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PREPARATION AND MELTING POINTS OF PURE DI- AND TRI-IODIDE OF PHOSPHORUS

BY FRANK E. E. GERMANN AND RALPH N. TRAXLER

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Introduction

A number of methods have been described for the preparation of the iodides of phosphorus which give products of varying degrees of purity. Possibly the oldest procedure is that of the direct union of the solid elements. The reaction is accompanied by a considerable evolution of heat and the reaction velocity is still appreciable at —24°. It is accordingly regarded advisable to cut down the vigor of the reaction by means of a solvent for the separate elements. The reaction is then brought about very satisfactorily by mixing the two solutions and removing the solvent by distillation, or effecting a separation by cooling the solution in a freezing mixture.

The usual procedure for the preparation of phosphorus di-iodide is to add slowly two gram atoms of iodine to a solution of one gram atom of white phosphorus in carbon disulfide. Similarly, phosphorus tri-iodide is prepared by mixing three gram atoms of iodine with one gram atom of white phosphorus in carbon disulfide. When these methods are used, the melting point of the di-iodide is 110° and of the tri-iodide 55°. Other methods which have been used are the making of the di-iodide by reducing the tri-iodide by shaking with mercury, and by the interaction of iodine and liquid hydrogen phosphide. According to Abegg[1] the di-iodide is also formed when iodine, dissolved in glacial acetic acid, acts on phosphorus trichloride. The equation which is given for the reaction is $2PCl_3 + 10I = P_2I_4 + 6ICl$.

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[1] Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, **1907,** vol. III^3, p. 418.

Besson[2] was the first to realize that the phosphorus tri-iodide prepared by Corenwinder,[3] Ouvrard,[4] and Snape[5] was not pure, and that the melting point obtained by them, namely 55°, was too low. Snape[5] prepared the tri-iodide by the interaction of potassium iodide and phosphorus trichloride, according to the reaction $3KI + PCl_3 = 3KCl + PI_3$, followed by extraction with and recrystallization from carbon disulfide. Besson[2] explained the low melting point as being due to the use of carbon disulfide in which the tri-iodide was too soluble to make possible a separation of the impurities by recrystallization. Concerning this he states, "If it is advisable to use carbon disulfide in the formation of phosphorus di-iodide, since it is only slightly soluble in this medium, crystallizing from it readily, it is not advisable in the case of phosphorus tri-iodide, which is extremely soluble in this solvent. In order to effect a separation, it must be evaporated to dryness, or to a sirupy consistency, followed by considerable chilling, which leads to a product of only relative purity."

Accordingly, Besson made use of the reaction $3HI + PCl_3 = PI_3 + 3HCl$, using dry hydriodic acid and passing it into phosphorus trichloride alone, or dissolved in carbon tetrachloride. On recrystallizing from the latter solvent, he obtained a product which melted at 61° in place of the older value of 55°.

Jaeger and Doornbosch[6] made use of the tri-iodide, which they prepared by the method of Besson but which, according to a personal communication from Professor Jaeger, was recrystallized from carbon disulfide which had been shaken with mercury just before using. They also report a melting point of 61°, which shows that the great solubility is not the cause of the low melting point obtained by others. This point, however, has been passed over unnoticed.

A simplified method for the preparation of pure phosphorus tri-iodide directly from pure white or red phosphorus and iodine in a medium of carbon disulfide has been described by Traxler and Germann.[7] The method is much shorter, and less complicated and tedious in execution than that of Besson, which depends on the interaction of hydriodic acid and phosphorus trichloride in carbon tetrachloride. The method consists in mixing two solutions, one of white phosphorus and the other of iodine, in the atomic ratio of one to three in carbon disulfide which has been shaken with mercury and distilled just before using. The same precautions are taken when recrystallizing from carbon disulfide. It was shown that the free sulfur present in ordinary, redistilled carbon disulfide

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[2] Besson, *Compt. rend.*, **124**, 1347 (1897).

[3] Corenwinder, *Ann. chim. phys.*, [3] **42**, 129 (1854).

[4] Ouvrard, *ibid.*, [7] **2**, 224 (1894).

[5] Snape, *Chem. News*, **74**, 27 (1896).

[6] Jaeger and Doornbosch, *Z. anorg. Chem.*, **75**, 261 (1912).

[7] Traxler and Germann, *J. Phys. Chem.*, **29**, 1119 (1925).

was responsible for the formation of compounds which lowered the melting point of the phosphorus tri-iodide prepared in such a solvent.

The object of the present investigation was to subject the method for preparing phosphorus tri-iodide to a more careful analysis, and to investigate the formation of phosphorus di-iodide.

