Summary

Iodine has been found to distribute itself between heavy water and carbon tetrachloride in the molarity ratio 1:103 at infinite dilution at 25°, as compared with a corresponding ratio of 1:85 for ordinary water.

KUNMING, CHINA RECEIVED FEBRUARY 21, 1944

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Molecular Structures of Phosphoryltribromide, Thiophosphoryltribromide, Thiophosphorylmonofluorodibromide, and Thiophosphoryldifluoromonobromide

BY J. H. SECRIST AND L. O. BROCKWAY

Interesting deviations from predicted single covalent bond radii have been observed in the molecular structures of halogen derivatives of non-metals, especially those of silicon and phosphorus.[1,2] Phosphoryl and thiophosphoryl fluorides and chlorides having been previously studied,[3,4,5] it seemed desirable to extend this type of investigation to the phosphoryl and thiophosphoryl bromides and to two mixed thiophosphoryl halides, $PSFBr_2$ and PSF_2Br, which had been prepared and furnished us by Professor H. S. Booth of Western Reserve University. The unusual shortening effect on bond lengths of fluorine atoms in both organic and inorganic compounds has been a subject of investigation for some time.

In this study, the usual electron diffraction method was employed on the vapor of the compound. A constant wave length of 0.0592 Å. for the electron beam was used, the camera distance varying between 99.0 and 101.5 mm. Temperatures were maintained on the samples sufficient to furnish vapor pressures of 50–100 mm. at the time of photographing. To reach this vapor pressure in the case of the solids $POBr_3$ and $PSBr_3$, a special electrical heating coil was used around the sample holder to maintain temperatures at 50–60°. Room temperature was satisfactory for the compound $PSFBr_2$, and −35 to −27° for the compound PSF_2Br.

Radial distribution curves for each compound were calculated from the distribution function of Pauling and Brockway, $D = \Sigma\, c_k(\sin s_k r)/(s_k r)$, where C_k is given by I_k, the visually estimated relative intensity, multiplied by the factor s_k^2 exp. $(-as_k^2)$. The exponential factor is set equal to 0.1 for the largest ring. These curves are shown in Fig. 1.

Phosphoryl Tribromide.—Phosphoryl tribromide was prepared from phosphorus tribromide by addition of bromine and subsequent treatment with phosphorus pentoxide.[6] The product boiling between 188 and 190° was recrystallized from anhydrous ether (m. p. 55–56°).

Theoretical intensity curves for the eight most favorable models are shown in Fig. 2. In calculating these models, trigonal symmetry through the P-O axis was assumed in each case. The models vary in decreasing order of BrPBr angle from 112° in model A to 103° in model H. The main difference in the curves appears at minima 3 and 4 and beyond peak 8. The photographs showed minimum 3 to be less deep than 4; and peaks 3 and 5 heavier than peak 4. This makes curve A inferior, as peaks 3 and 4 here are of about the same height. Regular gradations in the depth of minima 3 and 4 occur from top to bottom in Fig. 2. Curves F, G and H are, therefore, increasingly inferior in this respect to curves B, C, D and E. In curve H, the order is actually reversed for these two minima; moreover, peaks 6 and 7 show the wrong relative intensity in H. The conclusion is that curves C, D and E fit the observed features most closely, with B and F on the border line.

TABLE I

PHOSPHORYL TRIBROMIDE

Max.	Min.	s_0	c_k	s_C/s_0	s_D/s_0	s_E/s_0
	2	5.23	−44	0.922	0.924	0.893
3		6.27	44	.918	.928	.901
	3	7.11	−34	.918	.933	.913
4		8.00	32	.892	.905	.884
	4	8.93	−44	.899	.906	.879
5		9.87	47	.915	.920	.891
	5	10.86	−24	.919	.927	.897
6		11.85	24	.911	.919	.894
	6	12.62	−14	.915	.921	.896
7		13.54	14	.918	.923	.895
	7	14.64	− 8	.916	.922	.890
8		15.58	8	.921	.928	.895
	8	16.42	− 4	.930	.936	.907
9		17.41	3	.916	.926	.902
	Average			.915	.923	.896
	Average deviation			.006	.006	.006
	P-O, Å.			1.427	1.440	1.398
	P-Br			2.040	2.058	2.088
	O-Br			2.855	2.898	2.930
	Br-Br			3.331	3.332	3.333

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(1) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(2) A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937).

