

ACTIVE PHOSPHORUS

By

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Thesis submitted to the Faculty of Graduate  
Studies and Research of the University of Manitoba  
in partial fulfillment of the requirement for  
the Degree of Master of Science

From the Chemistry Department  
of the University of Manitoba  
under the supervision of  
Dr. H. Gesser



1960  
no date ?

### ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the Research Corporation who supported this work and to the National Research Council for a summer assistantship.

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## ACTIVE PHOSPHORUS

*Sir:*

An early attempt to produce phosphorus atoms by a condensed discharge proved unsuccessful.<sup>1</sup> In view of the work of Winkler and co-workers<sup>2</sup> on the reactivity of active nitrogen it was felt that a comparative study with phosphorus might prove informative.

An apparatus similar to that used for nitrogen<sup>2</sup> was tried for phosphorus. Argon, as a carrier gas, was passed through a bulb containing phosphorus at a temperature from 25 to 100°. The flow rate of argon was about 50 micromole/sec. at a pressure of approximately 1 mm. in the reaction bulb. When only argon was allowed to flow through the discharge, no decomposition of reactants was observed. Similarly no reaction was observed when P<sub>4</sub> was allowed to mix with reactant with no discharge. A definite reaction was obtained between phosphorus, swept through the discharge with argon, and ethylene, propylene, butene-1, propane, methane, ammonia, and hydrazine. Phosphine was the major gaseous constituent produced in all cases. The reactions also were observed when a microwave discharge was used to generate the "active phosphorus."

Gas chromatographic analysis on the products of methane-active phosphorus reactions indicated at least six volatile products. Phosphine, methylphosphine and ethane were obtained in very small quantities. The ethane was approximately 2% of the phosphine fraction. A considerable amount of solid was deposited in the reaction zone during an experiment. This, along with red phosphorus, appears to be the solid phosphorus hydrides.

It also was found that with a new discharge tube and a clean-walled apparatus, a liquid was produced in relatively large quantities. It was shown not to be P<sub>2</sub>H<sub>4</sub> from physical properties and elementary reactions.

Further work along with the identification of the "liquid" product is now being pursued.

Grateful acknowledgment is made to the Research Corporation for supporting this work.

(1) N. M. Gopshtein and S. Z. Roginskii, *J. Phys. Chem. (USSR)*, **7**, 587 (1936).

(2) D. A. Armstrong and C. A. Winkler, *J. Phys. Chem.*, **60**, 1100 (1956).

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RECEIVED OCTOBER 9, 1959

## ACTIVE PHOSPHORUS

### ABSTRACT

An early attempt to produce phosphorus atoms by a condensed discharge proved unsuccessful. In view of the work of Winkler and co-workers on the reactivity of active nitrogen it was felt that a comparative study with phosphorus might prove informative.

An apparatus similar to that used for nitrogen was tried for phosphorus. Argon, as a carrier gas was passed through a bulb containing phosphorus at a temperature from 25° C to 100° C. When only argon was allowed to flow through the discharge, no decomposition of reactants was obtained. A definite reaction was obtained between phosphorus swept through the discharge with argon, and ethylene, propylene, propane, methane, acetylene, methylene chloride, ammonia and hydrazine. Phosphine was the major gaseous constituent produced in all cases. The same products were obtained when a microwave discharge was used to generate the active phosphorus.

Gas chromatographic analysis on the products of methane-active phosphorus reactions indicated at least six volatile products. Phosphine, methylphosphine and ethane were identified; all with the exception of phosphine were obtained in very small quantities. The ethane was about 4% of the phosphine fraction. A considerable amount of solid was

deposited in the reaction zone during any one experiment. These besides red phosphorus appear to be solid hydrides.

It was also found that with a new discharge tube and a clean-walled apparatus, a liquid was produced in relatively large quantities. It was shown not to be biphosphine from physical properties and elementary reactions.

The discussion of the results contains several proposed mechanisms based on activated states of phosphorus atoms and molecules.



## INTRODUCTION

Since the discovery of the existence of free radicals by Gomberg (1) in 1900 it has become increasingly apparent that many reactions can be resolved into certain fundamental transformations which generally involve free atoms or radicals. Many have studied the reactions of various free atoms and radicals in an effort to gain some understanding of these fundamental transformations.

Rice (2) and co-workers obtained evidence to substantiate the existence of such radicals as ethyl,  $C_2H_5$ , and methyl,  $CH_3$ , in thermal decompositions of hydrocarbons soon after such radicals were proposed by Taylor (3). Wood (4) demonstrated that hydrogen atoms could be pumped out of a glimmering discharge in hydrogen and carried for considerable distances before they recombined. Bonhoffer (5) made extensive investigations of the chemical properties of atomic hydrogen and Steacie (6) studied a number of reactions of hydrogen and deuterium atoms. More recently Foner and Hudson (7) have done some work with hydrogen atoms in connection with H and  $O_2$  reactions. Considerable work has been done by Foner and Hudson and Robertson (8) in studying the production of  $HO_2$  radicals which seems to be of great importance in oxidation reactions.

Wood's method has also been applied to oxygen by a number of investigators among whom were Harteck and Kopsch (9) and Gieb (10). In dealing with oxygen atom reactions it was found that ozone,  $O_3$ , was



formed. At low pressures and at temperatures from room temperature upward, however, this proved to be relatively unimportant and the only "active" modification of oxygen was acknowledged to be atomic oxygen. Schiff and co-workers (11) have studied oxygen atoms, ozone and reactions of these. The work with both H and O atoms is often undertaken simultaneously because of the importance of reactions involving these two elements.

Rodebush and Klingelhoeffer (12) produced atomic chlorine by means of a high-frequency discharge. A fast flow system was used in order to prevent atom recombination. Schwab and Fries (13) prepared atomic chlorine by Wood's method. They found that the atoms recombined on the electrodes. This proved to be the main difficulty in producing atomic chlorine. Schwab investigated atomic bromine by Wood's method and found that almost every collision of a bromine atom with the wall led to recombination. As a result it was not possible to investigate reactions of bromine with other substances by this method.

The subject of active nitrogen produced by a discharge has a voluminous literature and a review of some of the more important reactions of active nitrogen would provide a background for the discussion of the possibility of some "active" phosphorus reactions. Therefore a brief outline of some pertinent nitrogen atom reactions will be given.

### Active Nitrogen

When a sufficiently strong electrical discharge is passed through nitrogen at low pressures a visible yellow afterglow persists after the discharge is stopped. This was first studied by Lewis (14). Strutt (15) then observed that the nitrogen afterglow was chemically active and proceeded to study its nature and active component. He was able to produce an afterglow which lasted for as long as six hours and to show that the afterglow intensity was greater at lower than higher temperatures. He also found that the glow was enhanced by small traces of foreign gases such as oxygen and hydrocarbons.

Strutt obtained nitrides of mercury, zinc, sodium, arsenic, cadmium, and sulphur in reactions of these elements with active nitrogen. Organic compounds such as acetylene, pentane, ethyl and methyl halides, ethylene dichloride and ethylidene dichloride reacted with active nitrogen to form hydrogen cyanide as a primary product. Benzene was reported to yield hydrogen cyanide and traces of cyanobenzene which was identified only by its odor.

The effect of the walls of vessels on the afterglow of nitrogen was examined by Herzberg (16). After finding it impossible to obtain the afterglow in clean quartz tubes and in Pyrex vessels, he concluded that the condition of the vessel wall seemed of primary importance. As a result of a series of experiments conducted by Strutt and Baker (17) and Tiede and Domcke (18) it was concluded that the shape of the discharge tube influenced the ease and ability of producing an afterglow.

