XLIII.—*The Use as a Drying Agent of Phosphoric Oxide treated with Ozone.*

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DURING some preliminary experiments with two McLeod gauges constructed for measuring very small gas pressures, it was found necessary to direct special attention to the way in which phosphoric oxide used as the drying agent comported itself. The problem, at first sight comparatively simple, proved on investigation to be difficult of solution; the difficulty arose, not from any intrinsic cause, but was rather the result of an intimate association of the problem with two others of a cognate nature to be dealt with in a further communication.

It is well known that by distilling phosphoric oxide in the presence of oxygen and spongy platinum, a product having a very high degree of purity may be obtained, but the process is admittedly lengthy, tedious, and costly; and this is markedly so when considerable quantities are required; moreover, it is by no means easy to obtain the purified compound in the light, powdery form so essential for perfect and rapid drying. But when phosphoric oxide is used for drying gases, it need not be *chemically* pure; the requirements of the physicist are fully met if two conditions are complied with. (1) The oxide must be free from all substances having measurable vapour pressures; and (2) impurities which, by reacting with water or mercury vapour or with the gas that is being dried, give rise to gaseous matter of a kind other than that which is under observation must be removed or changed into harmless products.

In order to investigate the matter somewhat fully, samples of the purest phosphoric oxide obtainable were at various times purchased from different firms. All the samples were found to contain phosphorous oxide. In six samples the amount varied within the limits of 0·43 and 1·06 per cent.; but a seventh sample (α) was so nearly free from phosphorous oxide that, when tested, many hours elapsed before a faint cloud of mercurous chloride appeared, and on evaporating an aqueous solution, no hydrogen phosphide was detected. Four of the samples were chosen for comparative experiments, but before the experiments were carried out three of the samples were purified. One (K_1) was distilled in the presence of oxygen and spongy platinum; two others (K_2, K_3) were freed from injurious impurities by the method described below; the fourth (α), containing the trace of phosphorous oxide already alluded to, was used as received.

Purification of the Samples K_2 *and* K_3.—These two samples were rendered eminently suitable for drying gases by proceeding as follows :—

A U-tube (subsequently used as a drying chamber) was loosely filled with the oxide, and the inlet and outlet tubes were lightly plugged with asbestos fibre; the U-tube was then set up within a small air-bath, and an ozone generator was attached. Next, the temperature of the bath was slowly increased while a continuous stream of air, previously freed from aqueous vapour and carbon dioxide and powerfully ozonised, was passed through the charged tube. During this period the escaping gas was frequently tested with potassium iodide and starch, and when it was found to be highly and continuously charged with ozone at the temperature of 300° or rather more, it was concluded that the purification of the oxide had been accomplished. The behaviour of the impurities in the two samples may here be noted.

Sample K_2.—At all temperatures below 160° there was no appreciable diminution in the quantity of the escaping ozone, but from that point upwards the presence of ozone became less and less marked until, at 175°, it was entirely lost. On temporarily reducing the temperature to 170°, traces of ozone were again detectable. The temperature of the bath having again been raised to the higher value of 175°, a continuous stream of ozonised air was maintained. After the expiration of twenty-five minutes, the indicator showed that ozone had reappeared in quantity, and it was therefore concluded that some impurity (P_4O_6?) had no been fully oxidised. At this stage of the experiment a white, crystalline deposit was observed in the projecting part of the tube, and this on analysis proved to be pure phosphoric oxide. Whenever phosphoric oxide, rendered impure by the lower oxide, is treated in the way described above, similar deposits are invariably produced, and the more marked the impurity the greater is the quantity of the crystalline deposit. Finally, on raising the temperature of the bath, it was found that throughout the whole range 175—303° ozone freely escaped from the heated oxide; whence it appears that all oxidisable impurities were completely satisfied with oxygen at the lower temperature of 175°. The purified compound was subsequently examined for phosphorous oxide; its aqueous solution remained for hours quite unaffected both by silver nitrate and also by mercuric chloride.

Sample K_3.—This sample contained foreign matter calculated as 0·43 per cent. of phosphorous oxide. When heated with ozone, the behaviour of K_3 differed from that shown by K_2. Three distinct stages of oxidation were noted; these occurred within small ranges of the respective temperatures 147°, 197°, and 220°. Each stage, although of brief duration, was sharply defined.