(3) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

(4) D. P. Stevenson and H. Russell, Jr., *ibid.*, **61**, 3264 (1939).

(5) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(6) E. Berger, *Compt. rend.*, **146**, 400 (1908).

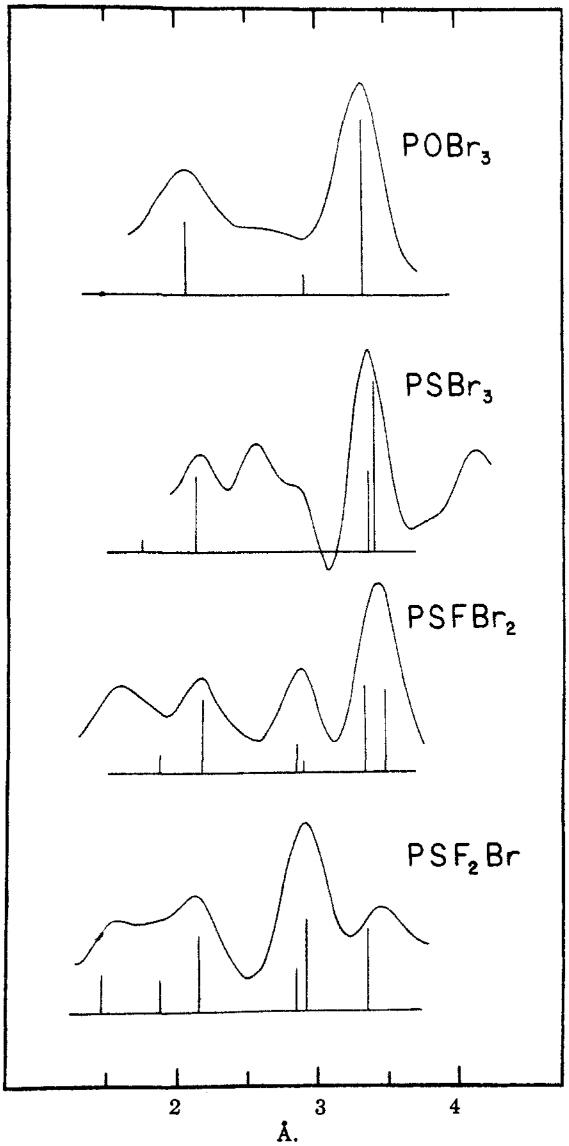

Fig. 1.—Radial distribution curves. The vertical lines mark the distances associated with the stronger terms in the intensity functions for the final molecular models.

The s/s_0 values for these three curves are given in Table I, together with the s_0 and c_k values.

If trigonal symmetry is assumed for this molecule, the molecular structure of all the models calculated are fixed by points on a two-dimensional parameter chart as shown in Fig. 3, using as axes the ∠BrPBr and the bond length ratio P–O/P–Br. The angle parameter can be determined within about 3°, but the low scattering power of oxygen relative to the phosphorus and the three bromine atoms makes the determination of the other parameter less certain. C and D are two of the better models in Fig. 2 but it is not possible to exclude other models having considerably different P–O/P–Br ratios. The values of the heavier scattering pairs, P–Br and Br–Br, are fixed by the results in Table I at 2.06 ± 0.03 Å. and 3.33 ± 0.03 Å., respectively, with ∠BrPBr = 1.08 ± 3°. The P–O distance is estimated at 1.44 ± 0.10 Å.