### The Nature of Active Nitrogen

Numerous theories have been proposed to explain the properties of active nitrogen and these have in turn involved normal and metastable atoms, excited molecules,  $N_2^+$  ions and  $N_3$  as major constituents.

Throughout his work, Strutt assumed that the chemical reactivity of the afterglow was due to atomic nitrogen. This belief was opposed by Saha and Sur (19) who argued from classical quantum concepts that active nitrogen consisted of excited molecules having about 8.2 e.v. of energy.

Direct evidence to support the presence of atoms in the afterglow was obtained by Wrede (20) who made use of the relative rates of diffusion of the atoms and molecules through an orifice. He was able to show the presence of concentrations of nitrogen atoms as high as 40% in the glowing nitrogen stream.

Jackson and Broadway (21) performed a Stern-Gerlack experiment on active nitrogen and obtained visible evidence for the existence of atoms in active nitrogen. The atoms were detected on a film of silver nitrate with which they reacted, leaving a trace which was interpreted as indicating their presence.

A mass-spectral investigation of active nitrogen has been reported by Jackson and Schiff (22). They found that  $4S$  atoms, that is, atoms in ground state, were present and that there was no evidence of metastable atoms. Tanaka (23) and Broida (24) have found evidence for the  $2D$  atom (the first excited state of nitrogen atoms) in active nitrogen and they

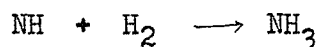
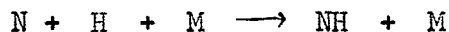
estimate its concentration at 1% of the total atom concentration.

Schiff also reports the possibility of  $N_2^+$  and  $N_3$  being present but could not determine their presence directly. Winkler (25) and co-workers have studied reactions of active nitrogen which indicate unambiguously that there are at least two reactive species in active nitrogen.

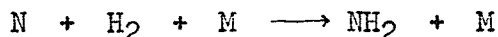
### Reactions of Nitrogen Atoms

#### Hydrogen:

In an effort to detect the presence of atoms in active nitrogen Lewis (26) investigated the reaction of hydrogen atoms with active and molecular nitrogen, and molecular hydrogen with active nitrogen. He found that in no case was hydrazine detected and that only when hydrogen atoms and active nitrogen were reacted did he detect ammonia. Stiener (27), in a more extensive investigation obtained hydrazine and traces of ammonia as products of the reaction of molecular hydrogen with active nitrogen. It was found, however, that hydrogen had diffused back into the discharge tube where it reacted in atomic form with nitrogen atoms. The mechanism proposed for the ammonia formation was



where M represented a third body. The mechanism proposed for hydrazine formation was



### Ethylene:

The reaction of nitrogen atoms with ethylene was first studied quantitatively by Greenblatt and Winkler (28). The products of the reaction, trapped in silica gel cooled with liquid nitrogen, were identified as hydrogen cyanide, ethane, and a viscous polymer. The yield of hydrogen cyanide increased linearly with increase in flow rate of ethylene until a maximum after which the yield of hydrogen cyanide was constant despite a further increase in flow of ethylene. The constant yield of hydrogen cyanide was higher with higher nitrogen atom concentrations. The amount of ethane formed increased from undetectable quantities at low flow rates of ethylene to about 30% of the ethylene input at higher ethylene flow rates. The reaction mechanism suggested was:



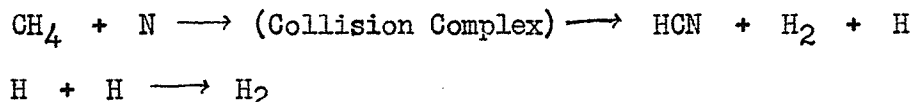
An activation energy of 6.9 kcal/mole as an upper limit was calculated from collision yields with 0.1 as the assumed steric factor.

This reaction has been re-investigated in greater detail by Versteeg (29). By poisoning the walls of the reaction vessel with phosphoric acid and using dry nitrogen he found that it was possible to eliminate the polymer as a primary product. In addition to hydrogen cyanide and ethane, Versteeg was able to identify methane, hydrogen, cyanogen and acetylene. Methane, acetylene and cyanogen were obtained in increasing amounts up to

the point of the total reaction of ethylene beyond which the yields decreased slowly with further increase in flow rate of ethylene. An essentially similar mechanism to that of Greenblatt and Winkler was proposed.

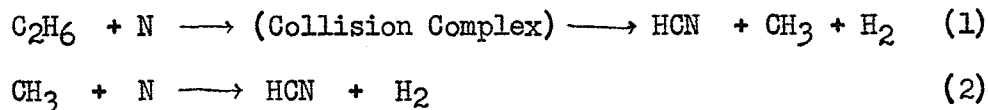
#### Methane:

Blades and Winkler (30) investigated the reaction of nitrogen atoms with methane at temperatures above 300° C and found hydrogen cyanide as the only condensible product. They were able to calculate an activation energy of 11 kcal/mole and a steric factor of  $5 \times 10^{-3}$  for the reaction. The mechanism suggested was:



#### Ethane:

The reaction of nitrogen atoms with ethane was studied (30) in the temperature range of 100° C to 295° C with hydrogen cyanide the only product found in measurable amounts. Above 165° C nitrogen atom consumption was complete when the ethane was in great excess. The reaction was second order with an activation energy of about 7 kcal/mole, and a steric factor of between  $10^{-1}$  and  $10^{-2}$ . The reaction mechanism suggested was:



The reaction of active nitrogen with methane and ethane were more recently re-investigated by Gartaganis and Winkler (31). They found that the production of hydrogen atoms had some effect on the production

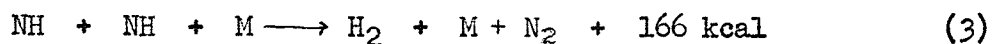
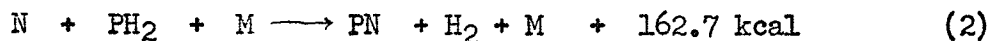
of hydrogen cyanide.

Several other hydrocarbons have also been reacted with active nitrogen and in general the mechanisms fall into two classes. The double bond attack where the active nitrogen shows a preference for the double bond site and the complex formation in the absence of a double bond, are slightly different in their paths to products. Evans and Winkler (32) have discussed some of these reactions and advanced an explanation on the basis of the components in active nitrogen. The ethane reaction was found to be considerably slower than the ethylene reaction.

#### Phosphine:

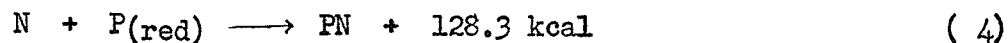
The reaction of nitrogen atoms with phosphine was studied by Wiles and Winkler (33). As it entered the active nitrogen stream phosphine extinguished the afterglow and a small, pale green reaction flame was observed. The main products of the reaction were hydrogen and an opaque, reddish brown polymer which formed on the walls of the reaction vessel. Chemical analysis showed that the polymer was the  $\alpha$  form of  $(PN)_n$ , phosphorus paranitride.

They concluded that the decomposition of one phosphine molecule required the consumption of two nitrogen atoms. On this basis they proposed the following mechanism:



where M is a third body.

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



is fast enough to maintain the concentration of phosphorus at a level too low for detection. Proof of reaction (4) was obtained by reacting active nitrogen with red phosphorus. Considerable  $(\text{PN})_n$  was formed.

In the reaction of hydrogen atoms with phosphine, Wiles and Winkler(34) found that red phosphorus and molecular hydrogen were the only products. It was postulated that hydrogen abstraction is followed by combination of  $\text{PH}_2$  radicals to give the products.



