

enough so that considerable data may be obtained in a relatively short period of time yet not so rapid as to prevent accurate measurement. The temperature coefficient is sufficiently small to allow the use of a rather wide temperature variation, which makes for precision in the determination of energies and entropies of activation.

The authors wish to express their appreciation of the advice and assistance given by Professor R. C. Elderfield during the extended absence of one of them (L. P. H.).

Summary

The acid and base catalyzed aldolizations of benzaldehyde with methyl ethyl ketone have been studied synthetically in detail. It was found that concurrent and consecutive reactions

may be totally eliminated by a careful selection of experimental conditions.

Kinetically, the base catalyzed reaction is first order with respect to the concentration of both aldehyde and ketone. The specific rate is linear in but not proportional to the square root of the analytically determinable concentration of the base. Medium effects are pronounced and the specific rate exhibits a parallelism to the initial concentration of either reactant.

The base catalyzed aldolization of benzaldehyde and acetone was also studied kinetically but in somewhat lesser detail.

Energy and entropy activation values lend additional support to the theory of Price and Hammett, concerning the effect of structure on the reactivity of carbonyl compounds.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HARVARD UNIVERSITY]

The Radioactive Exchange and Adsorption of Methyl Bromide with Several Inorganic Bromides

BY G. B. KISTIAKOWSKY AND JOHN R. VAN WAZER

Introduction

In order to add some data to the fund of information which will some day lead to a complete, general theory of heterogeneous catalysis, a quantitative study was made of the exchange of bromine isotopes between radioactive methyl bromide and several inorganic bromides. Aluminum bromide, barium bromide and potassium bromide were used since the first is a strong catalyst for certain reactions of methyl bromide, the second is a mild catalyst, and the third does not exhibit catalytic activity. The adsorption of methyl bromide on barium bromide was investigated in order to elucidate the mechanism of the exchange. Adsorption studies were not made on aluminum bromide because of the complicating action of impurities such as aluminum hydroxide.

Materials.—The radioactive methyl bromide was prepared in the following manner so that the measured radioactivity was due to Br^{80} with a thirty-four-hour half-life. Bromoform containing a trace of bromine was irradiated by slow neutrons in the Harvard Cyclotron. The free bromine containing a large fraction of the bromine radioactivity was then completely extracted from the bromoform by means of a cold solution of ammonium hydroxide. In order to avoid any complication of the exchange process by high energy bromine atoms coming from the iso-

meric transition of Br^{80} (4.4 hr.) to Br^{81} (18 min.) and also to be able to neglect the natural decay rate of the radioactivity in the calculation of exchange rates, the ammonium bromide was allowed to stand for thirty-six hours before it was used. During this time the aqueous extractions were evaporated on a steam-bath to pure, dry ammonium bromide. This salt was mixed with sulfuric acid and methyl alcohol and heated in a small reaction flask so arranged that the evolved gases were passed through four absorption columns, the first of which contained water, the other three concentrated sulfuric acid. The resulting pure dry methyl bromide with radioactive bromine was condensed in a trap cooled by dry-ice.

The barium bromide crystals used in the exchange studies were prepared by fusing dehydrated commercial C. P. barium bromide in a platinum boat within a furnace made from a porcelain tube. When the barium bromide had melted, the temperature of the furnace was slowly reduced and the furnace was evacuated. The barium bromide was then cooled under vacuum to *ca.* 100°. The resulting fused mass (probably a single crystal) was ground up in a mortar kept at 150° and the powder was shaken through a set of brass sieves also at *ca.* 150°. By this means, grains of a definite size and reproducible geometrical surface were obtained. Microscopic study showed that these grains were all crystalline conchoidal fracture particles with no visible surface cracks or fissures. The seventy-mesh particles had an average area of 3×10^{-3} sq. cm. and an average volume of 1.2×10^{-2} cu. cm. per particle. The barium bromide that was used for adsorption experiments was hydrated and dehydrated a number

of times in order to form sponge-like particles exhibiting a very large surface area.

The aluminum bromide was made by direct combination of the elements. Powdered aluminum was placed in a long-neck 50-cc. round-bottom flask and bromine was added to it dropwise. At the completion of the reaction a slight excess of aluminum was added and the neck of the flask was cleaned and sealed to a clean flask. Then by careful heating in a sand-bath the anhydrous aluminum bromide was distilled into the clean flask leaving a residue of aluminum and impurities. The flask containing the aluminum bromide was broken away from the other flask in a dry-box.

