[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 223]

CHEMICAL REACTIONS OF DRIED SUBSTANCES. I. AMMONIA AND PHOSPHORUS PENTOXIDE

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RECEIVED APRIL 1, 1929 PUBLISHED JULY 5, 1929

It was reported by H. B. Baker[2] that phosphorus pentoxide did not absorb thoroughly dried ammonia. Gutmann[3] was unable to duplicate these results but he failed to describe the purity of the phosphorus pentoxide and the method of introducing it into his apparatus. Baker[4] repeated his own experiments and reaffirmed his claim, suggesting that the presence of metaphosphoric acid would explain the absorption of ammonia observed by Gutmann. Recently, Robertson, Fox and Hiscocks[5] passed dried and purified ammonia through a tube of phosphorus pentoxide and confined it over mercury in contact with the pentoxide. They observed a slight reaction at first, after which no decrease in volume occurred during forty-eight hours.

In several of these investigations the experimental conditions were such that the ammonia might have partly saturated the phosphorus pentoxide before the observations were made. Furthermore, the possible formation of a protective film upon the pentoxide was not excluded. It appeared worth while, therefore, to repeat the experiments, avoiding these sources of uncertainty and taking the additional precautions made possible by modern, high-vacuum technique. The hazard of preliminary saturation of the phosphorus pentoxide may be eliminated by observing the pressure of ammonia *before* as well as after exposure to it and the possibility of film formation may be tested by exposing the gas to a fresh surface of the pentoxide after reaction with the first sample has ceased.

Baker dried his apparatus by heating the glass nearly to the softening point and simultaneously drawing through it a stream of air dried with sulfuric acid. Ammonia was prepared from ammonium chloride and dried over lime for several days. A thin glass tube containing sublimed phosphorus pentoxide was broken in a reaction chamber containing the dried ammonia and pressure changes were observed on a mercury manometer.

In the present investigation it was considered desirable to dry the apparatus by evacuation at elevated temperatures, to employ phosphorus

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[1] National Research Fellow.

[2] Baker, *J. Chem. Soc.*, **65**, 611 (1894).

[3] Gutmann, *Ann.*, **299**, 273 (1898).

[4] Baker, *J. Chem. Soc.*, **73**, 422 (1898).

[5] Robertson, Fox and Hiscocks, "Studies in the Infra Red Region of the Spectrum, II," *Proc. Roy. Soc. London*, **120**, 157 (1928).

pentoxide free from lower oxides[6] and observable quantities of metaphosphoric acid and to use ammonia which, after drying with dissolved sodium, had been triply distilled without further contact with any but dried and outgassed surfaces of pyrex glass and fused quartz.

Experimental Part

Apparatus.—The apparatus consisted essentially of purification trains for the reagents, a storage bulb for the ammonia and storage tubes for the phosphorus pentoxide, a quartz spiral manometer (connected by means of a graded seal) and suitable attachments for evacuating the system. A diagram appears in Fig. 1. The points at which various sections were sealed off during the manipulation are indicated by constrictions. Temporary separation of various parts was accomplished by the use of plunger stopcocks of the Richards type through which were made the connections described later.

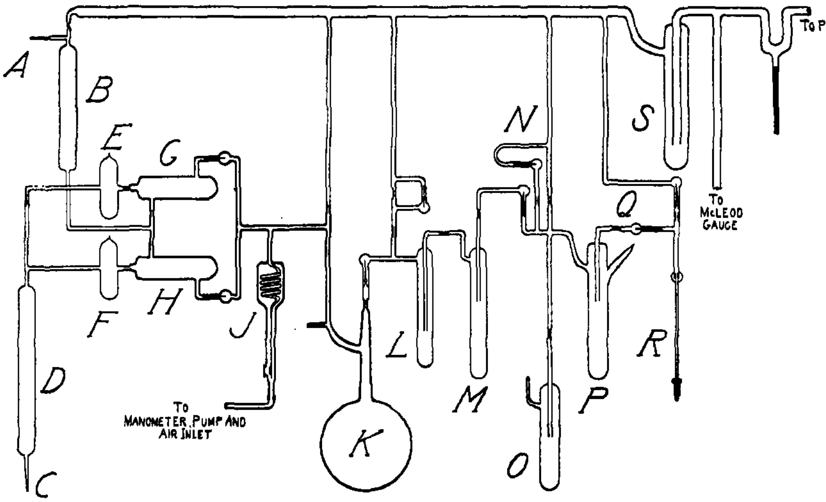

Fig. 1.—Apparatus for studying the reaction between dried ammonia and phosphorus pentoxide.

The iron cores were enclosed in glass sheaths to prevent contact between ammonia and the metal surfaces. A small mirror mounted on the indicator of the quartz manometer reflected the image of a straight filament upon a ground-glass scale placed at a distance of three meters. The manometer was used as a null instrument, balancing the pressures within it by external pressures which were read on a mercury manometer. Readings were accurate and reproducible to one millimeter. This auxiliary equipment is not shown in the diagram.