Materials and Apparatus

The *iodine* was purified by trituration with potassium iodide followed by sublimation. The *red phosphorus* was material which had not been exposed to the air for any length of time. This was washed with purified carbon disulfide to remove traces of white phosphorus. The *white phosphorus* was clean and dry when used and any old and oxidized surface was cut off and discarded. The *carbon disulfide* was the best grade obtainable. It was agitated in a glass-stoppered bottle with successive portions of pure mercury until all of the free sulfur was removed, which required prolonged agitation with several portions of mercury. The treatment was continued in every case until only a slight tarnish appeared on the bright surface of the mercury after several minutes of contact with the carbon disulfide. The solvent was filtered, distilled and used immediately.

Melting points were determined by two methods. The first method involved the use of a small amount of the powdered material which was placed in a very thin-walled capillary tube. The tube was fastened to the thermometer by means of a rubber band, in such a position that the material in the capillary was adjacent to the thermometer bulb. The thermometer and capillary were fitted by means of a cork into a test-tube full of concd. sulfuric acid when the acid was at the temperature of the experiment. The test-tube was fitted into a small, round-bottomed flask also filled with sulfuric acid. A reading glass was used in reading the temperatures. The second method involved the use of larger amounts of material and the obtaining of cooling curves. Twenty g. of the material to be examined was placed in a test-tube that was fitted with a cork and carried a thermometer and glass stirrer. This tube was fitted into a slightly larger tube, affording a thin air jacket around the inner tube. The tubes were placed in a sulfuric acid-bath. The temperature of fusion was then determined by the usual cooling-curve method.

Standardized thermometers graduated to 0.1° were used in all of the determinations.

Experimental Part

Phosphorus Tri-iodide. This was prepared by two different methods.

(1) Iodine was dissolved in carbon disulfide and to this solution washed red phosphorus was added in excess of the amount necessary to react with the iodine. After all of the free iodine had disappeared, the solution was filtered free from the residual red phosphorus and evaporated on a sand-bath until crystals just began to form. This point was not reached until the solution was very concentrated, which was in agreement with the observation previously made by Besson. The solution was then cooled and the resulting mass of crystals freed from the solvent by decantation, followed by gentle warming.

(2) A weighed amount of white phosphorus was dissolved in carbon disulfide. A quantity of iodine just sufficient to react with the phosphorus to give phosphorus tri-iodide (12.27 g. of iodine to 1 g. of phosphorus) was dissolved in carbon disulfide. The iodine and phosphorus solutions were well mixed, and it was made certain that none of either was lost. The resulting solution was evaporated as before. In both cases the solution remained dark red and opaque throughout the entire manipulation.

The crystals obtained by both methods, because of their rapid decomposition in moist air, were kept in a desiccator over calcium chloride. They agreed on analysis to the formula PI_3, and gave melting points of 61.0° by both the capillary-tube and cooling-curve methods. In the capillary-tube method, open, closed and evacuated tubes were used. Neither sealing the tubes containing air over the tri-iodide nor sealing the crystals in a vacuum had any noticeable effect on the melting point.

From the results recorded here it is clear that pure phosphorus tri-iodide, melting at 61.0°, can be obtained directly from pure iodine, and either yellow or red phosphorus, using carbon disulfide as a solvent, provided the carbon disulfide is purified by the removal of *all free sulfur* before use.

Phosphorus Di-iodide.—The preparation of phosphorus di-iodide was carried out by dissolving a weighed amount of white phosphorus in carbon disulfide. Iodine in quantity to react with the phosphorus to give the di-iodide (8.18 g. of iodine to 1 g. of phosphorus) was weighed out and dissolved in carbon disulfide. The solutions of iodine and phosphorus were thoroughly mixed, care being taken not to lose any of either solution. The resulting solution was at first dark brown, finally clearing to a transparent and beautiful red. This solution was evaporated at a low temperature on a sand-bath, the temperature not going above that causing incipient boiling of the carbon disulfide. If the temperature was allowed to become sufficient to cause rapid boiling of the solvent, the melting point of the resulting product was low, due, probably, to slight decomposition of the phosphorus di-iodide. The warm solution, when quite concentrated, but before any solid had separated out, was removed from the sand-bath and allowed to cool, whereupon clear-red, needle-like crystals were deposited. The mother liquor was drained off and the crystals freed from adhering carbon disulfide at the temperature used to evaporate the solution. The dried crystals, which gave on analysis the proportion PI_2, were kept in a desiccator over calcium chloride.

The melting point of the crystals was found to be 124.5°[8] by the capillary-tube method. Here again tubes open to the air and sealed tubes were used with identical results. Evacuated tubes gave low and irregular values, very probably due to the decomposition of the di-iodide under reduced pressure. If the temperature of the bath was brought up very slowly, a melting point considerably lower than the true one was obtained, that is, values of 122° or 123° were frequent. The best results were obtained by regulating the bath to a temperature of 114° before immersion of the melting-point tube, then raising the temperature at the rate of about 8° per minute.