The dry-box in which the aluminum bromide was always handled was kept anhydrous by trays of Dehydrite suspended around its sides. A pair of rubber gloves allowed free access to the interior of the box. The aluminum bromide was broken up in a mortar and sieved while in the box. Enough moisture was exuded from the rubber gloves to cause the aluminum bromide to fume slightly. This would, of course, add an indeterminate variable factor to the relationship between the geometrical surface and the active area for heterogeneous reactions.

The potassium bromide was carefully heated in an oven at 150° to remove adsorbed moisture and crushed in a hot mortar. Since the commercial sample used was especially pure and the salt does not form a stable hydrate, no special process of preparation was attempted.

Apparatus and Procedures.—The radioactive methyl bromide was kept in an evacuated tube cooled by an ether-dry-ice mixture. This tube was connected to a glass system so arranged that methyl bromide vapor at any given pressure could be put into either the vessel in which the exchange took place or an annular jacket surrounding the Geiger-Mueller tube with which the radioactivity was determined. The gas could also be condensed out of the exchange vessel and put into the counter jacket at a given pressure. Thus, the radioactivity of the gas could be measured before and after exchange.

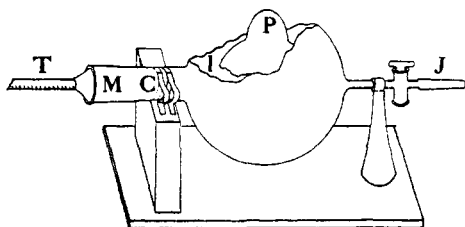


Fig. 1.—Solid-gas mixer: C, commutators leading to heating element; J, ground glass joint for attaching to filling system; M, large joint through which solid particles were added; P, protuberance for lifting solid particles; T, thermometer; I, insulation.

In the preliminary experiments the methyl bromide vapor was simply allowed to stand over the inorganic bromide with which the exchange was to take place. However, the rate of exchange was affected by variation of the exposed area of the inorganic bromide which indicated that diffusion between the solid particles was in part rate determining. In order to keep the gas well stirred and also to present all the faces of the solid particles to the gas during

the exchange process, the all-glass mixer shown in Fig. 1 was used as the exchange vessel. It could be filled or evacuated through the ground joint, J, and was heated by a wrapping of wire which led to the commutators, C. When the mixer was rotated, the cup-shaped protuberances on the walls picked up the solid particles and dropped them down through the methyl bromide vapor and over the thermometer, working in the same manner as a cement mixer. Before each run the mixer was evacuated and heated up to a temperature considerably higher than that of the run in order to remove adsorbed gases. Between runs the mixer was always kept evacuated. The usual procedure during a run was first to fill the mixer and the counter with fresh methyl bromide. While the mixer was rotating, the count of the unexchanged vapor was taken. The counter was then evacuated and refilled with the gas from the mixer.

The adsorption apparatus was of the usual design¹ and the temperature was maintained at different values by vapor-baths of boiling liquids.

Depth of Exchange.—In some of the experiments that were performed with barium and aluminum bromides all of the radioactivity was removed from the sample of methyl bromide. This occurred when the exchange was allowed to take place for a long period of time at an elevated temperature (150 to 300°). For these cases we can investigate the approximate depth in the crystal to which the exchange process must have proceeded so that only an undetectable amount of radioactivity was left in the gas. In these experiments the volume of methyl bromide gas in the mixer was 65 cc. and the ratio $P/T = 1$ mm. per °K.; thus 6.4×10^{20} molecules of methyl bromide were present. A volume of 6.5 cc. of the seventy-mesh barium bromide particles was in the mixer. Assuming 1.7 Å. as the average radius of the barium and bromide ions, we can say that there are *ca.* 10^{18} bromide ions in the geometrical surface layer of the barium bromide. Any allowances for fissures or irregularities could not account for a total area more than ten times larger than the geometrical area. Table I summarizes this information.

TABLE I

Material under consideration	Number of molecules therein
The sample of methyl bromide gas	6.4×10^{20}
The geometrical area of the barium bromide	1×10^{18}
The whole sample of barium bromide	6.4×10^{22}

Thus we see that not only the surface layer but approximately the upper 50 to 100 layers of the barium bromide crystals must be able to undergo exchange with the gas to remove half of the radio-

(1) Pease, THIS JOURNAL, 45, 1196 (1923).

activity. In order for the radioactivity to be so completely removed from the gas that no counts were experimentally observed, the exchange must