Method of Drying.—The glass and quartz surfaces were outgassed by evacuating through a liquid-air trap S with a mercury diffusion pump and a high-vacuum type of oil pump fifteen hours a day for five days. During this pumping the apparatus was intermittently heated with a blow torch until a yellow color was imparted to the flame and a high-tension discharge from a high frequency coil (which gives a one-inch spark in air) played upon the hot surfaces. After the third day no discharge from the heated

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[6] Biltz, *Ber.*, 27, 1257 (1894), observed that the presence of lower oxides caused absorption of the ammonia.

surfaces was observable. At the end of the five-day period the pumps could be disconnected for nine hours without a rise in pressure of more than 3×10^{-6} mm. of mercury. The direct leads to the pumps were then sealed off.

Materials.—Several brands of C. P. phosphorus pentoxide were tested for lower oxides and organic matter. The tests used for lower oxides were the mercuric chloride test advocated by Whittaker[7] and the silver nitrate test suggested by Finch and Peto[8] which is claimed to be the more sensitive by Finch and Fraser.[9] Our observations confirm this claim. One brand which was nearly free from these impurities was selected and further purified by sublimation at 800° in a stream of oxygen according to the directions of Finch and Fraser[9] and obtained in the highly pure and voluminous form which they described. Samples of this purified material were placed in the sublimation tubes E, F which were sealed off and evacuated. The surfaces of the storage tubes G, H were then outgassed and dried as described. The fine capillary C which terminated the inlet was broken and a stream of dry air entered through the phosphorus pentoxide protection tube D. The tip A of the second protection tube B was broken to provide an outlet and a slow stream of oxygen, dried by passage through an additional phosphorus pentoxide tube 80 cm. in length, was led through the sublimation train. Upon moderate heating, the pentoxide in the sublimation tubes readily sublimed and collected in the storage tubes as a voluminous deposit of feathery crystals and white powder. This material was apparently free from metaphosphoric acid, since it could be sublimed from one part of the tube to another without leaving any visible residue. The sublimation tubes together with the attached guard tube D were sealed off, the tip A of the second guard tube sealed and the storage tubes evacuated. Thus the storage tubes were protected by a guard tube of phosphorus pentoxide and a liquid-air trap. They were heated as hot as possible without driving out the pentoxide and treated with the discharge until a satisfactory vacuum and outgassing had been achieved, when they were sealed off from the vacuum line. Samples of the material which had collected in the connecting tubes were tested and found to be free from lower oxides.

Commercial anhydrous liquid ammonia was used as a starting material. This had been in contact with sodium in a special steel cylinder for four months. The outlet R of this cylinder was attached to the purification train with de Khotinsky cement. The connecting tubes between the tank and the first stopcock Q were pumped out but could not be heated, so the entering ammonia was redried by condensation at −78° into the first distillation tube, P, which contained metallic sodium. As soon as a sufficient quantity had collected, the lead from the tank was sealed off and the solution of sodium in the liquid ammonia allowed to stand for five hours.

One-third of the ammonia was distilled into a receiver O and discarded after sealing off this receiver. Baths of solid carbon dioxide in alcohol were used as refrigerants in all of the distillations. Hydrogen present in the vapors was now removed by connecting the first distillation tube through a stopcock N to the vacuum pumps. The ammonia was kept at −78° during this process and after the pumping was completed the vacuum connection was sealed off. Connection was then made to the second distillation tube M, one-half of the remaining ammonia distilled into it and this sample twice fractionated, retaining only the middle third at each step. Economy of apparatus and manipulation was achieved by returning the first third of each distillate to the residue and discarding them together.

Before allowing a sample to evaporate from the third distillation tube L into the storage bulb K, connection was made to the vacuum pumps for a short time to ensure

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[7] Whittaker, *J. Chem. Soc.*, **127**, 2221 (1925).

[8] Finch and Peto, *ibid.*, **121**, 692 (1922).

[9] Finch and Fraser, *ibid.*, **129**, 117 (1926).

complete removal of any residual traces of hydrogen. When the vacuum connection had been sealed off and the stopcock leading to the storage bulb opened, a deflection of the quartz manometer J was observed which was found to indicate a pressure of 46.0 mm. (of mercury) within the system. As the ammonia in the third tube was partly frozen to a white solid at this time, this value should correspond to the vapor pressure at the melting point. This pressure is given by Landolt-Börnstein[10] as 44.9 mm., thus providing a check upon the reliability of the manometer. The purified ammonia was allowed to evaporate until the storage bulb was filled to a pressure slightly below atmospheric when the third distillation tube and the stopcock were sealed off.

The Action of Dried Ammonia on Phosphorus Pentoxide.—The volume of the storage bulb, manometer and connecting tubes had been found to be 1124 cc. by allowing dried air to expand into this system from a bulb of known volume. Accordingly, by reading the pressure and noting the temperature of a water-bath surrounding the storage bulb, the amount of ammonia therein (0.742 g.) could be determined. The volumes of the two phosphorus pentoxide storage tubes (neglecting the volume of the pentoxide, itself) was also known and thus the drop in pressure, due to expansion alone, upon connecting these tubes with the bulb could be calculated.