### Phosphorus

In 1936, Gopstein and Roginski (35) attempted to produce phosphorus atoms in a manner similar to the method used to produce active nitrogen. The experiments were conducted with a high voltage direct current discharge system with the entire apparatus at a high temperature. The attempt failed with the conclusion that the possibility of obtaining phosphorus atoms outside the discharge region was very slight if not impossible. They reported that as soon as the discharge was turned on large amounts of red phosphorus immediately began to form on the walls of the discharge tube. It was reported that phosphorus atoms recombine by way of collisions in the gas phase to give  $P_2$  which eventually gave red phosphorus by recombination on the walls. It is the extension of this study which comprises the subject matter of this investigation.

At temperatures above  $800^\circ\text{C}$ , phosphorus vapour, which is usually in the form of  $P_4$  molecules is measurably dissociated into  $P_2$  molecules. The  $P_2$  molecule has been studied extensively by spectrographic means (36). At temperatures below  $800^\circ\text{C}$  the degree of dissociation of the  $P_4$  vapour into  $P_2$  molecules is negligible being only a few percent dissociated at this temperature. The greater the pressure and temperature the greater was the  $P_2/P_4$  ratio.

Each of the major allotropic modifications of phosphorus exhibits more than one variety. There are two crystalline forms of white phosphorus, six varieties of red phosphorus and two black forms. It is

believed by some that only one liquid phosphorus modification exists since vapour pressure curves of white and red phosphorus appear to be different sections of the same straight line.

The reaction of solid white phosphorus with air or oxygen has been quite extensively investigated and the phenomenon has been shown to involve a branching chain mechanism. Oxygen or compressed air causes white phosphorus to emit a greenish glow which can be made to appear downstream from the phosphorus when the gas is blown over it. In addition to glowing, white phosphorus may also oxidize very rapidly and burn with a bright yellow flame which may extend for a considerable distance from the phosphorus surface from which it proceeds. Under most conditions, the main product of the reaction between phosphorus and gaseous oxygen is phosphorus pentoxide, although the tetroxide, trioxide and perhaps lower oxides can also be produced under the proper conditions (37).

White phosphorus changes to amorphous red phosphorus when heated in a closed system at moderately high temperatures. During the early part of the conversion process, the reaction mixture consists of particles of red phosphorus suspended in white phosphorus. Ultraviolet radiations accelerates the conversion of  $\alpha$ -white phosphorus to amorphous red phosphorus. Addition of iodine or sulphur to liquid white phosphorus also accelerates the conversion process.

### The Hydrides of Phosphorus

#### The PH Molecule:

Spectra taken of mixtures of phosphorus vapour and hydrogen at very high temperatures show the existence of a molecule, PH, which does not exist at room temperatures (38). The estimated value for the fundamental stretching frequency is  $\nu = 2380 \text{ cm}^{-1}$  and the force constant is  $3.25 \times 10^5 \text{ dynes/cm}$ . The P-H distance in this molecule has been found to be  $1.43 \text{ \AA}$  which corresponds to a single bond. This means that the molecule has the following structure  $\cdot\overset{\cdot}{\text{P}}\text{H}$ .

#### Phosphine:

The most common preparative method for phosphine involves treatment of alkaline earth metal phosphides or other highly reactive phosphides with water. From careful analysis of the infra red (39) and microwave spectra (40) it is known that all three hydrogens are equivalent with a P-H distance of  $1.419 \text{ \AA}$  and an H-P-H angle of  $93.7^\circ$ . The physical constants of phosphine indicate that there may be some association in the liquid (41) but that this association is probably small as compared to water or ammonia. Phosphine shows little or no evidence of hydrogen bonding (42).

The oxidation of phosphine is similar in many respects to the oxidation of white phosphorus. A cloud, which is luminous in the dark and conducts electricity, forms in phosphine-oxygen mixtures just before explosion occurs. This action is similar to the glow observed in the oxidation of phosphorus. The products obtained from the reaction

between phosphine and oxygen consist of the various oxyacids of phosphorus plus water.

#### The Lower Hydrides of Phosphorus:

Four lower hydrides of phosphorus of apparently definite composition have been prepared. One,  $P_2H_4$ , biphosphine, is a clear colorless liquid which has been characterized fairly well (43). The other three are yellow to red colored solids which have been represented by the empirical formulas  $P_2H$ ,  $P_9H_2$  and  $P_5H_2$  respectively. The yellow solid hydride  $P_2H$ , studied by Stock (44) is said to be formed in reactions yielding phosphine or biphosphine, or by thermally decomposing biphosphine. The substance,  $P_9H_2$ , a red solid, was first reported by Stock, who obtained it by the thermal decomposition of  $P_2H$  above  $100^\circ C$ . Hackspill (45) reported that a solid having the composition  $P_5H_2$  could be prepared by heating Stock's  $P_2H$  to  $80^\circ C$ .

#### Organic Phosphines:

There are a number of organic derivatives of phosphine in which one, two, or three of the hydrogen atoms on the phosphorus are replaced by alkyl or aryl groups. These organic phosphines can be prepared by a number of procedures and indeed Kosalopoff (46) lists more than twenty preparations.

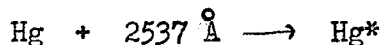
Generally speaking, the organic phosphines are all very reactive substances which possess the characteristic garlic-like odor of phosphine. All phosphines undergo oxidation, and react with sulphur and the halogens.

Although phosphine itself is not very basic the organic phosphines exhibit increasing basicity with increasing degree of substitution. Some organic derivatives of biphosphine are also known. A few of those which are discussed by Kosalopoff (47) are  $\text{Ph}_2\text{P}\cdot\text{PPh}_2$ ,  $\text{PhP}\cdot\text{POH}$  and  $\text{Me}_2\text{P}\cdot\text{PMe}_2$ .

### Methods of Producing Active Species

The simplest method of producing atoms is perhaps the thermal method. Thermal decompositions of many compounds proceed with the formation of atoms and radicals. For example by heating a metallic filament in the presence of hydrogen, Langmuir (48) produced atomic hydrogen.

Since atoms or radicals are involved in most photochemical reactions photolysis of compounds and elements such as the halogens and the hydrocarbons, produces free atoms and radicals. Some examples of radicals produced by photolysis are  $C_2H_3$ ,  $CH_3$ ,  $HS$ ,  $CH_3S$ ,  $CH_3O$ , and  $NOH$ . Flash photolysis has been used by Norrish and Porter (49) and Herzberg (50). Here gas-filled flash discharges of very high power are used. Using this method it has been possible to detect several free radicals in absorption spectra of the photolyzed gas. A substance which will absorb energy corresponding to some wavelength and then transfer this energy to the reactant which does not absorb at this wavelength is a photosensitizer and the reaction is a photosensitized reaction. An example of this is the mercury photosensitized reaction.



A corresponding system using thermal methods is effected by heating the reactant and a sensitizer to a temperature at which the reactant is stable but the sensitizer decomposes yielding atoms and radical which then initiate decomposition of the reactant.

There are two fundamentally different types of electrical discharge; the silent discharge and the disruptive discharge. The silent discharge includes a number of types, such as the ozonizer, semicorona, corona, glow and electrodeless discharge. The disruptive discharges, the arc and the spark are much more violent in nature. There is no doubt that the effects of these discharges are mainly thermal and correspond to a localized heating of the gas to 1500 ° C or higher (51).

More recently sonic and shock waves have been utilized in the production of atoms and radicals (52). The microwave generator is an example of a sonic discharge generator (53).

## EXPERIMENTAL

### Materials

Methane, ethylene, propane, propylene, and ammonia were obtained from the Matheson Company. The hydrocarbons and ammonia were simply given a trap to trap distillation, in which the first and last fractions were discarded, before they were introduced into the apparatus.

