for reactions of methyl bromide, the activation energy for the exchange with methyl bromide is 4.6 kcal. For barium bromide, which is a less active catalyst, the activation energy for the exchange is 12 kcal.; and for potassium bromide, which is not a catalyst, the rate of exchange is too slow to detect.

2. From determinations of the adsorption of methyl bromide on barium bromide, the differential heat of adsorption was found to be *ca.* −3 kcal. It is concluded that the rate determining step in the barium bromide–methyl bromide exchange is the exchange between the adsorbed methyl bromide and the barium bromide crystals. The significance of this step was discussed.

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

The Fluorination of Thiophosphoryl Bromide. The Thiophosphoryl Bromofluorides[1]

BY HAROLD SIMMONS BOOTH AND CLARENCE ARTHUR SEABRIGHT[2]

In contradistinction to the fluorination products of phosphorus tribromide,[3a] those of phosphoryl tribromide[3b] were quite stable. Furthermore, whereas the fluorination of sulfur monochloride by antimony fluoride, with or without a catalyst, gave only decomposition without fluorination, the fluorination of thiophosphoryl chloride with the same reagent proceeded smoothly to yield the stable chlorofluorides.[4] Hence it was of interest to establish whether thiophosphoryl bromide could be fluorinated easily to give stable bromofluorides.

Experimental

Thiophosphoryl tribromide[5] was prepared by the reaction of phosphorus pentabromide and phosphorus pentasulfide: $P_2S_5 + 3PBr_5 = 5PSBr_3$. The fluorination of thiophosphoryl bromide took place at 60–70° without a catalyst and the pressure was varied according to the product desired.[6] At atmospheric pressure chiefly thiophosphoryl fluoride was obtained. The main product at 40 mm. pressure was thiophosphoryl monobromodifluoride and at 15 mm. pressure the dibromomonofluoride was the major product. The reaction is noticeably exothermic. In all cases the generator head temperature was 20–25°.

The products were separated and purified by fractional distillation in a suitable column.[7] The identity of the PSF_3 was established by chemical analysis, and by determination of its boiling point and gas density. The two new compounds were established by their analyses and vapor densities.

Analysis.—Samples for analyses were condensed in weighed glass bulbs connected to the apparatus with conical joints. When filled the bulbs were sealed off at a constriction. After warming to room temperature the two portions of the sample tube were weighed and the weight of the sample determined. The sample was then frozen and the tube broken and dropped into a closed flask containing potassium hydroxide solution.

Thiophosphoryl monobromodifluoride reacted slowly with the alkaline solution at room temperature but thiophosphoryl dibromomonofluoride showed no apparent reaction even after standing for twenty-four hours. However, both liquids reacted with the alkali on heating on a steam-bath and were decomposed in a few hours. The solution was then heated on a steam-bath for fifty hours to ensure complete decomposition. A few cc. of 30% hydrogen peroxide was added to oxidize sulfides and sulfites to sulfates and the excess oxygen boiled off. Bromine was determined gravimetrically as silver bromide and sulfur as barium sulfate. The phosphorus was precipitated as ammonium phosphomolybdate and then dissolved and reprecipitated as magnesium ammonium phosphate, and finally ignited to magnesium pyrophosphate.

TABLE I

ANALYSES

	Phosphorus		Sulfur		Bromine	
	Theoret.	Found	Theoret.	Found	Theoret.	Found
PSF_2Br	17.14	17.18	17.71	17.76	44.15	44.16
		17.19		17.61		44.12
$PSFBr_2$	12.82	12.95	13.25	13.42	66.06	65.95
		12.78		13.40		66.12

Physical Properties.—Physical properties were established according to methods standard in this Laboratory.[6,7,8,9] Vapor pressures were run on different samples of the substances. From the combined data from three separately prepared samples of each compound, the vapor pressure equations given in Table II were derived. The physical properties of the thiophosphoryl bromofluorides

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[1] Presented at the St. Louis meeting of the American Chemical Society, April 8, 1941.

[2] From a portion of a thesis submitted by Charles Arthur Seabright in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, May, 1940.

[3] (a) Booth and Frary, THIS JOURNAL, **61**, 2934 (1939); (b) Booth and Seegmiller, *ibid.*, **61**, 3120 (1939).

[4] Booth and Cassidy, *ibid.*, **62**, 2369 (1940).

[5] See "Inorganic Syntheses," Vol. II, for details of this preparation.

[6] For technique of this generation see Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939).

[7] Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

[8] Booth, Elsey and Burchfield, THIS JOURNAL, **57**, 2064 (1935).

[9] Booth and Herrmann, *ibid.*, **58**, 63 (1936).

as shown in Table II, lie between those of the thiophosphoryl trifluoride and the tribromide. The compounds are colorless liquids and freeze to white solids. Since they attack mercury at elevated temperatures the critical constants could not be determined.

