the concentration dependence data in the following section which shows that the intensity is independent of the solvent in concentrations between 2.0 and 13.0 *M*. A 100° decrease in temperature for isopropyl alcohol produces about a 60% increase in intensity. This increase in intensity is best explained qualitatively by one of the two explanations in the previous section. The viewpoint of Mulliken[25] which takes into account the ability of various solvents to serve as electron donors affords the best explanation.

Intensity Data for Isopropyl Alcohol in Different Solvents.—The concentration dependence of the apparent integrated OH band intensity of isopropyl alcohol in diethyl ether, triethylamine and carbon tetrachloride is illustrated in Fig. 13. These data indicate that at room temperature the intensity of the bonded OH frequency is relatively independent of the solvent until the concentration of the alcohol is reduced to about 2.0 *M*. The small variations in the concentration range could possibly be due to a dielectric effect. The most striking result is the manner in which the intensity varies with continued dilution. For carbon tetrachloride, which should be an inert solvent, the intensity of the bonded OH frequency decreases when the solution is diluted below 2.0 *M;* and at about 0.2 *M* the free OH stretching frequency appears at 3620 cm.$^{-1}$. With continued dilution the bonded OH frequency disappears while the band due to the "free" OH stretching frequency increases in intensity. At extreme dilutions, the intensity of the OH stretching frequency approaches 0.48×10^4 liter mole^{-1} cm.$^{-2}$, which is the value quoted by Barrow.[5] With the two solvents which are electron donors, the effect upon intensity for these two solvents is in the same order as their order of basic strength. With continued dilution, the intensity for the bonded OH frequency for isopropyl alcohol becomes 3.0×10^4 and 4.8×10^4 liter mole^{-1} cm.$^{-2}$ in diethyl ether and triethylamine, respectively. These values agree with those quoted by Barrow[5] for these solvents.

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THE REACTION OF ACTIVE NITROGEN WITH PHOSPHINE[1]

BY D. M. WILES[2] AND C. A. WINKLER

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada

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The main products of the reaction between active nitrogen and phosphine are molecular hydrogen and the α-form of $(PN)_n$. Conversion of one molecule of phosphine to phosphorus paranitride appears to require two nitrogen atoms. It is suggested that the primary step is abstraction of hydrogen and that the resulting PH_2 radicals react further with nitrogen atoms to form the nitride.

Introduction

The physical properties and chemical behavior of active nitrogen have been variously attributed to the presence of atoms, ions and electronically excited molecules. A recent re-examination of the problem[3] indicates that the main reactive species is atomic nitrogen. However, the unusual results obtained in the reactions of active nitrogen with ammonia, and with mixtures of ammonia and ethylene,[4] suggested that a second active species, perhaps vibrationally excited molecules,[3] might also be present.

In an effort to obtain further information about the possible existence of such a second active species, experiments have now been made with phosphine, as an analog of ammonia, with the results outlined in the present paper.

Experimental

The apparatus and general techniques have been described in earlier papers from this Laboratory (*e.g.* ref. 5). The methods of preparation and purification of phosphine also have been outlined previously.[6]

Nitrogen (99.9% pure) from a cylinder was passed through a tube containing copper turnings at 400°, through a trap immersed in liquid nitrogen and into the discharge tube through a capillary flow meter at a flow rate of 1.15×10^{-4} mole/sec. The pressure in the reaction system, with the discharge operating, was 1.35 mm. Active nitrogen concentrations were estimated by measuring the amount of HCN produced in the ethylene–active nitrogen reaction.

Phosphine flow rates were measured in a series of "blank" experiments in which PH_3, collected in the product trap, was distilled into a removable trap containing silver nitrate solution. The precipitated silver was removed by filtration, and excess silver nitrate was titrated with thiocyanate solution[7]; unreacted phosphine was determined in the same way.

Results and Discussion

The relations between the rate of phosphine decomposition and phosphine flow rate at two temperatures are shown in Fig. 1. The curves at 83 and 290° are typical of a reaction in which there is complete consumption of one reactant in the presence of excess of the other. As it entered the active nitrogen stream, phosphine extinguished the afterglow and a small, pale-green reaction flame was observed. The main products of the reaction were

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[1] Financial assistance from the National Research Council of Canada.

[2] Holder of National Research Council Studentships 1955–1956, 1956–1957.

[3] H. G. V. Evans and C. A. Winkler, *Can. J. Chem.*, **34**, 1217 (1956).

[4] (a) G. R. Freeman and C. A. Winkler, THIS JOURNAL, **59**, 371 (1955); (b) D. A. Armstrong and C. A. Winkler, *ibid.*, **60**, 1100 (1956).

[5] P. A. Gartaganis and C. A. Winkler, *Can. J. Chem.*, **34**, 1457 (1956).

[6] D. M. Wiles and C. A. Winkler, THIS JOURNAL, **61**, 620 (1957).

[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1952.

hydrogen and an opaque, reddish-brown polymer which formed on the walls of the reaction vessel. Its non-volatility, color, behavior in hot and cold concentrated H_2SO_4 and insolubility in the usual solvents suggested that the polymer was the α-form of $(PN)_n$, phosphorus paranitride. Chemical analysis[8] confirmed its identity.

