THE POSSIBLE EXISTENCE OF THE CATION POBr⁺₂ AND SOME PROPERTIES OF PHOSPHORUS OXYBROMIDE. GALLIUM TRIBROMIDE, AND THEIR IONIC 1:1 ADDITION COMPOUND

N. N. GREENWOOD and I. J. WORRALL Department of Chemistry, The University, Nottingham, England

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Abstract—Phase studies show that phosphorus oxybromide reacts with gallium tribromide to form a 1:1 addition compound melting at 154.0° . This complex is less stable than the corresponding chloro-compound, POCl₂+GaCl₄-, but otherwise has similar properties and is considered to contain the new non-metal cation POBr₂⁺. At $161\cdot2^{\circ}$ the molten compound has a density of $2\cdot875$ g ml⁻¹, a dynamic viscosity of 4.92 cP, and a specific conductivity of $1.0 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. The density, surface tension, viscosity, and related properties of the reacting components POBr₃ and Ga₂Br₆ have been determined over a range of temperature and the conductivity of both liquid and solid phosphorus oxybromide has been shown to be $<4\cdot10^{-8} \Omega^{-1} \text{ cm}^{-1}$.

THE addition compound between gallium trichloride and phosphorus oxychloride is a good electrical conductor⁽¹⁾ and has been shown by Raman spectroscopy to contain the ions $POCl_2^+$ and $GaCl_4^{-.(2)}$ These results prompted an investigation of the corresponding bromo-system, for, although the $GaBr_4^-$ ion is known,⁽³⁾ the cation $POBr_2^+$ has not previously been reported. Indeed, even the parent donor and acceptor compounds phosphorus oxybromide and gallium tribromide have received scant attention in recent years and little is known about their physical properties. For this reason the density, surface tension, and viscosity of these compounds were determined over a range of temperature and the results used to calculate the activation energy of viscous flow, parachor, surface free energy, and related properties. The electrical conductivity of molten gallium tribromide is known to be small⁽⁴⁾ and phosphorus oxybromide was found to be a non-conductor. It was originally intended to compare these properties with those of the 1:1 addition compound, GaBr₃·POBr₃, which had been found from phase studies, but the complex underwent some decomposition above the melting point and this restricted the amount of information obtainable from it. However, sufficient data were obtained to show that the compound was appreciably ionized in the molten state.

EXPERIMENTAL

Phosphorus oxybromide was prepared by adding the calculated amount of bromine to phosphorus tribromide and then heating the phosphorus pentabromide so formed with a slight excess of phosphorus pentoxide for several days at 70°.(5) The product was distilled from the all-glass preparation apparatus at atmospheric

New York (1946).

pressure and freed from remaining traces of phosphorus tribromide and hydrolysis products by vacuum fractionation at 80°. Final purification was effected by repeated fractional freezing of the molten compound in an evacuated vessel until cryoscopic homogeneity was attained. The m.p. was $56 \cdot 4^{\circ}$, as compared with the best literature values of $55^{\circ}-56^{\circ}$.^(5,6)

Gallium tribromide (m.p. $122 \cdot 5^{\circ}$) was prepared and purified as previously outlined.⁽⁴⁾ The measurement of density, surface tension, and viscosity under vacuum conditions has also been described⁽⁷⁾ as have the circuit and cells used to determine the electrical conductivity.^(1,4)



FIG. 1.—Preparation of mixtures of known composition for phase diagram.

The preparation under anhydrous conditions of mixtures of known composition for melting-point determinations presented some difficulty, as the involatility of the compounds at room temperature precluded manipulation by conventional vacuumline techniques. The apparatus used is shown in Fig. 1. A sealed tube of phosphorus oxybromide was opened and placed in the left-hand limb, which was then sealed at position 1. A similar tube containing gallium tribromide was weighed, broken open cleanly, and then sealed into the right-hand limb at point 2, after which the apparatus was evacuated and sealed off at point 3. The phosphorus oxybromide was melted into the burette tube, the gallium tribromide sublimed into the reaction vessel, and the unwanted sections of the apparatus drawn off at points 4 and 5. The weight of gallium tribromide used was found by difference and in two runs was 0.1824 g and 1.1763 g. Successive amounts of phosphorus oxybromide were poured into the reaction vessel from the Grade A 1 ml burette which was placed in a thermostated oil-bath at 62.3°, the weight added being calculated from the density of the ligand and the heights of the meniscus as measured on a cathetometer reading to 0.01 mm (0.14 mg). After each addition the contents of the reaction vessel were melted to