Hydrazine, white label grade, and methylene dichloride, certified spectrographically pure, were obtained from the Eastman Company and the Fischer Scientific Company respectively. The liquids were also given a trap to trap distillation in which only the middle fraction was kept as reactant.

Argon, 99.9% pure, was obtained from the Linde Corporation. Helium was supplied by the Matheson Company.

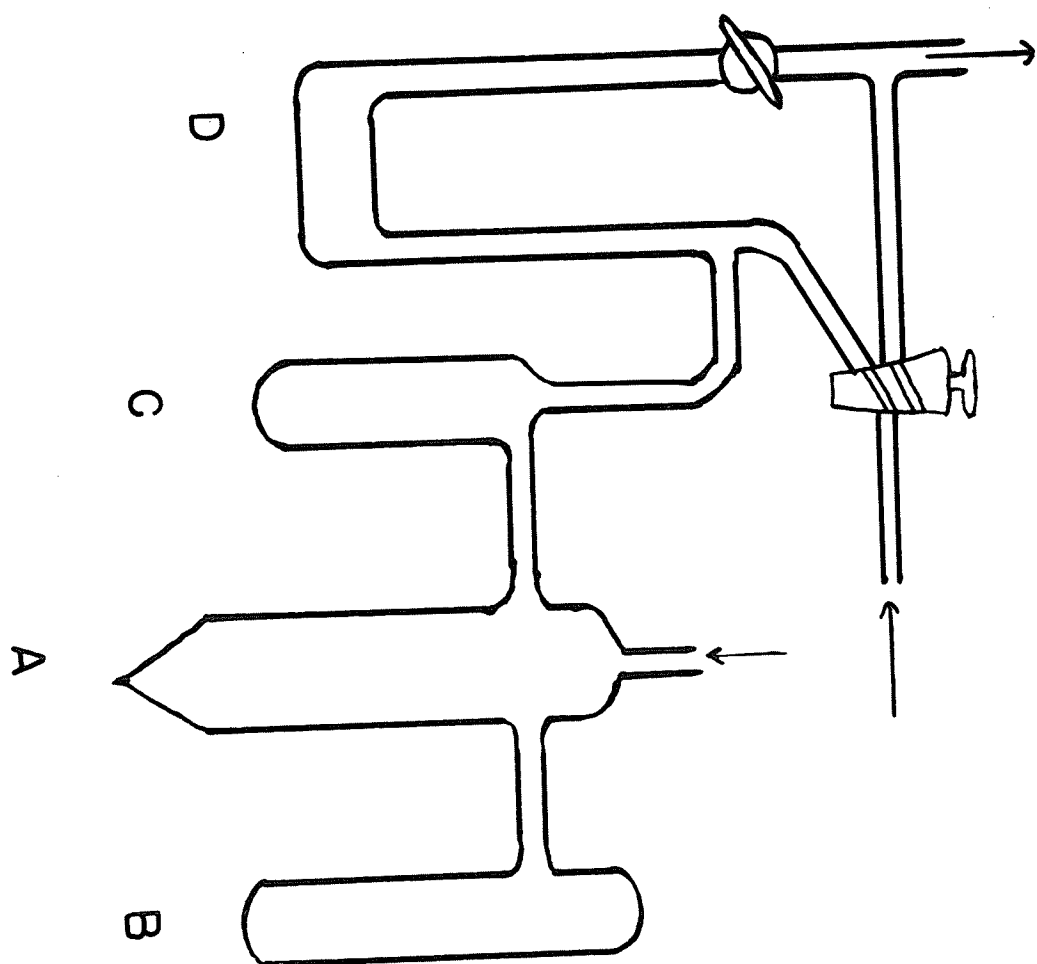
### Introduction of Phosphorus into the Apparatus

Phosphorus, N-F grade, obtained from the Fischer Company, was introduced into the apparatus by the following method. Molten phosphorus under hot water was allowed to flow into bulb A, Figure 1, with the aid of a separatory funnel. Care was taken that enough water to cover the phosphorus was allowed into the bulb in order to prevent oxidation of the phosphorus. The entry tube of A was then sealed off and with A at Dry



Figure 1

Diagram of Phosphorus Reservoir Apparatus



Ice-acetone temperature the apparatus was evacuated. The system was then shut off from the line and the water and about a third of the phosphorus was distilled into B using liquid nitrogen. B was then sealed off thus leaving essentially anhydrous phosphorus which was then distilled into bulb C. About a third of the original amount in A, which was then also sealed off from the line, was left in bulb A. The phosphorus was then distilled into reservoir D which was the phosphorus reservoir in the discharge line. C was then sealed off and removed from the apparatus.

#### Apparatus

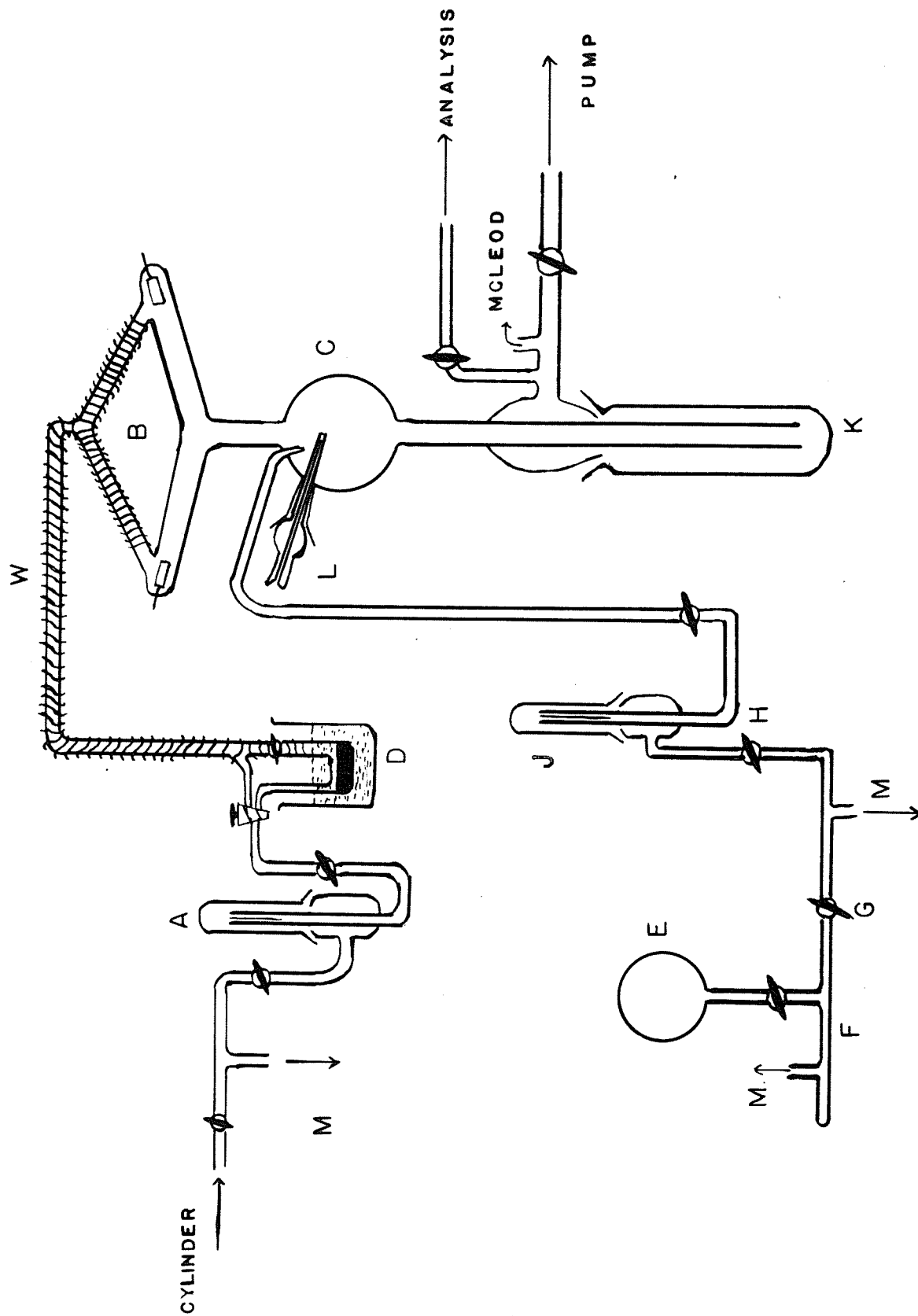
A diagram of the apparatus is shown in Figure 2. It was constructed entirely of Pyrex glass.