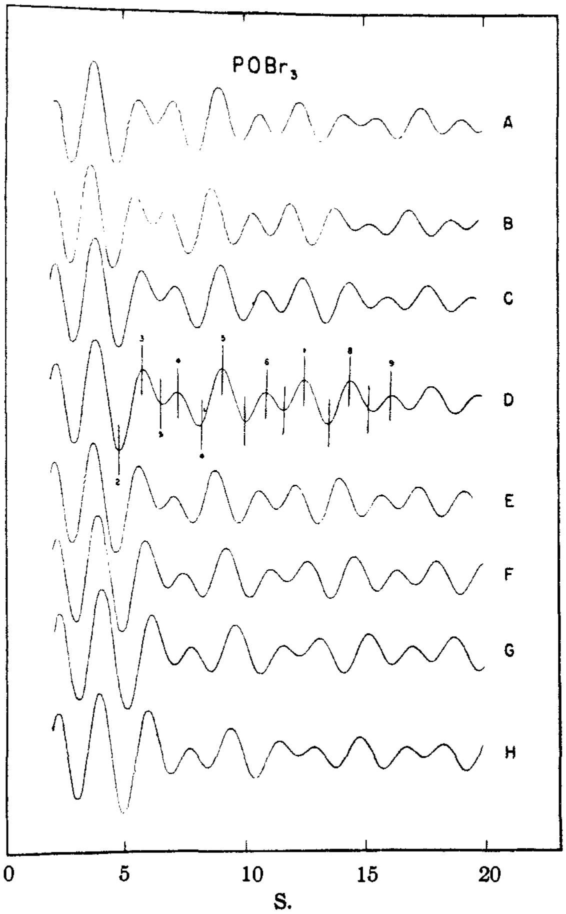

Fig. 2.—Electron scattering curves for $POBr_3$. The observed positions of the maxima and minima are marked on the best curve.

Radial distribution peaks (Fig. 1) occur at 3.29 and 2.06 Å., corresponding to the Br–Br distance and the P–Br distance, respectively. These results indicate a considerable shortening of the P–Br bond distance under 2.24 Å., the value calculated from the sum of the atomic radii and observed in a study of PBr_3.[2] In spite of large uncertainties, the P–O distance appears to be shorter than 1.57 Å., the distance calculated from tables of double-bond radii. Previous reports[1] on P–O distances for phosphoryl trichloride and fluorochlorides give results of 1.54 to 1.56 Å.

Thiophosphoryl Tribromide.—The sample of thiophosphoryl tribromide was prepared by passing dry hydrogen sulfide over phosphorus pentabromide. The product was recrystallized from carbon bisulfide (m. p. 38–39°).

Seven curves (Fig. 4) were calculated for the models shown on the parameter chart in Fig. 5, in which the scale is fixed by a value of 1.95 Å. for P–S in A, D and G and of 1.84 Å. in B, C, E and

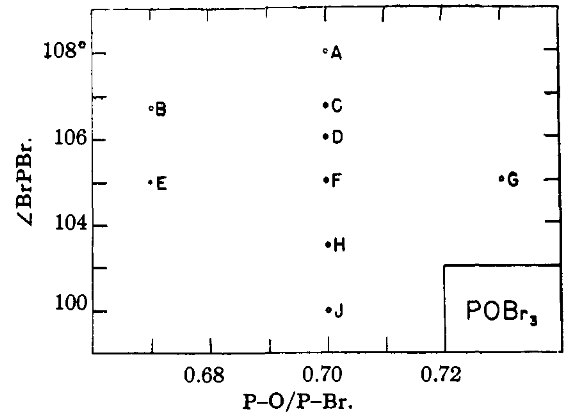

Fig. 3.—Chart showing the models calculated for $POBr_3$.

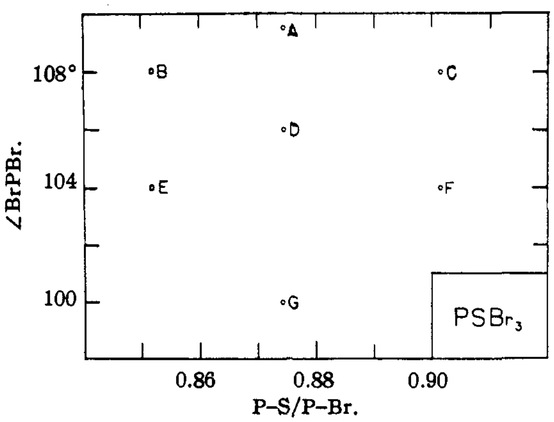

Fig. 5.—Chart of models calculated for $PSBr_3$.