 ⁽⁶⁾ A. BESSON C. R. Acad. Sci., Paris 124, 763 (1897); J. H. SECRIST and L. O. BROCKWAY J. Amer. chem. Soc. 66, 1941 (1944); W. GERRARD, A. NECHVATAL and P. L. WYVIL Chem. & Ind. (Rev.) 437 (1947).
⁽¹⁾ N. D. CATANINGO, and K. WINE, Linear and Chem. 3, 240 (1057)

⁽⁷⁾ N. N. GREENWOOD and K. WADE J. inorg. nucl. Chem. 3, 349 (1957).

obtain a homogeneous mixture, after which the melting point of the resolidified mass was determined by heating the vessel very slowly and observing the temperature of disappearance of the solid phase on a calibrated thermometer.

The 1 : 1 addition compound $GaBr_3 \cdot POBr_3$ was prepared by the same method, using a 5 ml burette. After purification by fractional freezing the m.p. was 154.0°. Above this temperature the complex became grey and opaque, but colourless crystals could be reobtained by allowing the liquid to solidify. Under these conditions it was not possible to measure physical properties over a range of temperatures except for the density, which appeared to be insensitive to the (partially reversible) decomposition occasioned by fusion. The m.p. itself also appeared relatively insensitive to the presence of the small amounts of decomposition products.

RESULTS

Phosphorus oxybromide. The density of phosphorus oxybromide was determined on a sample which had been vacuum-distilled into a fractional freezing unit and then transferred without breaking the vacuum into a double-capillary dilatometer. The results, which have been corrected for bouyancy and for thermal expansion of the glass, are given in Table 1 and may be represented by the equation:

$$d_4^{t} = 2.8335 - 2.487 \times 10^{-3}(t-55)$$

t°	62·3	65·5	69·6	75∙6	82·0	85·2	90·4	95·6
d₄t	2·8161	2·8068	2·8011	2∙7813	2·7664	2·7576	2·7453	2·7308
t°	99·8	104·4	110·2	114·6	120·2	125·0	130∙0	
d_4^t	2·7213	2·7096	2·6968	2·6858	2·6713	2·6594	2∙6474	

TABLE 1.-DENSITY OF LIQUID PHOSPHORUS OXYBROMIDE

These figures appear to be the first data on the density of liquid phosphorus oxybromide. RITTER⁽⁸⁾ found the density of the solid to be $d_4^{20} = 2.822$ on a sample which melted some 11° below the present m.p.; a value of $d_4^{20} = 3.23$ may be obtained by extrapolation of data⁽⁹⁾ obtained between -183° and -21° and, if an allowance of about 10 per cent is made for expansion on fusion, this latter value is seen to be reasonably consistent with the present figures.

The surface tension of phosphorus oxybromide was estimated in a separate run between 100° and the m.p. by measuring the lengths of liquid in the two capillaries of the dilatometer and making an appropriate meniscus correction. A least-squares treatment of the 11 values lead to the equation:

$$\gamma = 41 \cdot 2 - 0 \cdot 167(t - 55)$$

This represents the surface tension with a mean deviation of 1.7 dyne cm⁻¹. The corresponding surface free energy ($\omega = \gamma V_M^{2/3}$, where V_M is the molar volume) is given by

$$\omega = 895 - 3.22(t - 55)$$

⁽⁸⁾ H. RITTER Liebigs Ann. 95, 208 (1855).

⁽⁹⁾ W. BILTZ, A. SAPPER and E. WÜNNENBERG Z. anorg. Chem. 203, 277 (1932).

in which the Eötvös constant k has the rather large value of 3.22. The parachor, $([P] = V_M \gamma^{1/4})$, calculated from the 11 independent values of surface tension, had a mean value of 255.3 \pm 3.4, compared with a value of 254.3 calculated by McGowan's method.(10)

The viscosity of phosphorus oxybromide was measured in a sealed, all-glass, capillary viscometer having an overflow wier.⁽¹¹⁾ Outflow times varied between 175 and 275 sec. The results are summarized in Table 2, which lists the kinematic viscosity (v cS) the dynamic viscosity (η cP = vd_4^{t}) and the fluidity (ϕ cP⁻¹). The reproducibility of the data and the stability of the compound are shown by the fact that the viscosities at the first three temperatures in Table 2 were measured at the conclusion of the run when the thermostat had cooled down from 93°; graphically they are indistinguishable from the rest of the data.