TABLE II

BARIUM BROMIDE-METHYL BROMIDE EXCHANGE

CH ₃ Br pressure, mm.	Temp. of exchange, °C.	Time for exchanging, min.	R', counts/sec.	R, counts/sec.	$k \times 10^3$, min. ⁻¹
Sample 1. Activation energy = 10.7 kcal.					
405	136	75	43.4	15.0	14.1
363	121	59	55.3	35.1	7.8
324	108	92	53.7	36.0	4.3
474	158	42	22.0	16.2	7.3
681	227	40	22.0	6.6	30
288	96	63	32.9	29.3	15.1
375	125	69	31.6	24.9	3.3
Sample 2. Activation energy = 7.8 kcal.					
342	114	88	43.4	16.1	11.1
327	109	69	55.3	21.4	13.8
354	118	102	53.7	16.2	11.0
159	147	53	22.0	13.2	9.7
680	192	49	22.0	5.3	24
285	95	81	32.9	25.8	29.6
375	125	83	31.6	16.9	7.5
Sample 3. Activation energy = 13.1 kcal.					
$P/T = 1^a$	119	72	91.1	62.1	5.37
	82	76	86.8	81.8	0.79
	88	81	61.3	55.3	1.51
	114	80	62.6	42.0	4.98
	158	41	45.4	18.3	22.1
$1/2 P$	119	47	46.4	31.9	8.0
$2 P$	116	55	46.4	38.2	3.52
Sample 4. Activation energy = 12.8 kcal.					
$P/T = 1$	119	85	91.1	68.5	2.30
	88	101	61.3	58.8	0.48
	116	92	62.6	42.3	4.26
	210	52	62.6	65	43
	144	48	45.4	25.7	11.8
$1/2 P$	121	65	46.4	37.3	3.36
$1/2 P$	117	56	46.4	35.2	4.94
Sample 5. Activation energy = 12.2 kcal.					
$P/T = 1$	120	70	32.0	22.8	4.83
	209	54	47.3	ca. 0	Large
	147	60	52.1	22.5	14.0
	119	72	52.1	35.3	5.43
	95	160	42.7	32.0	1.81
Sample 6. Activation energy = 13.5 kcal.					
$P/T = 1$	120	88	32.0	22.0	4.29
	209	66	47.3	ca. 0	Large
	147	70	52.1	12.9	20.0
	120	87	52.1	31.9	5.66
	95	172	42.7	30.4	1.99

^a In these runs the number of methyl bromide molecules was kept constant by making the ratio of pressure in mm. to absolute temperature equal to unity. However, in certain of these runs the pressure was n times greater than this constant ratio demanded; these runs are denoted by the symbol nP where n is given its numerical value.

TABLE III

ALUMINUM BROMIDE-METHYL BROMIDE EXCHANGE

In order to keep the number of methyl bromide molecules constant, the pressure was so adjusted that $P/T = 1$ mm. per °A.

Temperature of exchange, °C.	Time for exchanging, min.	R', counts/sec.	R, counts/sec.	$k \times 10^3$, min. ⁻¹
Sample 1. Activation energy = 4.6 kcal.				
25	75	24.3	2.0	3.3
25	33	24.3	6.9	3.8
22	76	72.3	19.5	1.73
31	37	63.3	26.2	2.4
35+	40-	63.3	35.0	1.50
47	32	39.3	12.7	3.5
48	24	39.3	13.3	4.6
65	23	39.3	5.1	8.9
Sample 2. Activation energy = 4.6 kcal.				
24	35	37.7	8.3	4.3
25	33	37.7	12.7	3.3
24	40	46.2	13.4	3.1
24	29	46.2	20.0	2.9
72	33	46.2	5.6	6.6
74	22	32.5	4.1	9.5
74	21	32.5	4.5	9.4

extend nearly all the way into each barium bromide particle. This is in accord with experiments² on the exchange between silver bromide and bromine in which the exchange extended throughout the entire solid. Therefore, this extreme depth of exchange in the solid appears to be a general phenomenon.

Exchange Data.—We can compute the data on the exchange rate as a first order reaction³ with respect to the loss of radioactivity from the sample of methyl bromide. Thus the rate constant, k , equals $(2.303/t) \log (R'/R)$, where R' is the counting rate of the pure methyl bromide corrected for pressure and background, and R is the corrected counting rate for the methyl bromide which was allowed to exchange during the time, t . Each sample of barium bromide was 6.5 cc. of the seventy-mesh, fused salt. Sample 1 of the aluminum bromide was 6.5 cc. of thirty- to sixty-mesh aluminum bromide. However, since the aluminum bromide had practically all adhered to the walls of the mixer when the first set of experiments was completed, the mixer was not cleaned out before the addition of the second sample of aluminum bromide, which was 6.5 cc. of the same mesh. Perhaps this explains the fact that the data on sample 2 are more self-consistent than those on sample 1. The volume of the mixer was 50 cc.