The argon from a cylinder was passed through a reducing valve into the line which was open to a manometer, M, placed before a flowmeter, A. The manometer was used to insure a constant pressure head in order that the flow of argon be as nearly constant as possible. From the flowmeter the argon was passed through a phosphorus reservoir, D, which was immersed in an oil bath equipped with stirrer, heater, and thermoregulator which enabled temperature control of the phosphorus reservoir.

The flow system for the reactant was such that a continuous range of constant flow rates could be obtained. It consisted of a calibrated volume F, adjoined to reservoir E, from which the reactant passed through a scratched stopcock G, into a ballast volume H, and then through flowmeter J. By keeping the pressure in the ballast volume constant during an experiment it was possible to maintain a constant rate of flow of

Figure 2

Diagram of Apparatus



reactant. The reactant flow was determined from the duration of the experiment and the volume of gas used, found from the change in pressure in the calibrated volume, with the use of the Ideal Gas Law.

The discharge tube, B, was of 22 mm. diameter tubing and 50 cm. long. A commercial nonex sealed cylindrical iron and tungsten electrode was sealed into each end. The argon and phosphorus vapour was introduced at each end of the tube below the electrodes so as to prevent formation of metallic phosphide on the electrode surface.

Several variations were used in order to lessen the possibility of electrode-phosphorus reactions and phosphorus-wall combinations. One modification successfully used was to seal the electrodes on to ground glass joints. This discharge tube was then able to be cleaned quite easily.

The discharge tube and reaction vessel, C, were connected by 15 cm. of 22 mm. tubing. The reaction chamber was a 500 ml. spherical bulb into which the reactant entered at the top through a small jet. A sheathed thermocouple, L, gave an indication of reaction temperature. The glass between the phosphorus reservoir, D, and the discharge tube was heated by asbestos covered chromel wire, W, to prevent any phosphorus from condensing. All condensible products of the reaction were frozen out in trap, K, which was cooled with liquid nitrogen.

The pumping system consisted of a Welch Duo-Seal vacuum pump, H-1402 B, which gave an ultimate vacuum of  $10^{-4}$  mm. of mercury and a pumping speed of 140 liters/min.

### Electrical Circuit

The active phosphorus was produced by a high voltage condensed discharge the circuit diagram of which is shown in Figure 3, and a Raytheon Mfg. Co. Microtherm (Model CMD 7) unit.

In the case of the microwave experiments the discharge tube and reaction bulb were replaced by a 40 cm. length of quartz tubing 16 mm. in diameter. The microwave director was then placed as close as possible to the quartz tube.

For the condensed discharge method the primary of a variac was connected to the secondary of a 110 V:220 V transformer. The secondary of the variac led to the primary of a second high voltage transformer. The output voltage across the transformer was thus capable of being varied from 0 to 4500 V. Two 866A mercury-filled rectifier tubes were used in parallel to rectify the current. The pulsating direct current from these tubes was used to charge a 4  $\mu$ f. capacitor through two 10,000 ohm resistors. A discharge occurred when the voltage on the condenser was sufficient to discharge through the spark gap and discharge tube. The rate of discharge was estimated to be 5 discharges per second.

### Analysis System

A diagram of the analysis system is given in Figure 4. An indication of the amount of product obtained in any reaction was given by the pressure in a calibrated volume, A, open to manometer, M. The products were analysed and separated with the use of a Leroy (54) still, B. The products were identified by comparison of the vapour pressure curves with

Figure 3.