ť	ν (cS)	η (cP)	ϕ (cP ⁻¹)	t°	v (cS)	η (cP)	ϕ (cP ⁻¹)
54.5	0.9627	2.729	0.3663	75.4	0.7312	2.035	0.4914
56.0	0.9459	2.679	0.3734	77.3	0.7154	1.987	0.5031
58.0	0.9181	2.594	0.3854	79.9	0.6930	1.921	0.5206
60.0	0.8957	2.527	0.3957	82·5 ₅	0.6737	1.863	0.5368
62.3	0.8690	2.446	0.4087	85·2 ₅	0.6561	1.810	0.5526
65-1	0.8378	2.353	0.4250	87·0	0.6442	1.774	0.5638
66.6	0.8177	2.294	0.4359	89-1	0.6356	1.734	0.5770
6 9·7	0.7863	2.199	0.4546	91-1	0.6169	1.693	0.5907
72.0	0.7641	2.132	0.4690	93·1 ₅	0.6043	1.655	0.6043
73.2	0.7534	2.101	0.4761	•			

TABLE 2.-VISCOSITY AND FLUIDITY OF PHOSPHORUS OXYBROMIDE

A plot of log η against $1/T^{\circ}K$ is slightly curved, the activation energy of viscous flow (E_n) decreasing from 3.21 kcal mole⁻¹ at the m.p. to 2.85 kcal mole⁻¹ at 90°. It may be noted that the latent heat of vaporization of phosphorus oxybromide is 10.9 kcal mole⁻¹,⁽¹²⁾ so that the ratio $\Delta H_{\rm vap}/E_n$ is in the range 3.4–3.8, in agreement with the theory of absolute reaction rates.

The electrical conductivity of a sample of phosphorus oxybromide which had been distilled under vacuum into a cell was too small to be measured with the apparatus used. This places an upper limit of $4 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ on the conductivity. The solid was also non-conducting.

Gallium tribromide. The density of molten gallium tribromide (Ga_2Br_6) is presented in Table 3. It corresponds to the equation

$$d_{4}^{t} = 3.1199 - 2.47 \times 10^{-3}(t-120)$$

which may be compared with the equation of KLEMM and TILK⁽¹³⁾ based on values between 139° and 230°.

$$d_4^{t} = 3.15_3 - 2.9_5 \times 10^{-3}(t - 120)$$

(10) J. C. MCGOWAN Rec. Trav. chim. Pays-Bas 75, 193 (1956).
(11) N. N. GREENWOOD and K. WADE J. sci. Instrum. 34, 288 (1957).
(12) M. VAN DRIEL Rec. Trav. chim. Pays-Bas 61, 748 (1942).
(14) M. VAN DRIEL Rec. Trav. chim. Pays-Bas 61, 748 (1942).

⁽¹³⁾ W. KLEMM and W. TILK Z. anorg. Chem. 207, 161 (1932).

The two other published values ⁽¹⁴⁾ are also higher than the present values but are not concordant: $d_4^{120} = 3.123, 3.138$.

t°	117·8	119·2	120·3	121·3	122·4	123·4	124·4	125·7
d₄ ^t	3·1256	3·1213	3·1189	3·1173	3·1138	3·1107	3·1090	3·1048
t°	127·7	129∙0	130·1	132·2	133·3	134·8	135∙9	
d₄t	3·1004	3∙0976	3·0941	3·0897	3·0869	3·0837	3∙0806	

TABLE 3.—DENSITY OF LIQUID GALLIUM TRIBROMIDE

The surface tension of gallium tribromide in the same temperature range may be represented to ± 2 dyne cm⁻¹ by the equation

$$\gamma = 35.5 - 0.15(t - 120)$$

This leads to a surface free energy equation

$$\omega = 1200 - 4.5(t - 120)$$

The lack of precision in the surface tension measurements is due to the fact that capillary diameters which are desirable for density measurements are not the optimum diameters for surface tension determinations. Nevertheless the results give a reasonable indication of the magnitude of the surface tension. The mean of ten concordant parachors calculated from individual values of the surface tension is $[P] = 482.0 \pm 2.5$. The mean of all 15 values is 482.7 ± 5.8 and the calculated value for the bridged dimer Ga₂Br₆ is 482.0.