(2) Kolthoff and O'Brien, *J. Chem. Phys.*, **7**, 401 (1939).

(3) McKay, *Nature*, **142**, 997 (1938).

From the experiments on the barium bromide samples 1, 2, 3 and 4, we see that the pressure (in the range of 200 to 1000 mm.) had no effect on the rate constant within experimental error. The best value for the activation energy of the barium bromide-methyl bromide exchange is 12 kcal., and for the aluminum bromide-methyl bromide exchange it is 4.6 kcal.

In the experiments on potassium bromide and also on sodium bromate no exchange was found. Calcium bromide showed an exchange of the same magnitude as that found with barium bromide. Although several experiments showing no exchange were made with ferrous and zinc bromides, the data are not considered significant because the salts that were used were impure and had incrustated surfaces. Qualitatively then the rate of bromine exchange is proportional to the catalytic activity of these salts.

Adsorption.⁴—When the methyl bromide was adsorbed on the microarborescent crystals of barium bromide such data as those plotted in Fig. 2 resulted. From this figure, which is typical of the entire set of adsorption experiments, we can see that the over-all process can be treated as if it were composed of a fast process (part AB of Fig. 2) and a succeeding slow process (B to D). Since the rates of the fast and slow processes are of an entirely different magnitude, the amount of methyl bromide adsorbed in the fast process may be considered to be measured at equilibrium.

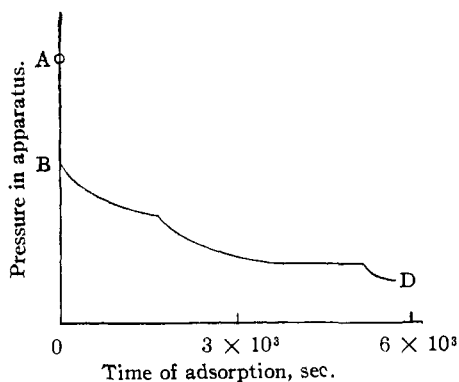


Fig. 2.—Adsorption curves: A. pressure of nitrogen which is equal in amount to the methyl bromide and thus closely approximates the pressure that the methyl bromide would have if none were adsorbed; B, value of methyl bromide pressure obtained by extrapolating the rate curve for slow adsorption back to zero time.

(4) The word adsorption is used here in the most general sense of condensation on a clean surface at a temperature above the boiling point of the adsorbate, regardless of whether the adsorbate is then absorbed or not.

Thus, we may plot isotherms for the fast process, *e. g.*, Fig. 3, and from these determine a differential heat of adsorption. For the sample of barium bromide, the isotherms of which are plotted in Fig. 3, the average value for the differential heat of adsorption is -4.0 kcal.; for another sample the differential heat of adsorption was calculated to be -2.5 kcal. Thus ΔH for the fast adsorption process is *ca.* 3 ± 1 kcal.

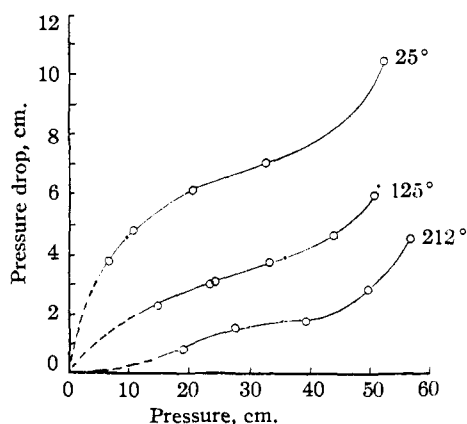


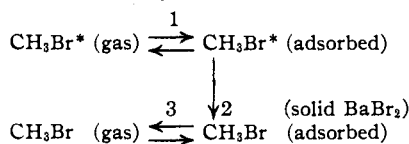
Fig. 3.—Fast adsorption isotherms.

The slow process is not reproducible and is composed of successive, apparently independent, steps, each one of which appeared to tend toward an equilibrium. In some experiments the pressure in the adsorption apparatus would decrease to a value stable for anywhere from a period of minutes to hours, then it would again decrease toward another metastable pressure value. In other experiments the pressure-time curve would exhibit a cusp and the pressure would undergo a sharp decrease before a metastable pressure was reached. Each step of the slow process could be fitted to the rate equation $-dP/dt = k(P - P_E)P/P_E$ where P is the instantaneous pressure at time t , and P_E is that metastable pressure toward which the value of P tends with increasing time. The stepwise appearance of the pressure-time curve could not have been caused by a disintegration of the barium bromide particles, since, when the adsorption apparatus was evacuated and a run was repeated, the pressure time curves of the two runs were the same except for the fact that the cusps in the slow processes did not coincide.