F. Trigonal symmetry was assumed in all cases. Curve A shows peak 7 heavier than peak 6, contrary to the photographs. In both curves A and B, minimum 6 is too shallow and peak 9 does not appear as strong as observed. Curves E and G are objectionable because of the approximately equal depth of minima 3 and 4. The photographs show minimum 4 somewhat deeper than 3. It is concluded that curves C, D and F fit the observed pattern most reliably, and their deviations from observed s values are satisfactorily small. The s/s_0 ratios for these curves, together with the c_k and s_0 values, appear in Table II. From the tabulated results the following values are given: P–S = 1.89 ± 0.06 Å.; P–Br = 2.13 ± 0.03 Å.; ∠BrPBr = 106 ± 3°. The larger uncertainty associated with the P–S estimate is due to the relatively small scattering power of the single P–S pair. The prominent peak in the radial distribution curve at 3.37 Å. for this compound (Fig. 1) represents the unresolved Br–Br and S–Br distances, which are nearly equal in length and both of which possess relatively strong scattering powers.

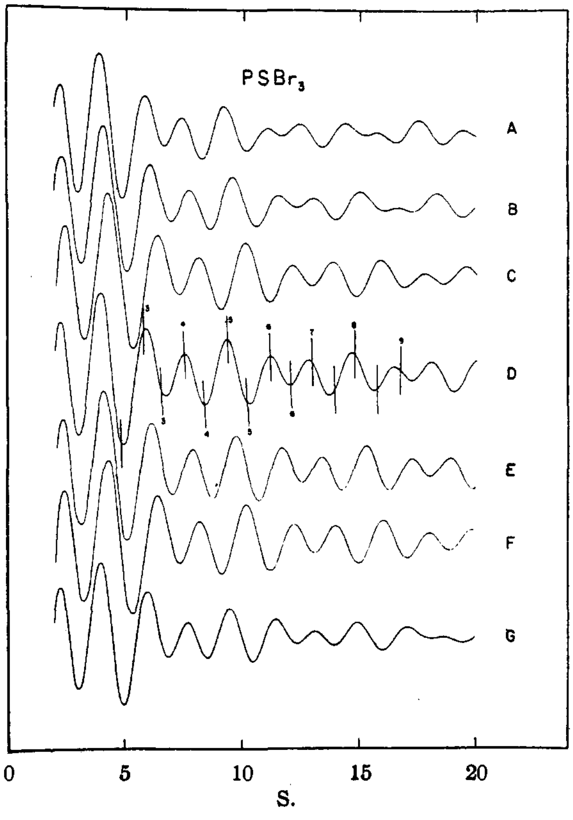

Fig. 4.—Electron scattering curves for $PSBr_3$.

TABLE II

THIOPHOSPHORYL TRIBROMIDE

Max.	Min.	s_0	c_k	s_C/s_0	s_D/s_0	s_F/s_0
	2	5.01	−22	1.057	0.971	1.069
3		5.97	42	1.051	.977	1.069
	3	6.78	−33	1.070	.989	1.082
4		7.79	59	1.038	.960	1.048
	4	8.69	−64	1.041	.961	1.050
5		9.69	55	1.042	.958	1.050
	5	10.59	−48	1.048	.967	1.060
6		11.60	39	1.042	.962	1.055
	6	12.52	−38	1.032	.958	1.047
7		13.47	23	1.029	.950	1.038
	7	14.47	−21	1.025	.945	1.035
8		15.37	8	1.034	.952	1.043
	8	16.40	− 4	1.031	.953	1.043
9		17.43	3	1.019	.946	1.035
	Average			1.040	.961	1.052
	Average deviation			0.010	.010	0.011
	P–S, Å.			1.914	1.874	1.936
	P–Br			2.122	2.143	2.146
	S–Br			3.318	3.354	3.440
	Br–Br			3.432	3.421	3.387

The P–Br distance in this compound also is shorter than the predicted value from the sum of the atomic radii, though not as much shorter as in $POBr_3$. The P–S distance also is shorter than that calculated from tables of double-bond atomic radii (1.95 Å.). Previous reports on PSF_3 and $PSCl_3$[4,5] give results of 1.85 and 1.94 Å., respectively, for the P–S bond.