The viscosity of gallium tribromide was measured over a period of three days to check reproducibility and stability. Times of outflow were similar to those observed for phosphorus oxybromide and varied between 225 and 275 sec. The results are collected in Table 4 which also indicates the sequence of measurements. The activation energy of viscous flow decreases slowly from 3.94 kcal mole⁻¹ at the m.p. to

No.	t°	ν (cS)	η (cP)	No.	t°	ν (cS)	η (cP)
17	117.6	0.9766	3.052	11	128.0	0.8639	2.678
16	118.8	0.9623	3.004	10	129.0	0.8535	2.644
15	119.8	0.9502	2.965	12	130.0	0.8435	2.611
14	121.0	0.9363	2.919	4	131.3	0.8335	2.577
13	122.0	0.9267	2.887	5	132.5	0.8228	2.542
1	123.4	0.9096	2.830	6	133.6	0.8117	2.505
19	124·2	0.9014	2.803	7	135.0	0.7999	2.465
2	125.1	0.8935	2.776	8	136-3	0.7888	2.429
18	126.1	0.8817	2.738	9	137.4	0.7800	2.400
3	127.1	0.8732	2.709				

⁽¹⁴⁾ W. C. JOHNSON and J. B. PARSONS J. phys. Chem. 34, 1210 (1930).

3.70 kcal mole⁻¹ at 135° . This is less than the latent heat of evaporation, 14.3 kcal mole^{-1 (15)} by a factor of 3.6-3.8 as expected.

Gallium tribromide-phosphorus oxybromide. The existence of an addition compound $GaBr_3 \cdot POBr_3$ was established by the melting-point diagram shown in Fig. 2 which was obtained by adding successive amounts of phosphorus oxybromide to



FIG. 2.—Phase diagram of the system gallium tribromide-phosphorus oxybromide.

known weights of gallium tribromide. The maximum m.p. is 155° and occurs at the 1 : 1 ratio; this m.p. is slightly above that of the purified complex (154.0°) since, in phase studies, the mixture is heated slowly until the last disappearance of the solid



FIG. 3.—Variation of conductivity with time after fusion.

phase, whereas the m.p. quoted for the pure compound was the temperature of first appearance of liquid when individual crystals were heated.

The density of the complex over a range of temperature may be represented by the equation

$$d_4^{t} = 2.8855 - 1.62 \times 10^{-3}(t - 155)$$

⁽¹⁵⁾ W. FISCHER and O. JUBERMANN Z. anorg. Chem. 227, 227 (1936).

Because of the tendency for the complex to undergo some decomposition above the m.p., the true surface tension could not be measured, but the complex gave a reproducible value of the viscosity when measured at $161 \cdot 2^{\circ}$:

$$v = 1.712 \text{ cS};$$
 $\eta = 4.921 \text{ cP}.$

The conductivity of the complex increased with time at $161 \cdot 2^{\circ}$, but reached a steady value of $2 \cdot 302 \ \Omega^{-1} \ cm^{-1}$ after 3 hr. This variation is plotted in Fig. 3. Zero time is the time at which melting began, and the first reading, taken 20 min later when thermal equilibrium had been established at $161 \cdot 2^{\circ}$, was $1 \cdot 540 \times 10^{-3}$. Extrapolation to zero time gives a conductivity of about $1 \cdot 0 \times 10^{-3}$.

DISCUSSION

Before the structure of the addition compound GaBr₃·POBr₃, is discussed two points which arise from the properties of the components will be considered. The first concerns the parachor which can now be calculated accurately by means of the modified table of atomic parachors due to McGowan.⁽¹⁰⁾ In an earlier paper⁽⁷⁾ GREENWOOD and WADE pointed out that no satisfactory method for reproducing the parachor of compounds of gallium had been devised. Values calculated from McGOWAN's original table,⁽¹⁶⁾ using an extrapolated value for gallium itself, gave 418.0 for gallium trichloride instead of the observed value of 392.0; with the modified table the calculated value becomes 392.6, in excellent agreement with the experimental value. For gallium tribromide the experimental and calculated values are identical, 482.0. The parachor has an unenviable history in structural chemistry and it would be rash to claim that the present results imply further evidence for the already wellestablished bridged dimer structure of the gallium halides (the calculated values for 2GaCl₃ and 2GaBr₃ being 429.8 and 519.2 respectively). Nevertheless, it is important to establish that at least one scheme can be used for computing the parachor of compounds containing gallium, since this serves as an admirable check on the experimental values of the surface tension.