By the cooling-curve method the highest solidification temperature obtained was 124.0°. This value was obtained by heating the mass to about 126°, allowing it to cool slowly without stirring to 120°, during which

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[8] Jaeger and Doornbosch (Ref. 6) mention obtaining a value of 124° for the melting point of phosphorus di-iodide. They used purified carbon disulfide freed from sulfur by shaking with mercury for the recrystallization of their phosphorus tri-iodide, and undoubtedly used the same solvent for the preparation of phosphorus di-iodide. However, no statement is made as to the method used.

operation the mass remained liquid, and then by agitation inducing solidification, causing the temperature to rise. A satisfactory solidification temperature was not obtainable when supercooling was prevented. When the liquid mass was heated above 126° the resulting solidification temperature was much too low. The low values obtained by the cooling-curve method and in the capillary method when slow heating was employed, are undoubtedly due to slight decomposition of the di-iodide at or above its melting point. Besson[2] states that phosphorus di-iodide, when heated under 15 mm. pressure at 100–120°, yields a sublimate of phosphorus tri-iodide and a residue of red phosphorus. This same or other decomposition reaction undoubtedly takes place even under atmospheric pressure to an extent sufficient to cause an appreciable lowering of the melting point if the compound is exposed to high temperatures for any length of time. It may be noted here that heating the di-iodide to 170° causes the appearance of notable quantities of iodine vapor.

In view of the above experiments, it would appear that 124.5° was the most satisfactory value for the melting point of pure phosphorus di-iodide.

Discussion of Results

From the above results it is evident that the value commonly given in the literature and tables of constants for the melting point of phosphorus di-iodide, 110°, is much too low. This great difference and the difference between the accepted value of 61° for the melting point of phosphorus tri-iodide and the value of 55° obtained for crystals from ordinary impure carbon disulfide may be accounted for by the presence of a compound of phosphorus, sulfur and iodine formed when carbon disulfide containing free sulfur is used. Adding very small amounts of sulfur to purified carbon disulfide, which was later used as the solvent for the preparation of both iodides, gave crystals with a low melting point. The properties of the compounds formed between the three elements would point to $P_4S_3I_2$ as being the compound which causes the lowering in the melting points of both the iodides of phosphorus.[7]

The preparation of pure phosphorus tri-iodide by the use of either red or white phosphorus and a solution of iodine in purified carbon disulfide is less complicated and tedious than Besson's method, using phosphorus trichloride in carbon tetrachloride. In regard to the phosphorus di-iodide, this compound can easily be prepared in a very pure condition, using iodine and white phosphorus in purified carbon disulfide. The melting point of the resulting crystals is found to be considerably higher than the figure usually given.

By recognizing the obstacles in the way of preparing the iodides of phosphorus in a pure condition and the simple means for the removal of these obstacles, the compounds may be prepared easily and with confidence as to their state of purity.

Summary

1. Phosphorus tri-iodide has been prepared, using red phosphorus and a solution of iodine in carbon disulfide from which the free sulfur has been removed.

2. Phosphorus tri-iodide has been prepared by the interaction of solutions of iodine and white phosphorus in purified carbon disulfide.

3. The crystals of phosphorus tri-iodide obtained by both methods of preparation were found to melt at 61.0°.

4. Phosphorus di-iodide was prepared by the interaction of solutions of iodine and white phosphorus in purified carbon disulfide.

5. The crystals of phosphorus di-iodide obtained gave a melting point of 124.5°. This value is 14.5° higher than the commonly accepted value for the melting point of this compound, and should be adopted to replace the old value of 110°.

6. The presence of a compound of phosphorus, sulfur and iodine, probably $P_4S_3I_2$, is suggested as the cause of the low melting point of the two iodides of phosphorus. This will be true whenever they are prepared or recrystallized from carbon disulfide which has not had the free sulfur, which is always present, removed immediately before using.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY]

THE DIFFUSION OF OXYGEN THROUGH SILVER

BY F. M. G. JOHNSON AND P. LAROSE

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In a previous paper[1] an apparatus was described for the investigation of the rate of diffusion of oxygen through silver. The rates of diffusion under various conditions of temperature and pressure as well as for different thicknesses of silver were given. The results were summed up in the equation $X = (1.71\sqrt{p}/10^{43}h)T^{14.62}$, where X is the rate of diffusion in cc. per sq. meter per hour, p the pressure of oxygen in mm. of mercury, h the thickness of silver in mm. and T the absolute temperature. (NOTE.—$\sqrt{p/h}$ was printed by error instead of $\sqrt{p}/h$ on pp. 1387 and 1389 of Ref. 1).

This paper is a continuation of the previous one.

Further investigation has shown that a general equation can represent the results of the diffusion of gases through metals for all cases so far investigated.

Apparatus

The apparatus used to obtain the results of Table I was that described in the first paper. That for the other results was practically the same, ex-

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[1] Johnson and Larose, THIS JOURNAL, **46**, 1377 (1924).