Diagram of the Electrical Circuit



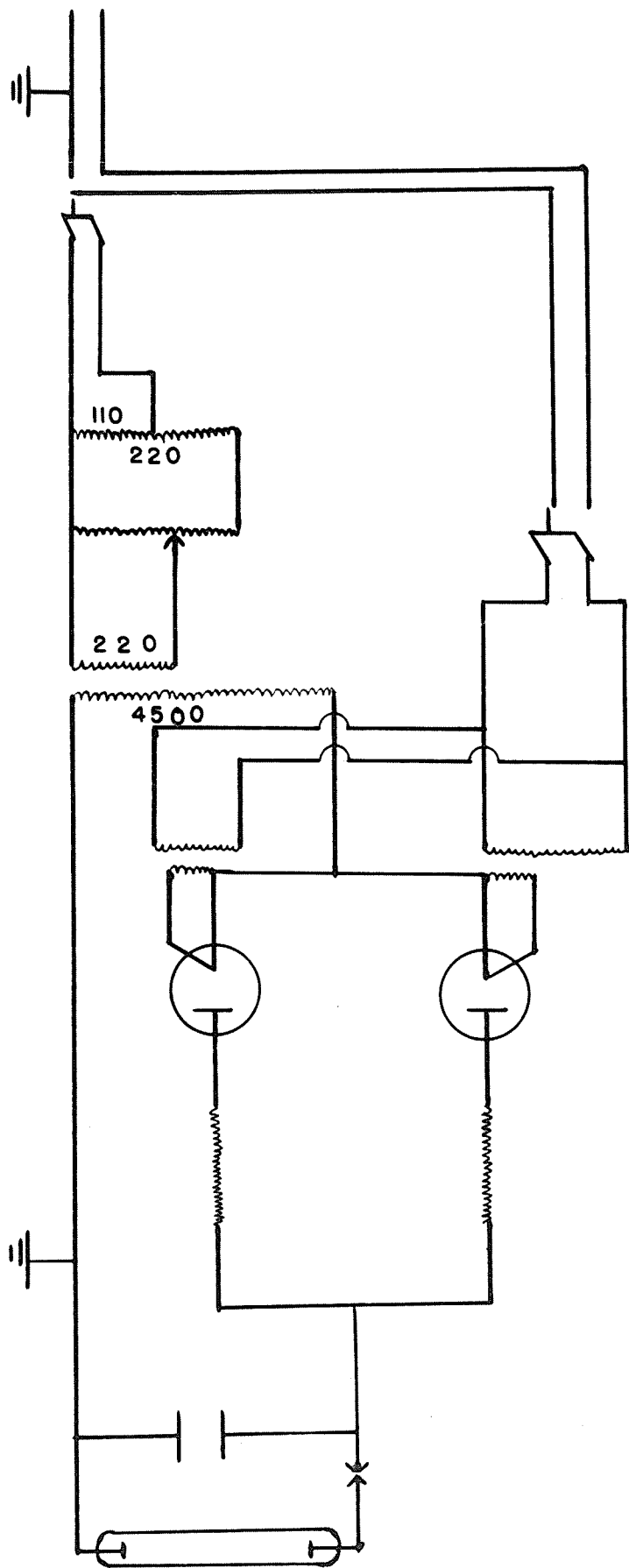
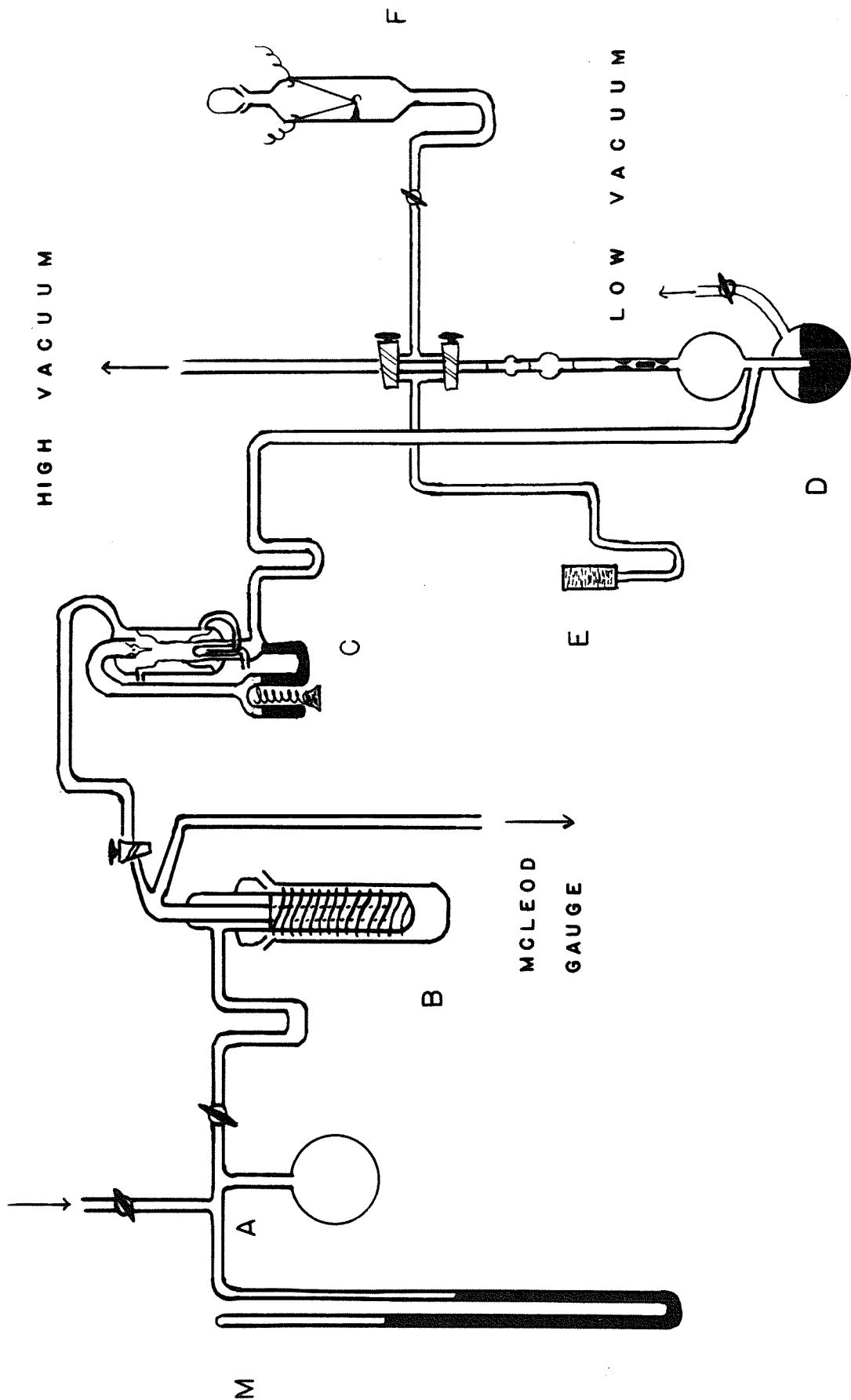


Figure 4

Diagram of Analysis System

REACTION CHAMBER



those for the various pure substances which were considered as possible products of the reaction. A mercury diffusion pump, C, aided the speed of separation. A calibrated gas buret and Toepler pump, O, was used in order to estimate relative amounts of products.

When sufficient product was obtained in any one fraction a Perkin Elmer, Model 21, infra red instrument was used for identification purposes. Vapour pressure versus temperature curves shown in Figure 5, were used for indicating the temperature at which good separation could be obtained.

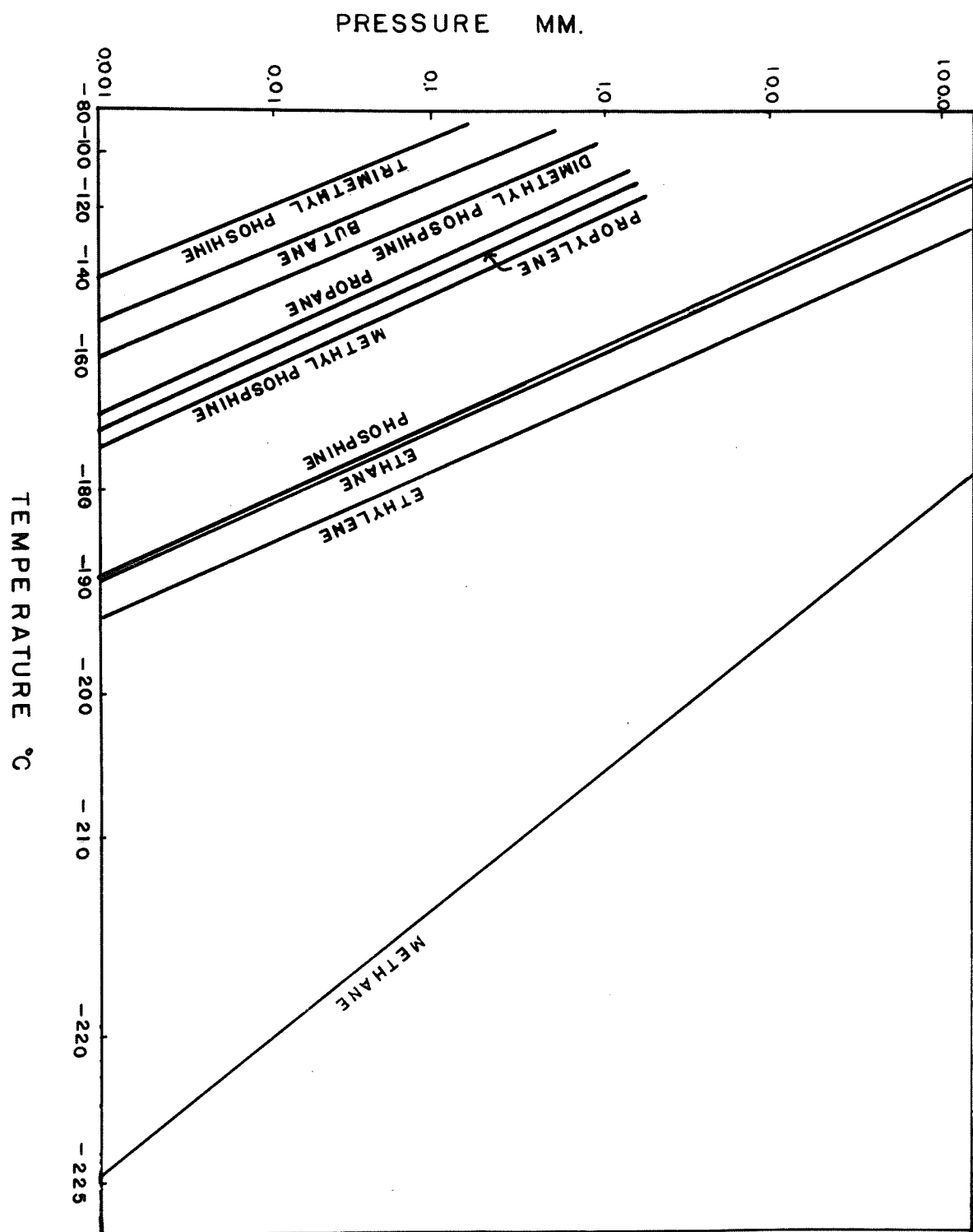
A copper oxide furnace, E, and a platinum wire combustion chamber, F, were used in order to obtain carbon content of some of the phosphorus compounds produced.