The second property for discussion is the viscosity. Complex formation is accompanied by a considerable increase in viscosity of the system, the viscosity of the complex at its m.p. being approximately twice those of the donor and acceptor compounds at their melting points; the disparity would be even greater if the comparisons were made all at the same temperature. It has also been shown that the activation energies of viscous flow for phosphorus oxybromide and gallium tribromide have values agreeing with those expected from the known heats of evaporation of these compounds. Of more interest is an alternative representation of viscosity by an equation involving the fluidity ($\phi = \eta^{-1}$) and the specific volume ($v = d^{-1}$):

$$v=b+B\phi$$
,

where b and B are constants. Linear plots were obtained in this way for both the parent compounds, values for Batschinski's constant B being obtained from the slope. For phosphorus oxybromide $B = 5 \cdot 13 \times 10^{-2}$ ml cP g⁻¹; for gallium tribromide $B = 5 \cdot 60 \times 10^{-2}$ ml cP g⁻¹. The magnitude of B is often taken as being roughly proportional to the size of the flow unit in a liquid. It is therefore interesting ⁽¹⁶⁾ J. C. McGowan Chem. & Ind. (Rev.) 495 (1952).

to observe that the values for the two bromides are both *less* than those for the corresponding chlorides (POCl₃, 6.45×10^{-2} , Ga_2Cl_6 , 5.75×10^{-2})⁽¹⁾ despite the fact that their molar volumes are greater. Other instances of this type of reversal may be found in the literature, for example the trichlorides and tribromides of phosphorus and arsenic, and the tetrachlorides and tetrabromides of silicon and tin.⁽¹⁷⁾ It may be argued that the size of flow units on a molecular scale is not necessarily proportional to the bulk molar volume of a liquid and that chlorides might be more likely to associate or interact than the bromides, but such interaction seems unlikely, especially in those halides which are highly symmetrical such as the gallium trihalides and the tetrahalides of silicon and tin.

The electrical conductivity of phosphorus oxybromide is $<4.10^{-8} \Omega^{-1} \text{ cm}^{-1}$ and that of liquid gallium tribromide is $7.10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at its melting point. By contrast, the complex GaBr₃·POBr₃ has a conductivity of $1.0 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ when first melted at 161·2°, and this value increases during 3 hr to a constant value of $2.3 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. It is unlikely that the conduction is due entirely to traces of decomposition products, firstly because the compound shows appreciable conductivity immediately on melting (although time is required for complete fusion and the attainment of thermal equilibrium), and secondly because the conductivity rapidly reaches an equilibrium value of the same order of magnitude as the initial conductivity. If one assumes that ionic mobility is viscosity-controlled, as it normally is in such selfionizing complexes, then the ionic concentration required to give the observed conductivity is about 0·1 M; such a concentration of impurity would certainly lower the m.p. of the compound, but this is not observed.

In fact, there is no reason to suppose that the conductivity is not due predominantly to self-ionic dissociation of the molten complex. The initial conductivity of 1.0×10^{-3} Ω^{-1} cm⁻¹ corresponds to a molar conductivity, μ , of $0.21 \ \Omega^{-1}$ cm² and a reduced conductivity, $\mu\eta$, of $1.0 \ \Omega^{-1}$ cm² cP. These values are strikingly similar to those of the corresponding chloro-complex GaCl₃·POCl₃ at its m.p. of 118.5° : $\kappa = 1.26 \times 10^{-3} \ \Omega^{-1}$ cm⁻¹, $\mu = 0.227 \ \Omega^{-1}$ cm², and $\mu\eta = 0.442 \ \Omega^{-1}$ cm² cP.⁽¹⁾ It seems reasonable to suppose, therefore, that the structures of the two complexes are analogous. The Raman spectrum of molten gallium trichloride-phosphorus oxychloride has been interpreted exclusively in terms of the ions POCl₂⁺ and GaCl₄⁻⁽²⁾ and it is suggested that the present complex should be formulated as POBr₂+GaBr₄⁻. An unequivocal demonstration of the presence of the new cation POBr₂⁺ by Raman spectroscopy may prove difficult because of the opacity which develops on fusion, but it is hoped to prepare analogous complexes, for example with aluminium or indium tribromides, in the hope that these may prove more amenable to structural investigation by physical techniques.

⁽¹⁷⁾ G. P. LUCHINSKI J. gen. Chem., Moscow 7, 2116 (1937).

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