TABLE II

PHYSICAL PROPERTIES

	PSF_2Br	$PSFBr_2$
Boiling point,[a] ° C.	35.5 ± 0.1	125.3 ± 0.1
Freezing point, ° C.	−136.9 ± 0.5	−75.2 ± 0.1
Liquidus range	172.4	200.5
Liquid density	1.940 at 0	2.390 at 0
Molecular weight (by the gas density method)	182	
Heat of vaporization,[b] cal.	6775	8351
Trouton's constant	22.0	21.0

[a] From a plot of the vapor pressure data. [b] Calculated by the Clausius–Clapeyron equation.

Vapor pressure of PSF_2Br from 0 to 760 mm.

$\log p = (-1484.8/T) + 7.6970$ (av. deviation of data from the equation = +0.05 mm. Maximum deviation = +7.6 mm.)

Vapor pressure of $PSFBr_2$ from 0 to 760 mm.

$\log p = (-1827.3/T) + 7.4674$ (Av. deviation of data from the equation = −0.17 mm. Maximum deviation = +3.2)

Chemical Properties.—A small amount of $PSFBr_2$ was distilled into each of a number of tubes containing various materials and the tubes sealed off. They were allowed to stand for two weeks at room temperature and then observed. There was no visible reaction with lead, tin, zinc or sulfur. Iron was corroded on the surface with the formation of a white solid and the liquid turned yellow. Copper was severely attacked with the formation of white, red and black solids. In one month the copper wire appeared to be almost entirely destroyed. The surface of pieces of silver became yellow. The thiophosphoryl dibromomonofluoride in contact with sodium iodide turned red, probably due to formation of free iodine. A finely powdered silica became gelatinous and swelled. A piece of paraffin dissolved to form a clear solution; on cooling this solution to 0° it solidified to a white opaque solid; on warming to 25° it became liquid again.

Various other properties of thiophosphoryl dibromomonofluoride were noted during the course of the studies. It begins to react with mercury at about 70°. It does not attack nichrome wire noticeably at room temperature. It is miscible with acetone and carbon tetrachloride. The reaction with water and dilute potassium hydroxide at room temperature is slight, if any. The liquid appeared unchanged even after standing in contact with potassium hydroxide solution for twenty-four hours. On heating to 100° reaction takes place slowly. It fumes slightly in air and has a peculiar, but not sharp, odor.

Thiophosphoryl monobromodifluoride is somewhat more reactive than the dibromomonofluoride. It reacts slowly with cold potassium hydroxide solution and vigorously with hot caustic. It attacks mercury slightly at 35–40°. In general, both thiophosphoryl bromofluorides are more inert than most of the inorganic non-polar halides.

Discussion

The remarkable thermal stability of the "phosphoryl" type of halofluorides, as shown by the products of the partial fluorination, of $POCl_3$,[10] $PSCl_3$,[4] and of $POBr_3$,[3b] is here again exemplified in the thiophosphoryl bromofluorides. In fact, of all of these, surprisingly, the thiophosphoryl bromofluorides are the most resistant to hydrolysis. In the past this has been explained by Willy Lange[11] as due to the formation of salts of intermediate fluophosphoric acids which are difficult to hydrolyze completely. However, the inertness of thiophosphoryl dibromomonofluoride to cold alkaline solution even after twenty-four hours of contact would indicate the inertness resided in the first stage of hydrolysis and requires further elucidation.

The great strength of the sulfur–phosphorus bond as shown by its non-reaction with the fluorinating agent both in the case of $PSCl_3$ and in the case of $PSBr_3$ as contrasted with our experience with S_2Cl_2 merits considerable study.

As in the case of phosphoryl tribromide,[3b] phosphorus tribromide,[3a] and as found by Schumb and Gamble[12] in the fluorination of $SiBr_4$ by SbF_3, no catalyst was necessary. We have explained this in the past by assuming the presence of small amounts of free bromine due to thermal decomposition of the bromide. In view of the greater stability of thiophosphoryl bromide, if this is the true explanation, then extremely small amounts of the catalyst suffice.

The lessened reactivity of fluorination products of $PSBr_3$ was to be expected from the evident exothermic character of the reaction, but the greater inertness and stability of the monofluoro derivative as compared with the difluoro compound was unexpected.

The liquidus ranges of these new compounds are unusually long as is the case with the parent substance, $PSBr_3$, although no other evidence of association was observed.

Summary

The fluorination of thiophosphoryl bromide by anhydrous SbF_3 without a catalyst yields the known gas PSF_3, and two new volatile liquids, PSF_2Br boiling at 35.5° and $PSFBr_2$ boiling at 125.3° the latter unusually resistant to alkaline hydrolysis. Other physical and chemical properties are given.

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(10) Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939).

(11) Willy Lange, *Ber.*, **60B**, 962 (1927); **62B**, 786-792 (1929).

(12) Schumb and Gamble, THIS JOURNAL, **58**, 994 (1936).