Since the area of the barium bromide particles used in the adsorption work could not be measured, no estimate could be made of the amount of

adsorption on the fused crystals used in the exchange experiments. However, the shape of the fast adsorption isotherm would be the same for both the fused and arborescent crystal particles. If the abrupt changes in the rate of slow adsorption are due to some property of the crystal form of the barium bromide particles, it is very possible that the fused crystals used in the exchange might not exhibit this rate phenomenon.

The Rate Determining Step in the Methyl Bromide-Barium Bromide Exchange.—The radioactive exchange between methyl bromide and barium bromide is represented by the system of chemical equations given below



Let us investigate the energy requirements of this system of equations. Since the fast adsorption isotherm has the S-shape that is associated with multimolecular adsorption and since there is a large amount of adsorption in this process, it seems probable that the entire adsorbing surface is covered in the fast adsorption process. Even if this is not so, the active centers for adsorption must be covered in this, the first adsorption process. Radioactive exchange must take place between the crystals of barium bromide and those adsorbed molecules closest to the crystal surface. It is also reasonable to expect that the active centers for adsorption would also be the most active part of the surface for exchange if the ability to exchange varied over the surface of the crystals. Therefore, step 1 in the mechanism of radioactive exchange given above must have the same energy values that were found for the fast adsorption process. For step 1, the activation energy is nearly zero and ΔH is *ca.* -3 kcal.

Since the over-all reaction and the reaction in step 2 are both only isotope exchange reactions, there can be no heat change in the process, and the energy level before the reaction must equal the energy level after the reaction for both cases. This means that the heat and activation energy of step 3 must both be equal to those of step 1. But the observed activation energy for the over-all exchange is *ca.* 12 kcal. Therefore, the rate determining step in the exchange process is step 2, or the exchange between the adsorbed methyl bromide and the barium bromide solid. The acti-

vation energy for the rate determining step is then 12 to 15 kcal. depending on the character of adsorption.

We may express the rate constant for exchange in the following manner, if the rate determining step is unimolecular.

$$k = r\nu e^{-E/RT}$$

where r is the ratio between the number of adsorbed molecules that can participate in the rate process and the number of molecules in the gas. For a unimolecular reaction we can take roughly the frequency factor⁵ as equal to *ca.* 10^{13} . From the fast adsorption isotherms, it seems that the adsorbing surface was nearly completely covered with a film of molecules at the pressures used in the exchange experiments. If the entire first layer of adsorbed molecules can participate in the rate determining step, the ratio r in the above equation is not much less than 10^{-3} .

$$\therefore k = (10^{-3})(10^{13})e^{-15000/800} = 10^2$$

at temperatures around 100° .

The rate constant thus calculated turns out to be some 10^6 times faster than the experimental values. The possibility that reaction occurs only on some selected ("active") parts of the surface which would reduce the theoretical frequency factor, seems to be rather improbable because the entire crystal has been found to undergo the exchange process. Slow reaction on the surface, of a type different from the unimolecular mechanism, cannot be excluded, of course, but the more probable explanations are that the rate determining step is either (1) diffusion of ions or (2) diffusion of methyl bromide molecules through the crystal. In this connection the observed "slow adsorption" of methyl bromide in barium bromide is undoubtedly significant, but its detailed correlation with the exchange data is not clear. In experiments⁶ on the diffusion of hydrogen and halogens into potassium halide crystals it was shown that dissociation did not occur during diffusion. Thus, it is possible that the methyl bromide diffused through the crystal lattice undissociated.

Summary

1. The exchange of bromine between methyl bromide and various inorganic bromides has been studied by means of a radioactive tracer. For aluminum bromide, which is an active catalyst

(5) $\nu = \frac{kT}{h}$.

(6) Mollwo, *Ann. Phys. Lpz.*, **29**, 394 (1937).

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.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 12, 1943

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

The Fluorination of Thiophosphoryl Bromide. The Thiophosphoryl Bromofluorides¹

BY HAROLD SIMMONS BOOTH AND CLARENCE ARTHUR SEABRIGHT²

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 tribromide⁵ 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_2Br 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

(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. 11, 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*, **67**, 2064 (1935).

(9) Booth and Hertmann, *ibid.*, **58**, 63 (1936).