Thiophosphoryl Monofluorodibromide.—This compound was prepared by H. S. Booth of

Western Reserve University[7] by the fluorination of $PSBr_3$ with anhydrous SbF_3 without a catalyst at 60–70°.

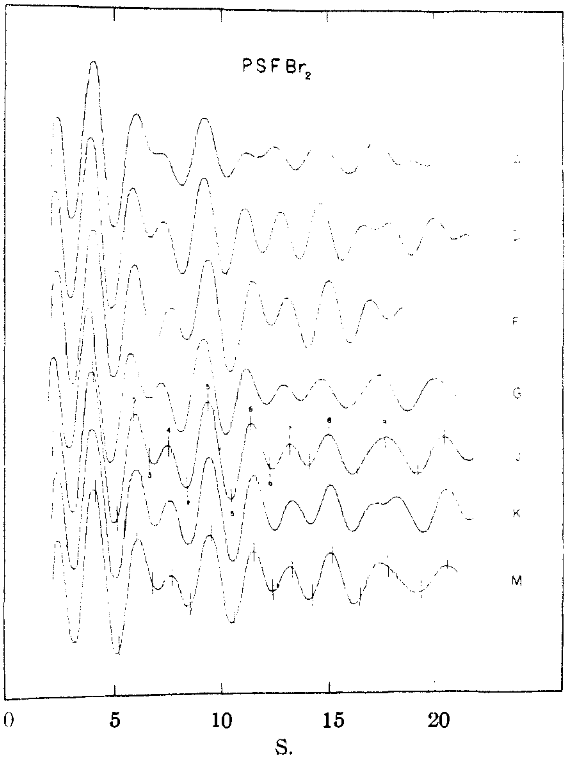

Fig. 6.—Electron scattering curves for $PSFBr_2$.

It is evident that this molecule cannot have the symmetry assumed for $POBr_3$ and $PSBr_3$, and a two-dimensional parameter chart would be inadequate to describe the structure. Table III gives the internuclear distances for twelve calculated models. Values chosen for these models were assigned on the basis of best estimates for these distances in similar previously determined compounds, and from the major peaks of the radial distribution curve. The assumption was made in every model except M that angles FPBr and BrPBr were equal. This assumption, although arbitrary, becomes a reasonable one when one considers that the position of the fluorine atom in the molecule will be uncertain because of its low scattering power so that fairly large variations in its position will have little effect upon the curves. To test the plausibility of this argument, model M was constructed to agree exactly with model J with respect to all distances not involving the fluorine atom, while the length of the P–F bond was made 1.60 Å. in model M as compared to 1.52 Å. in model J. In spite of the considerable change in this bond distance, it is evident that curve M closely resembles curve J. Consequently, the P–F distance must be reported with a relatively large uncertainty.

TABLE III

MOLECULAR MODELS CALCULATED FOR $PSFBr_2$

Model	P–S, Å.	P–Br, Å.	P–F, Å.	∠BrPBr
A	1.95	2.23	1.52	109½°
B	1.79	2.20	1.52	106°
C	1.59	2.23	1.52	106°
D	1.95	2.23	1.52	106°
E	1.68	2.20	1.52	103°
F	1.65	2.23	1.52	103°
G	1.95	2.23	1.52	100°
H	1.78	2.23	1.52	100°
J	1.88	2.20	1.52	100°
K	1.84	2.19	1.50	100°
L	1.78	2.19	1.50	100°
M	1.88	2.20	1.60	100°

Theoretical intensity curves for the seven best models appear in Fig. 6. Curve A is inferior because of the lack of a sharp fourth peak, observed in the photographs, which in this curve is no more than a shoulder on peak 3. The sixth minimum is also much too shallow. Curve D is objectionable because of a split peak at the ninth maximum, which is not observed. Curve E gives a third minimum about as deep as the fourth, not in agreement with the photographs. Curve K is also inferior due to the split ninth peak. Curves G, J and M seem to fit the observed curve most closely, qualitatively and quantitatively, and their s/s_0 values, with the s_0 and c_k values, appear in Table IV. The corrected distances for these models show close agreement with respect to the heavier scattering atomic pairs. Final estimates are: P–Br = 2.18 ± 0.03 Å.; P–S = 1.87 ±