When the stopcock leading to the first pentoxide tube was opened a very rapid drop in pressure occurred which only continued for less than one minute. Thereafter the pressure fell very slowly. During the reaction some of the pentoxide near the ammonia entrance shrank considerably in volume and took on a glassy appearance. In other parts of the tube its appearance was not so markedly changed. Since the tube became heated, during the reaction, one hour and fifteen minutes was allowed for cooling and the pressure then determined. Upon standing thirteen hours the pressures dropped 7.4 mm. (of mercury) more. The second pentoxide tube was then connected and a similar effect was observed. The data for these pressure changes appear in Table I. The third column lists the pressures in mm. of mercury before opening the pentoxide tubes, the fourth the new pressures calculated for expansion only, the fifth the new pressures observed, the sixth the drop in pressure due to absorption.

TABLE I

PRESSURE CHANGES DURING RAPID REACTION

Tube no.	Volume, cc.	P_1	P_2 (calcd.)	P_2 (obs.)	P (abs.)	Temp., °C.
I	52	713	682	532.5	149.5	21.3
II	47	525.1	505	122.9	382.1	20.3

The system was allowed to stand for two days after these observations were made and the pressure read from time to time. These values, corrected for temperature variations, together with the time intervals are given in Table II.

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[10] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Berlin, **1923**, Vol. II, p. 1345.

TABLE II

PRESSURE CHANGES SUBSEQUENT TO RAPID REACTION

Pressure, mm.	122.8	119.8	113.9	102.8	92.0
Time, min.	0	85	320	1370	2810

The second pentoxide tube was then heated to 74° in a water-bath but no effect upon the pressure was observed beyond that calculated for expansion. This indicates the occurrence of a true reaction as opposed to mere adsorption.

Finally, dry air was admitted to the system and the two pentoxide tubes were sealed off. These were weighed, broken open, cleaned out with water and reweighed. By subtracting from the total weight of the contents of each tube the weight of ammonia absorbed in that tube as calculated from the pressure drop, the amount of pentoxide originally present was determined. These data appear in Table III, where Col. 2 gives the amounts of phosphorus pentoxide in each tube, Col. 3 the amount of ammonia actually absorbed and Cols. 4 and 5 give the amount calculated upon the assumption that one and two moles of ammonia, respectively, react per mole of pentoxide.

TABLE III

ABSORPTION OF AMMONIA BY PHOSPHORUS PENTOXIDE

Tube no.	P_2O_5, g.	NH_3(obs.), g.	NH_3 (calcd., 1 mole), g.	NH_3 (calcd., 2 moles), g.
I	3.060	0.162	0.366	0.732
II	5.635	.435	.673	1.346

It was noticed that, whereas part of the contents of the pentoxide tubes was glassy in appearance and dissolved but slowly in water, other portions reacted vigorously, indicating the presence of unused pentoxide. The aqueous solutions were tested and the absence of lower oxides in the reaction product was demonstrated.

Conclusions

There is, of course, no known method of establishing the precise degree of dryness actually attained in an investigation of the kind here described. It is the opinion of the authors, however, that the procedure employed was at least equal, and in some respects superior, to that described by the previous investigators.

It is a noteworthy fact that the amount of ammonia absorbed in the period of rapid reaction was insufficient to saturate the available phosphorus pentoxide. This is evident from Table III upon comparing the observed absorption with that calculated even upon the assumption that only one mole of ammonia reacts with one mole of the pentoxide. The actual difference is probably much greater, for the nature of the reaction products obtained by various investigators[11] indicates that at least *two* molecules of the gas are involved in the reaction. This marked retardation of the absorption cannot be ascribed to the removal of residual traces of moisture from the ammonia since a rapid absorption again took place when a fresh surface of the pentoxide was exposed. The effect may be explained by assuming the formation of a protective film of the reaction product upon the phosphorus pentoxide. This assumption is compatible with the appearance and character of the reaction product obtained.

No indications of such film formation have been reported by the previous workers and the information which they give is not sufficient to determine to what extent their observations may have been influenced by this effect.[12]

Summary

1. Pure phosphorus pentoxide has been found to absorb appreciable quantities of carefully dried ammonia rapidly.
2. Evidence has been obtained indicating that the reaction product forms a protective film upon the pentoxide which retards further absorption.

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[11] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," London, **1928**, Vol. VIII, pp. 708–711.

[12] After this paper was submitted for publication our attention was called to an article by H. Tramm [*Z. physik. Chem.*, **105**, 356 (1923)]. He found that phosphorus pentoxide reacted with ammonia dried by Baker's procedure or by dissolving sodium in the liquid ammonia. However, he reported that ammonia dried by passage over sodium wire and then through liquid sodium–potassium alloy did not react with the pentoxide. He did not consider the possible influence of the formation of a protective film upon the pentoxide and it appears from the description that the ammonia was first admitted at low pressure into the pentoxide tube. Under such conditions film formation might occur without a very noticeable heat effect and thus the disappearance of a small amount of ammonia at the beginning of the experiment might have been unnoticed. Since he did not state his criterion for reaction, it seems advisable to reserve judgment upon his experiment until it has been repeated.