This second purified sample, when examined for phosphorous oxide, was, like K_2, found to be free from that impurity.

The oxidation of impurities as outlined above is easily effected, and the method involves but little attention or skill. The phosphoric oxide retains its loose, bulky form, and, other conditions being equal, a gas in contact with it is therefore most quickly dried. Also there is the added advantage that the purified compound, being already in situ, is not subsequently and of necessity exposed to the dampness of the air. To determine their efficacy as drying agents, the four samples of oxide were severally examined as follows.

Sample α.—A drying chamber was charged with the oxide and then fused to a tube leading to a Sprengel pump and afterwards highly exhausted, and in order to effect a very complete removal of aqueous vapour from the internal surfaces, some weeks were allowed to pass before accurate measurements of the gas pressure were made, but during this period the pump was almost daily used.

When the oxide had been in the apparatus for fourteen weeks, the gas (air) pressure was reduced until the value as determined by the attached McLeod gauge was 0·00017 mm., then, leaving the pump at rest, measurements of the steadily growing gas pressure p were carried out during successive days. On the ninth day, $p = 0{\cdot}00181$ mm.; the increase in p was therefore 0·00174 mm., a mean daily rate of 0·00019 mm. After the conclusion of the first series of observations, the pump was again brought into frequent use during another five weeks, and then a second series of daily pressure readings carried out. Starting with $p = 0{\cdot}00041$ mm., the value had by the eighth day become 0·00133 mm., the difference being 0·00092 mm., which equals a mean daily rate of 0·000115 mm. Proceeding as before and making frequent use of the pump during an additional seventeen weeks, a third and final series of observations, also extending over eight days, was obtained. In this last series of experiments with sample α, the initial and final values of p were respectively 0·00068 and 0·00123 mm.; the growth in p was therefore 0·00055 mm., and this equals a mean daily rate of 0·00007 mm. The final rate observed is 2·5 times smaller than that obtained in Series II.

Samples K_2 and K_3.—The chambers containing these two samples of purified oxide were fused to separate pumps, and high vacua produced and maintained within them for many weeks; then, leaving the pumps at rest, the residual air pressures, p, were measured once on each of nine successive days. It was thus found that the mean daily growth in p equalled 0·000031 mm. for K_2, whilst that for K_3 was 0·000034 mm.

Concluding experiments, calculated to throw light on the behaviour of sample α as recorded above, were at this juncture carried out with phosphorous oxide newly prepared by Thorpe and Tutton's method; these I now describe.

Phosphorous Oxide.—A drying chamber was charged with the oxide and fused to the pump, which still retained the purified phosphoric oxide K_3, and the whole apparatus was exhausted as rapidly as possible. The fall-tube of the pump was quickly stained, and in consequence of this the reduction of the gas pressure p was a matter of difficulty, and some twenty hours elapsed before the clicking sound so characteristic of the approach to a high vacuum was heard. On arresting the action of the pump at any time during the first days of the experiments, p increased with abnormal rapidity, and this fact suggested that a continuous formation of gas was taking place. Exact measurements made after the expiration of three days showed that p was increasing at the mean daily rate of 0·0166 mm. By using the pump freely during a period of six weeks, this rate was reduced to 0·004 mm., and similarly during an additional two weeks, the mean daily rate was reduced to the small value of 0·00038 mm.

Before discussing the results, I would disarm possible criticism by reminding chemists that no claim is here put forth for chemical purity; those desiring "chemically pure" phosphoric oxide will set about the task of preparing it in some other way. The point which I desire to stress is that although in this instance chemical purity of the highest degree was not attained, we yet do by the method adopted for purifying samples K_2, K_3 secure possession of phosphoric oxide the purity of which is such that when the substance is used for drying hydrogen, oxygen, nitrogen, air, or helium (all of which have been critically tested during the past ten or twelve years), no measurements of a purely physical character subsequently conducted with those gases are in the least degree likely to be affected; and this being so, phosphoric oxide purified by ozone fulfils in each of the cases cited above the requirements of the physicist.