TABLE IV

THIOPHOSPHORYL MONOFLUORODIBROMIDE

Max.	Min.	s_0	c_k	s_G/s_0	s_J/s_0	s_M/s_0
2		4.20	32	0.945	0.971	0.971
	2	5.25	−19	.950	.968	.971
3		6.09	36	.979	.993	1.003
	3	6.79	−29	1.001	1.020	1.034
4		7.70	52	0.956	0.982	0.987
	4	8.56	−35	.967	.988	.984
5		9.55	84	.976	.992	.988
	5	10.61	−31	.977	.992	.988
6		11.55	52	.982	.997	.996
	6	12.42	−20	.988	1.006	.998
7		13.37	34	.980	0.996	.987
	7	14.30	−14	.972	.990	.987
8		15.24	20	.976	.993	.992
	8	16.54	− 6	.973	.984	.982
9		17.88	6	.984	.996	.976
	9	19.44	− 5	.976	.994	.989
10		20.67	4	.979	.995	.997
	Average			.974	.991	.990
	Average deviation			.010	.008	.010
	P–S, Å.			1.899	1.863	1.861
	P–Br			2.172	2.180	2.178
	Br–Br			3.331	3.340	3.336
	F–Br			2.834	2.854	2.911
	S–Br			3.487	3.469	3.465

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[7] H. S. Booth and C. A. Seabright, THIS JOURNAL, 65, 1834 (1943).

0.05 Å.; P–F = 1.50 ± 0.10 Å.; ∠BrPBr = 100 ± 3°. The radial distribution curve (Fig. 1) gives major peaks at 3.43, 2.87 and 2.17 Å. These values agree well with the above results, the 3.43 value corresponding to the unresolved Br–Br and S–Br distances; the 2.87 value to the F–Br distance; and the 2.17 value to the P–Br distance.

The P–Br distance is less than the sum of the atomic radii, while the P–S value agrees closely with that determined in $PSBr_3$. It is interesting to note that the BrPBr angle, which is 108° in $POBr_3$ and 106° in $PSBr_3$, decreases to 100° in $PSFBr_2$. The angle thus decreases with increasing P–Br bond length.

Thiophosphoryl Difluoromonobromide.—This compound, like the monofluorodibromide, was prepared by Booth and Seabright by the controlled fluorination of $PSBr_3$ with SbF_3 as described above.[7]

The irregular nature of the molecule again precludes the use of a two-dimensional parameter chart to describe the structure. To simplify the problem of constructing models, the FPBr angle was made equal to the FPF angle in all models but U. Model U was constructed to agree with the heaviest scattering distances of the best previous models, with the weaker scattering distances somewhat altered. The problem of the choice of models here is somewhat less simple than in the case of $PSFBr_2$, where the presence of two heavy bromine atoms made the calculation of the distances involving these two atoms considerably more accurate, whereas the positions of the lighter atoms were relatively uncertain. In this molecule, the scattering powers of atomic pairs are much more evenly distributed. A larger number of models was therefore necessary to approach a reasonably accurate estimate of the structure. Table V gives the distances for twenty calculated models, of which the theoretical intensity curves for the eight best are shown in Fig. 7. The radial distribution curve (Fig. 1), which gave major peaks at 2.12, 2.89 and 3.42 Å., indicating strongly scattering pairs at these distances, was used as a starting point for most models.