#### Procedure for Typical Experiment

Trap, K, was cooled to liquid nitrogen temperature and the system was evacuated to  $10^{-3}$  mm. The line to the argon cylinder was then opened to the pump to remove any air which may have leaked in by way of cylinder connections. The argon flow was then started and the discharge turned on to ensure that the electrical circuit was in order. The argon was then passed over the phosphorus in the reservoir which had previously attained the desired constant temperature, and then into the discharge. After a few minutes, the reactant was allowed to flow into the reaction vessel. The experiments were run for times varying from fifteen minutes to an hour.

Figure 5

Vapour Pressure versus Temperature Curve



In the case of the microwave discharge experiments the length of an individual experiment was governed by rate of deposition of red phosphorus in the glow region. When the tube was completely covered the discharge extinguished itself. Under the conditions of the experimental runs used this "cut-off" occurred about twenty minutes after the phosphorus flow was begun. This difficulty was not encountered in the condensed discharge method, and the length of an experiment was governed by the time needed to introduce sufficient reactant to form a volume of gas products which could be handled comfortably in the Leroy Still.

The products formed in the reaction and excess reactant were then removed from trap, K, and enclosed in a calibrated volume open to a manometer. In the case of methane as reactant, the products of the reaction were the only gases present in trap, K.

After expanding and condensing the gases several times, and pumping to  $10^{-4}$  mm. at liquid nitrogen temperatures the gases were analysed in the Leroy still. Separations were effected at temperatures which allowed efficient separation with a minimum of contaminants. From the still the pure fractions were pumped into calibrated volumes by a Toepler pump where their pressure, volume and temperature could be read. This data allowed the products formed to be estimated in moles and mole percent of total amount of products.

From the Toepler pump the gases were withdrawn into a Perkin Elmer infra red gas cell, or into a capillary fitted with ball joints which could be attached to a PYE argon gas chromatograph. The gases were also

withdrawn into gas storage tubes for wet reagent tests.

A copper oxide furnace and a platinum wire combustion chamber were placed at the exit of the Toepler pump in order that combustion experiments be easily undertaken. These were used in order to estimate carbon content of the various fractions taken from the Leroy still.



## RESULTS

Ethylene was the first reactant used in an attempt to prove the existence of a chemically reactive species of activated phosphorus. In view of the work with nitrogen atoms this seemed a logical starting point. A comparison between amount of reactant used with excess reactant and products indicated that a reaction had taken place. In one experiment, which lasted 4.5 minutes,  $6.78 \times 10^{-4}$  moles of ethylene were used and the amount of product and unreacted ethylene was  $4.36 \times 10^{-4}$  moles. Separation of excess ethylene left only trace amounts of gaseous product. Aqueous silver nitrate solution was blackened by the ethylene-product fraction. This suggested that phosphine was a product and since an ethylene-phosphine mixture cannot be separated by the Leroy still, it seemed that propylene might be a better reactant since propylene and phosphine can be separated by distillation.

In the experiments with propylene, four gaseous products were found. In one experiment, which lasted for sixty-five minutes,  $5.32 \times 10^{-4}$  moles of propylene were used and the amount of product and excess reactant was  $6.72 \times 10^{-4}$  moles of which  $5.07 \times 10^{-4}$  moles were excess propylene. Phosphine, proven by infra red spectrum analysis, amounted to approximately 60% of the total amount of product. The actual amount found was  $1.06 \times 10^{-4}$  moles. The infra red spectrum of the excess propylene showed absorption bands foreign to the propylene spectra. This pointed to the probable

existence of a product with a vapour pressure similar to that of propylene. The "extra bands", whose frequencies were between  $720\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$ , corresponded approximately to a carbon-phosphorus linkage. Thus, from these indications methyl phosphine can be postulated as a possible product. The third product,  $5.0 \times 10^{-6}$  moles, had vapour pressures corresponding to that of dimethylphosphine. Due to the small amount, however, an identification was not attempted. The final product had vapour pressures corresponding to a  $C_5$  hydrocarbon and comprised about 30%,  $5.1 \times 10^{-5}$  moles, of the total product. In a copper oxide combustion  $2.88 \times 10^{-5}$  moles of this product was combusted giving  $2.63 \times 10^{-5}$  moles of carbon dioxide and approximately  $1.2 \times 10^{-5}$  moles of water. This would indicate a phosphorus-hydrogen-carbon compound which contained at least one hydrogen and one carbon per molecule. However, one cannot place much faith in a combustion of a carbon-phosphorus compound since many oxy-acids form in combustions of compounds of this type (55). The amount of water is likely a lower limit of the true amount formed.

It was decided then to study the nature of the attack and to determine if the carbon-carbon double bond played any significant part in the mechanism as it does with nitrogen atoms. With this in view,  $C_3H_8$ , propane, was used as a reactant and phosphine was again obtained as a product. In the propylene experiment with the phosphorus reservoir temperature at  $25^\circ\text{C}$  and flow rate of propylene  $1.2 \times 10^{-5}$  moles/min.,  $1.63 \times 10^{-6}$  moles of phosphine were formed per minute and, in comparison,  $1.74 \times 10^{-6}$  moles/min. were formed, under the same conditions when propane was used as reactant. This then suggested that the carbon-carbon double bond played no especially important role in the production of phosphine under these

conditions. In view of this result methane was then chosen as a reactant since it is a non-condensable gas at liquid nitrogen temperatures and therefore unreacted methane would not mask any of the products.

For the experiments with methane as reactant argon was used as a carrier gas instead of helium which was used previously. It was found that with helium a 1% decomposition of hydrocarbon was obtained as a blank when phosphorus was absent. This presented the possibility of free radical hydrocarbons reacting with phosphorus. Generally the amount of reaction was of the order of 30 - 50% when based on total products produced. It would seem unlikely that the 1% decomposition of hydrocarbon could precipitate a reaction of this magnitude. With the aid of argon and a spark gap in the direct current discharge unit this decomposition was negligible. This is due to the less energized environment in the system: the metastable state of argon has an energy of 11.6 ev. as opposed to 19.7 ev. for helium.

An estimation of the phosphorus flow rate was also attempted. The phosphorus was swept into the liquid nitrogen trap by the argon for a known time. The phosphorus was then removed, oxidized to the pentoxide and estimated by the ammonium molybdate method. The value obtained when the flow rate of argon was  $50 \times 10^{-6}$  moles/sec. and a phosphorus reservoir temperature of  $27^{\circ} \text{C}$  was  $1.6 \times 10^{-8}$  moles/sec. This estimation is rather a hazardous operation due to the difficulty of working with phosphorus in air. The flow of argon was kept at about  $50 \times 10^{-6}$  moles/sec. for all experiments.

The data for the production of products from the methane-phosphorus reaction conducted with phosphorus reservoir temperature at 60° C is shown in Table I and is plotted in Figure 6 as a function of the flow rate of methane.

A microwave generator was then tried in the hope that experiments could be run for longer times thereby obtaining more products. However it was found that the opposite occurred. The efficiency is greatly decreased as compared to the condensed discharge. For example, the amount of phosphine produced from methane in a microwave experiment with the phosphorus reservoir temperature at 60° C was just a trace as compared to the  $10^{-4}$  moles produced in a condensed discharge experiment. However the same products were obtained using both methods.