We have seen that, in the presence of phosphorous oxide, reduction in the pressure of a gas is difficult; and that with the attainment even of a moderately high vacuum, on bringing the pumps to rest, the growth in the pressure p acquires an abnormally high rate, and, further, that although this rate decays, it persists for weeks. The exceptional increment for p is, however, understood when we remember that the interaction of aqueous vapour and *finely divided* phosphorous oxide such as we used results in the ready formation of hydrogen phosphide. Now the formation of this gas proceeds at the greatest rate when the aqueous vapour present is a maximum quantity, that is, during the earlier stages of drying. With the complete removal of aqueous vapour by phosphoric oxide, the production of hydrogen phosphide necessarily terminates, and so from this time forth the attainment of a high vacuum is a possibility. But since the boiling point (173°) of phosphorous oxide is not high, the vapour pressure even at the ordinary temperature must be appreciable, and therefore when the lower oxide is present in the drying chamber, it will be impossible to establish vacua of the highest order. The truth of these remarks receives confirmation from the results of the experiments with sample α cited above. But in addition to the disturbing factor introduced by hydrogen phosphide, a secondary and one of even more importance arises from the appearance of free hydrogen. An analysis of the dark substance removed from the fall-tube of the Sprengel pump revealed the powder as mercury phosphide; this substance was in all probability formed in accordance with the equation

$$2PH_3 + 3Hg = 3H_2 + Hg_3P_2.$$

It therefore follows that during the reaction between hydrogen phosphide and mercury there were substituted 3 vols. of hydrogen for 2 vols. of hydrogen phosphide, and in consequence of this the pressure was still further augmented.

In confirmation of the above interpretations, the following two experiments are cited.

Experiment 1.—After the whole apparatus had been cleaned, dried, and exhausted, a very small quantity of hydrogen phosphide obtained from pure phosphonium iodide and subsequently purified and dried, was introduced. Using the McLeod gauge as though we were about to measure a gas pressure, the bulb and most of the capillary tube were charged with mercury; the cistern was then lowered and when the mercury had left the gauge the whole interior surface was found to be covered with a highly uniform film having a golden tint; this film extended upwards within the capillary tube to the highest point reached by the mercury, but not beyond. From the conditions under which the film of mercury phosphide was formed it was concluded that electrical charges, produced by the friction between the mercury and the glass, initiated the chemical change. Holding this view, I was led to try the following experiment.

Experiment 2.—A clean dry tube was charged with pure mercury and set up as a barometric column; some hydrogen phosphide, prepared as for experiment 1, was then introduced, and the volume of the gas under normal temperature and pressure determined. A clean iron wire having been passed up through the column of mercury, the upper end of the tube was fitted with a tin-foil cap; the wire and the cap were then joined to an induction coil, and a glow discharge was set up within the hydrogen phosphide. The volume of the gas at once began and continued to increase steadily, and at the same time a golden, iridescent film appeared within the tube; the general appearance of this film was similar to that of the film obtained in the McLeod gauge during experiment 1. When the volume of the gas had increased by 15 per cent., the tube was pierced by the discharge and the experiment abruptly terminated, but as the available evidence was now sufficiently complete, no repetition of the experiment was required. The film, when subjected to analysis, was found to be, as expected, mercury phosphide.

On reviewing our data in the light of the evidence adduced, it is at once apparent that although the sample of oxide α contained but a mere trace of phosphorous oxide, yet even so its quality as a drying agent was markedly affected, and when the oxide was finally tested after a lapse of thirty-six weeks, the daily growth in the pressure on arresting the action of the pump was still some ten times greater than would probably have been the case if the oxide had previously been treated with ozone.

With regard to the two samples, K_2, K_3, which had been subjected to the influence of ozonised air, their superiority over the unpurified sample of oxide α is at once revealed by comparing the respective data (*vide supra*) for the three several samples. Contrasted with phosphoric oxide purified by distillation in oxygen, the ozonised oxide is sometimes found to absorb aqueous vapour more rapidly than the sublimed compound; this, however, appears to happen only when the latter in condensing forms a somewhat compact mass with a more restricted surface; apart from this, the two modes of purification yield phosphoric oxide identical in merit as drying agents.

In conclusion, it may be remarked that as the various experiments were comparative and differential rather than absolute, the slight effect on the increment in the pressure p following an attenuation of the gas skins upon the internal surfaces of the apparatus has not here been taken into account; such a course being obviously unnecessary.

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