TABLE V

MOLECULAR MODELS CALCULATED FOR PSF_2Br

Model	P–S, Å.	P–Br, Å.	P–F, Å.	∠FPF
A	1.95	2.23	1.52	$109\frac{1}{2}°$
B	1.92	2.05	1.52	$109\frac{1}{2}°$
C	1.95	2.23	1.52	106°
D	1.65	2.20	1.52	106°
E	1.89	2.10	1.52	106°
F	1.78	2.14	1.52	106°
G	2.03	2.03	1.52	106°
H	1.85	2.12	1.52	106°
J	1.83	2.18	1.42	106°
K	1.91	2.10	1.52	106°
L	1.84	2.14	1.51	$104\frac{1}{2}°$
M	1.81	2.19	1.52	103°
N	1.76	2.18	1.52	$102\frac{1}{4}°$
O	1.95	2.23	1.52	100°
P	1.76	2.20	1.56	100°
Q	1.99	2.20	1.47	100°
R	1.72	2.18	1.59	100°
S	1.67	2.23	1.52	100°
T	1.78	2.12	1.66	100°
U	1.87	2.14	1.42	106°

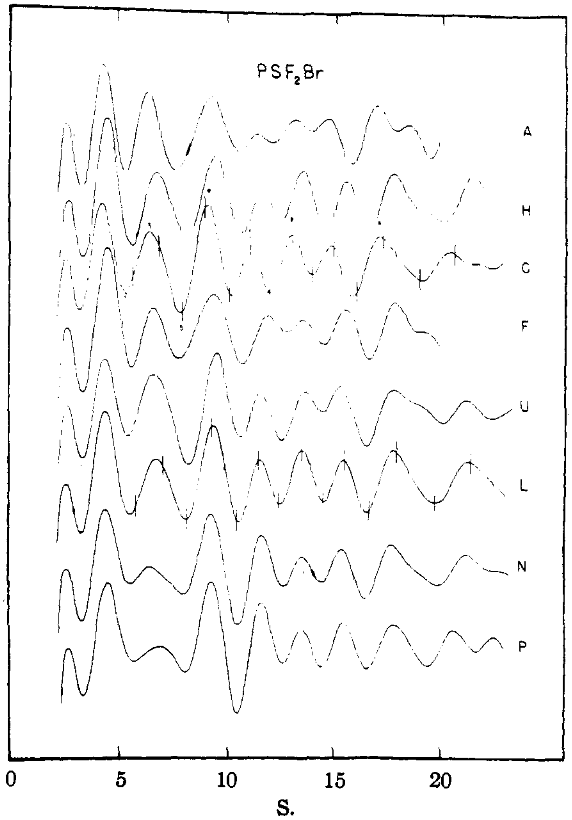

Fig. 7.—Electron scattering curves for PSF_2Br.

Curve A is inferior because the depth of minima 2 and 3 are about equal, contrary to observation, which showed minimum 3 deeper than 2. Also peaks 5, 6 and 7 are much smaller than observed. Curve H is also wrong at minima 2 and 3. Curve P displays a much too weak third peak, and minima 2 and 3 of too nearly the same depth. The models displaying the closest resemblance to the observed pattern are models C, L and U; and their s/s_0 values, together with the s_0 and c_k values, appear in Table VI. The corrected distances for the heavier scattering pairs in these models show close agreement, and the final estimated internuclear distances for this molecule are: P–Br = 2.14 ± 0.04 Å.; P–S = 1.87 ± 0.05 Å.; P–F = 1.45 ± 0.08 Å.; ∠FPBr = 106 ± 3°. The radial distribution peaks at 2.12, 2.89 and 3.42 Å. correspond reasonably well, respectively, to the P–Br distance, the unresolved F–Br and S–F distances, and the S–Br distance.

The P–Br distance is again evidently less than

TABLE VI

THIOPHOSPHORYL DIFLUOROMONOBROMIDE

Max.	Min.	s_0	c_k	s_C/s_0	s_L/s_0	s_U/s_0
	2	5.87	−23	0.908	0.959	0.939
3		7.08	39	.915	.968	.948
	3	8.21	−24	.965	.998	1.011
4		9.32	56	.984	1.014	1.032
	4	10.48	−32	.980	1.016	1.024
5		11.47	20	.971	1.016	1.016
	5	12.41	−21	.974	1.012	1.019
6		13.49	15	.971	1.005	1.015
	6	14.46	−15	.970	1.008	1.003
7		15.48	7	.959	1.003	0.994
	7	16.63	− 7	.958	1.001	.996
8		17.90	6	.959	0.999	.998
	8	19.66	− 5	.973	1.007	1.022
9		21.35	5	.956	0.999	0.994
	Average			.963	1.002	1.004
	Average deviation			.015	0.011	0.019
	P–Br, Å.			2.141	2.144	2.149
	F–Br			2.909	2.916	2.922
	S–Br			3.350	3.357	3.363
	S–F			2.794	2.826	2.761
	P–S			1.872	1.844	1.877
	P–F			1.459	1.513	1.426

