction between  $\text{PCl}_3$  and  $\text{PF}_3$  in a hot tube. This method is unsatisfactory as a method of preparation due to side reactions with the glass to form  $\text{POF}_3$  and  $\text{SiF}_4$  which are extremely difficult to remove from  $\text{PF}_2\text{Cl}$  by distillation.

Two new gases ( $\text{PFCl}_2$  and  $\text{PF}_2\text{Cl}$ ) were obtained and  $\text{PF}_3$  was restudied, using improved technique, with melting and boiling points as follows:

TABLE VII

CRITICAL CONSTANTS OF  $\text{PCl}_3$ ,  $\text{PFCl}_2$ ,  $\text{PF}_2\text{Cl}$  AND  $\text{PF}_3$

|  | $T_c, ^\circ\text{C.}$ | $P_c, \text{atm.}$  |
|--|------------------------|---|
| $\text{PF}_3$  | $-2.05 \pm 0.02$       | 42.67   |
|  | $-2.05 \pm .02$        | 42.70   |
| Mean   | $-2.05 \pm .02$        | 42.69   |
| Source: mixture of $\text{PF}_3$ from fluorinating $\text{PCl}_3$ and also $\text{PFCl}_2$ by Swarts reaction. |                        |   |
| $\text{PF}_2\text{Cl}$   | $89.17 \pm 0.05$       | 44.62   |
|  | $89.16 \pm .05$        | 44.59   |
| Mean   | $89.17 \pm .05$        | 44.61   |
| Source: fluorination of $\text{PFCl}_2$ by Swarts reaction   |                        |   |
| $\text{PFCl}_2$  | $189.88 \pm 0.05$      | 49.60   |
|  | $189.80 \pm .05$       | 48.99 Best value  |
| Mean   | $189.84 \pm .05$       | 49.3  |
| Source: Swarts reaction from $\text{PCl}_3$ <sup>18</sup>  |                        |   |
| $\text{PCl}_3$ <sup>18</sup>   | $285.5^a$              | Critical pressure not measurable by the closed tube method. |

<sup>a</sup>  $t_c$  measured by the closed tube method.

(17) Booth and Swinehart, *THIS JOURNAL*, **57**, 1337 (1935).

(18) Br. Pawlowski, *Ber.*, **16**, 2633 (1883).

|                        | 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).