Comparison of the experimental results given in Fig. 1 with plateau values determined in the present study for the HCN yield from ethylene (9.9×10^{-6} mole/sec. HCN at 83°, 19.9×10^{-6} mole/sec. HCN from 250 to 450°) make it possible to suggest a mechanism for the active nitrogen–phosphine reaction. The increase with temperature of the limiting hydrogen cyanide yield in the reaction of active nitrogen with ethylene may be explained by assuming that the rate of production of hydrogen cyanide by decomposition of $N-C_2H_4$ complexes increases with temperature relative to the rate of recombination of nitrogen atoms by collision of the complexes with nitrogen atoms.[9] Hence, if the actual flow rate of active nitrogen is taken to be that corresponding to the HCN plateau at 290°, phosphine decomposition occurred at 83 and 290° to the extent of 41 and 53%, respectively, of the flow rate of active nitrogen. The difference in these two values might be due to a difference in the effectiveness of phosphine itself as a catalyst for the recombination of nitrogen atoms at the two temperatures.

On the basis of these considerations it would appear that decomposition of one phosphine molecule required the consumption of two nitrogen atoms. If this be true, a possible mechanism for the reaction of phosphine with active nitrogen would be

$$N + PH_3 \longrightarrow NH + PH_2 + 1.7 \text{ kcal.} \quad (1)^{10}$$

followed by

$$N + PH_2 + M \longrightarrow PN + H_2 + M + 162.7 \text{ kcal.} \quad (2)$$

$$NH + NH + M \longrightarrow N_2 + H_2 + M + 166 \text{ kcal.} \quad (3)$$

where M is a third body.

It seems likely that, as the flow rate of phosphine is increased beyond the point corresponding to complete consumption of nitrogen atoms, PH_2 radicals should react according to

$$PH_2 + PH_2 \longrightarrow P_2 + 2H_2 + 26.2 \text{ kcal.} \quad (4)$$

followed by

$$P_2 \longrightarrow P_{red} + 38.2 \text{ kcal.} \quad (5)$$

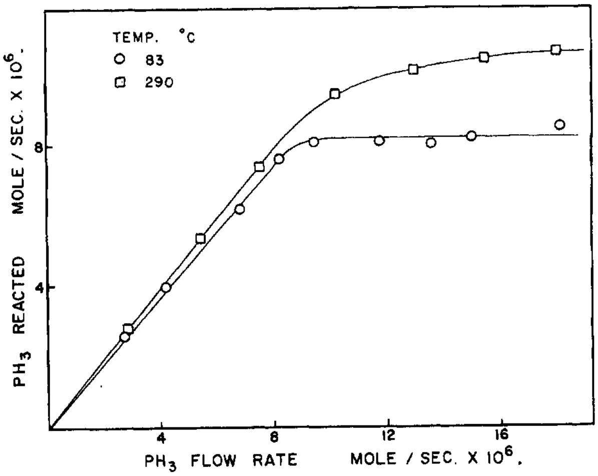

Fig. 1.

Failure to detect red phosphorus in the polymer layer might indicate that reaction 2 is very fast compared with (1), or that the reaction

$$N + P_{red} \longrightarrow PN + 128.3 \text{ kcal.} \quad (6)$$

is fast enough to maintain the concentration of phosphorus at a level too low for detection. On the other hand, experiments at sufficiently high flow rates of phosphine might reveal the presence of reactions 4 and 5.

Evidence for the occurrence of reaction 6 was obtained by depositing a relatively thick layer of red phosphorus on the clean wall of the reaction vessel by treating phosphine with hydrogen atoms. When this layer was subjected to attack by active nitrogen at 300°, considerable $(PN)_n$ was formed. Apparently nitrogen atoms can form the paranitride by reaction with phosphorus in the gas phase or at the surface.

A brief study also was made of the reaction of hydrogen atoms, produced in a condensed discharge, with $(PN)_n$. The reaction was found to be slow at 60°, more rapid at 300°, and the products were phosphine and a species, presumably nitrogen atoms, which reacted with propane to give HCN. The active nitrogen produced in this way was found to decompose ammonia, although to only a slight extent. This suggests that ammonia does react with atomic nitrogen, though perhaps slowly.

It is of interest to note that, of all the reactions of active nitrogen investigated to date,[11] the reaction with phosphine is the first one for which a satisfactory explanation of the experimental results has seemed possible by assuming the primary reaction to be hydrogen abstraction by atomic nitrogen.

Unlike the results obtained with ammonia as reactant, the data of the present study give no reason to suppose that an active species other than atomic nitrogen might participate in the reactions of active nitrogen.

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(8) The layer was removed in small flakes from the inner walls of the reaction system by leaching with NH_4OH solution, which presumably dissolved the underlying metaphosphoric acid used to poison the wall of the reaction vessel. Two samples of the well-washed and dried material (each 0.3 g.) were hydrolyzed for 48 hours in a sealed tube at 200°, following the procedure described by Moureu and Wetroff [H. Moureu and G. Wetroff, *Bull. Soc. Chem.*, [v] **4**, 1839 (1937)]. Analysis of the hydrolysis products showed that the polymer was 46.8% nitrogen and 46.5% phosphorus (atom % basis).

(9) W. Forst, H. G. V. Evans and C. A. Winkler, THIS JOURNAL, **61**, 320 (1957).

(10) Values for the heats of formation of most of the species in this and subsequent equations were obtained from U. S. Natl. Bur. Standards, Circular 500, "Selected Values of Chemical Thermodynamic Properties," Washington, 1952. For atomic nitrogen 112.5 kcal./mole was used; the values 83, 30 and 55 kcal./mole were estimated for NH, PH_2 and PH radicals, respectively.

(11) H. G. V. Evans, G. R. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).