In taking the averages of the s/s_0 values the last two were weighted at 1/3 and the preceding four at 2/3.

the 2.24 Å. distance calculated from the sum of the atomic radii. The P–S distance agrees with the figure obtained in $PSFBr_2$. The P–F distance agrees well with previously published results,[1] in spite of large uncertainties, and is much shorter than that calculated from the sum of the atomic radii (1.74 Å.).

TABLE VII

	$POBr_3$	$PSBr_3$	$PSFBr_2$	PSF_2Br
P–S, Å.	...	1.89 ± 0.06	1.87 ± 0.05	1.87 ± 0.05
P–F	...	...	1.50 ± 0.10	1.45 ± 0.08
P–Br	2.06 ± 0.03	2.13 ± 0.03	2.18 ± 0.03	2.14 ± 0.04
P–O	1.41 ± 0.07	...	...	...
∠BrPBr	108 ± 3°	106 ± 3°	100 ± 3°	...
∠FPBr	...	...	...	106 ± 3°

Acknowledgment.—The assistance of the Board of Governors of the Horace H. Rackham School for Graduate Studies in providing funds for the construction of the diffraction apparatus is gratefully acknowledged.

Summary

The molecular structures of four phosphoryl and thiophosphoryl bromides and fluorobromides have been investigated with the results shown in Table VII. The phosphorus–halogen distances are shorter than the corresponding sums of the single covalent atomic radii. The P–S and P–O distances are also shorter than the respective sums of double bond atomic radii. In $POBr_3$ the P–Br distance is shorter and the BrPBr angle is larger than in any other phosphorus–bromine compound.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 15, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

X-Ray Crystallographic Studies of Organic Sulfonates. I. The Quarter-hydrates of Certain Sodium 1-Alkane-sulfonates

BY L. H. JENSEN[1] AND E. C. LINGAFELTER

In connection with the study of paraffin-chain sulfonates as colloidal electrolytes, some apparent anomalies have appeared in the heats of solution. In order to explain these effects it is desirable to have some information concerning the crystal structures of the solid phases. Preliminary investigations have shown that the sodium-1-alkane-sulfonates form several hydrated phases. This paper is a report of the study of the quarter-hydrated phase of sodium 1-octane-, 1-decane-, 1-dodecane-, 1-tetradecane-, 1-hexadecane- and 1-octadecanesulfonate.

All compounds used in the course of the investigation were of the highest purity and had been prepared by previous workers in this Laboratory by the action of aqueous sodium sulfite on the corresponding alkyl halide.[2]

In all cases the crystals were grown from saturated solutions by slow evaporation of the solvent. The crystals were found to grow more rapidly and of sufficient size from mixtures of solvents of moderate dielectric strength. Most of the crystals were grown from mixtures of C. P. carbon tetrachloride and ethanol with or without small amounts of other miscible solvents. A small quantity of glycerol added to the solvent increases the thickness of the otherwise extremely thin laths. The stable solid phase formed in this manner is the quarter-hydrate in the range from a few per cent. water to at least 25% water.

The habit was found to be the same for all crystals obtained, thin tabular parallel to {001} and elongated parallel to the *a* axis. The tablet is outlined by {010} and {110} in most cases, and occasionally by {010}, {110} and {100}.

Data were obtained from Laue, rotation, oscillation and Sauter photographs. For all moving crystal photographs Cu Kα radiation was used.

The dimensions of the unit cells were deter-

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[1] Present address: College Station, Berrien Springs, Michigan.

[2] Reed and Tartar, THIS JOURNAL, 57, 570 (1935).