363. *The Use of Phosphoric Oxide as a Drying Agent for Hydrogen Chloride.*

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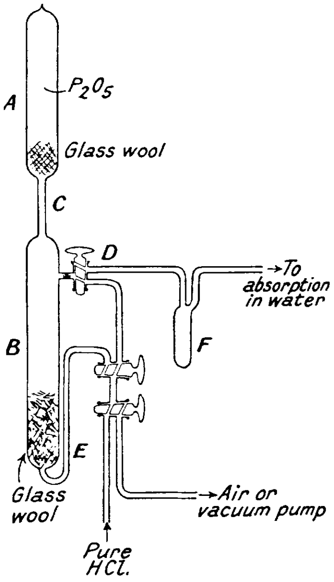
PHOSPHORIC oxide has often been used as a drying agent for hydrogen chloride, this treatment being followed in some cases, though not invariably, by condensation and fractionation of the hydrogen chloride. Several workers have, however, reported that a reaction occurs between the substances.

Bailey and Fowler (J., 1888, **53**, 755) found that hydrogen chloride kept in contact with phosphoric oxide was absorbed with the formation of phosphoryl chloride and metaphosphoric acid. They gave as the reaction : $2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$. They found that the hydrogen chloride was absorbed very slowly during the first few days and thereafter at an increasing velocity. They suggested that the initial slow rate "may merely indicate that it was necessary for the hydrogen chloride to expel the air mechanically retained by the phosphorus pentoxide before it could come into intimate contact with the latter." Gutmann (*Annalen*, 1898, **299**, 267), as a corollary to a failure to repeat Baker's experiment on the inhibitory effect of drying by phosphoric oxide on the reaction between hydrogen chloride and ammonia, examined the rate of absorption of hydrogen chloride by phosphoric oxide by measuring the change of pressure in what was almost a constant-volume apparatus: the rate of decrease of pressure during the first 12 hours was almost negligible, increased during the following 100 or so hours, and then fell off rapidly; *i.e.*, the rate of reaction was increasing whilst the pressure of the gas was decreasing. Baker (J., 1898, **73**, 422), in reply to Gutmann, stated that he had found that, whilst phosphoric oxide containing much metaphosphoric acid absorbed ammonia gas, yet distilled phosphoric oxide was practically without action both on ammonia and on hydrogen chloride, and he attributed Gutmann's failure to reproduce his experiments to the presence of metaphosphoric acid in his phosphoric oxide. Gray and Burt (J., 1909, **95**, 1633) also found that hydrogen chloride reacted with phosphoric oxide, forming a volatile phosphorus compound which was decomposed by mercury, a solid yellowish film being deposited on the glass surface of a Töpler pump, and that the formation of this compound was lessened by employing phosphoric oxide which had been distilled in a stream of oxygen. Baxter, Hines, and Frevert (*J. Amer. Chem. Soc.*, 1906, **28**, 770) found that when manganous chloride was fused in hydrogen chloride gas which had been dried by phosphoric oxide, an insoluble residue of manganese phosphate was obtained in a quantity which varied with the amount of moisture in the salt. These authors, and also Gray and Burt, found that hydrogen chloride, passed over phosphoric oxide and absorbed by water, gave a precipitate with ammonium molybdate solution.



On the other hand, there are a number of instances in which phosphoric oxide has been used in conjunction with hydrogen chloride without any obvious ill effects, which would suggest that it is the purity of the phosphoric oxide which determines whether or not reaction occurs between it and the hydrogen chloride.

EXPERIMENTAL.

Several g. of phosphoric oxide, free from lower oxides, were sealed in the tube *A* in the apparatus shown in the Fig. The apparatus was evacuated and warmed, and allowed to stand for several days in order to remove as much as possible of the moisture on the walls. The phosphoric oxide was then sublimed in a vacuum into the portion *B*, part of it being condensed on to the surface of the glass wool in the lower end of *B*. The apparatus was then sealed off at *C*. Hydrogen chloride, prepared from pure sulphuric acid and A.R. ammonium chloride, was passed over resublimed aluminium chloride, solidified in liquid air, and fractionated. *B* was cooled in liquid air, and several g. of the purified hydrogen chloride (admitted through *D*) were condensed on to the phosphoric oxide. *B* was then allowed to warm up, whilst hydrogen chloride gas was passed in through *E*. The issuing gas was condensed in the vessel *F*, which from the beginning of the experiment was immersed in liquid air, thus preventing, in addition, any back diffusion of moisture from the water-absorption vessel. When about 10 c.c. of solid hydrogen chloride had collected in *F* (*B* being gently warmed during the later stages to assist in the removal of any phosphoryl chloride which might have been formed), the contents were allowed to liquefy and were evaporated and absorbed in water, *F* also being heated at the end of the evaporation, and a current of purified hydrogen chloride passed through the apparatus. In these circumstances the question of diffusion of the hydrogen chloride into the phosphoric oxide (see Bailey and Fowler) did not arise. The resulting solution of hydrochloric acid gave a barely detectable coloration by the ammonium molybdate test. Several litres of moist air were then passed through *B*, and the experiment repeated, with similar results. *B* was then opened by cutting the seal at *C*, a few drops of water introduced, and *B* re-sealed. An experiment carried out as before yielded a solution of hydrochloric acid which gave an appreciable amount of precipitate with ammonium molybdate solution.

These experiments show clearly that there is no reaction when dry hydrogen chloride is passed over pure phosphoric oxide at the ordinary temperature, but that the presence of an appreciable amount of moisture or metaphosphoric acid is necessary for a reaction to be observed.

The slow reaction between hydrogen chloride and phosphoric oxide containing only a trace of metaphosphoric acid, and the rapid acceleration as the reaction proceeds, may be explained as follows. The hydrolysis of phosphoryl chloride is probably reversible to a small extent, $POCl_3 + 2H_2O \rightleftharpoons 3HCl + HPO_3$, the reversibility being generally unnoticed because the hydrolysis equilibrium is almost completely in favour of the free halogen acid. Nevertheless, if even a minute proportion of water is present at equilibrium, then, in the presence of a relatively large amount of phosphoric oxide, the reaction will proceed slowly towards the left, one molecule of metaphosphoric acid giving rise to two molecules of water and thence to four molecules of metaphosphoric acid : $2P_2O_5 + 2H_2O = 4HPO_3$. As a consequence, the amount of this acid in the system will increase with time, and the absorption of hydrogen chloride become faster and faster.

Although, as a result of using fairly pure phosphoric oxide in the first place and on account of the slowness of the reaction in the early stages, no serious contamination of the hydrogen chloride may occur when it is passed over phosphoric oxide, the fact remains that phosphoric oxide is not a suitable drying agent for hydrogen chloride, unless followed by condensation and fractionation.

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