Using the condensed discharge and a new discharge tube along with a phosphorus reservoir temperature of 80° C, slightly different results were obtained. The data for the production of products from the methane-phosphorus reaction conducted with phosphorous reservoir temperature at 80° C is shown in Table II.

In Experiment 34 with the new discharge tube,  $2.5 \times 10^{-5}$  moles of phosphine,  $6 \times 10^{-6}$  moles of methylphosphine and a small amount of liquid were produced. The methyl phosphine was identified by its vapour pressure, odor, and spontaneous combustibility in air. The liquid was soluble in acid and gave a black precipitate with silver nitrate which when dissolved in nitric acid gave a phosphate test with ammonium molybdate.

No consistent results were obtained by combustion of the liquid in a copper oxide furnace. This is due undoubtedly to the fact that phos-

TABLE I

The Yields of Products from the Reaction of Active Phosphorus with Methane

Temperature of Phosphorus Reservoir = 60° C

Experiment Number	Reaction Time	Flow of Methane	<u>Moles/Min. x 10<sup>6</sup></u>		
			$\text{PH}_3 + \text{C}_2\text{H}_6$	$\text{CH}_3\text{PH}_2$	$\text{CH}_3\text{PH}\cdot\text{PHCH}_3$
24	50.0 Min.	1.33	.86	.084	.20
23	50.0 "	2.34	.81	.37	.46
41	15.5 "	6.80	1.30	.37	.80
27	21.0 "	11.00	2.00	.14	.77
26	21.0 "	12.30	2.40	.12	1.18

Figure 6

Yields of Products with  
Phosphorus Reservoir Temperature at 60° C

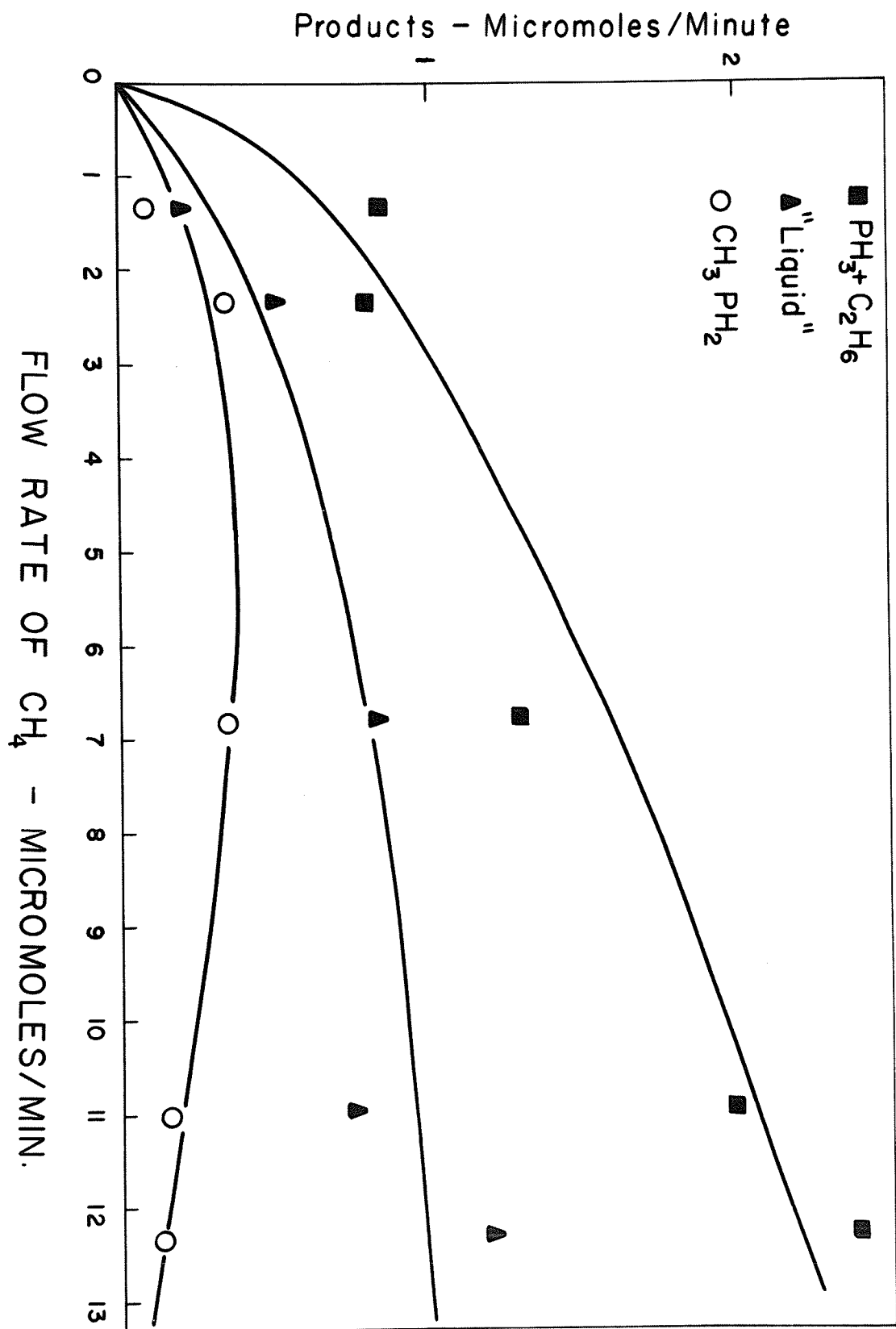


TABLE II

The Rate of Production of Products from the Reaction of Phosphorus with Methane  
at High Phosphorus Reservoir Temperatures

Experiment Number	Reaction Time	Temperature	Flow of Methane	$\text{PH}_3 + \text{C}_2\text{H}_6$	$\text{CH}_3\text{PH}_2$	Liquid
			<u>Moles/Min. x 10<sup>6</sup></u>			
34	26.5 Min.	80° C	15	.94	.22	.5 cc.
35	27.5 "	80° C	15	.57	1.12	.05 cc.
40	30 "	65° C	9	.31	.04	.1 cc.



phine and all its organic derivatives behave abnormally in oxidation reactions. Carbon dioxide was not found among the products of combustion. Washings of the combustion chamber gave a phosphate test thus showing that phosphorus pentoxide was formed in the combustion. The compound had a melting point of about  $-10^{\circ}\text{C}$  and a molecular weight (one determination by weight) of 44 grams/mole. The infra red spectrum showed absorption which might be explained by an acetylene linkage. Only one band at  $3200\text{ cm}^{-1}$  was shown on the spectrum. From this information the analogue to hydrogen cyanide is indicated, however a great deal more evidence is required to prove this. A nuclear magnetic resonance spectrum was suggested as a method of proving the existence of a compound of the type  $\text{H-C}\equiv\text{P}$  but not enough of this compound could be produced in order to do this.

The subsequent experiment, Experiment 35, gave similar results but much less liquid was produced. The discharge tube was by then well coated with a red brown deposit. The violet reaction flame, visible in the reaction vessel for the first experiment in the clean discharge tube was no longer visible because the walls had become quite covered with a reddish-brown non-volatile material. The next experiment produced no liquid product. A new discharge tube was then employed and again liquid was obtained as a product for the first experiment. It therefore seemed that the condition of the walls played an important part in the reaction mechanism. Different products might well be produced with varying degrees of wall contamination.

The experiments at  $80^{\circ}\text{C}$  proved to add to the difficulties of this

work as the amount of phosphorus brought into the discharge was quite large. This concentration undoubtedly affected both the state and amount of activated phosphorus.

For an experiment with the phosphorus reservoir at 80° C the volatile products were passed through a gas chromatographic column in order to determine the number of products in the methane-phosphorus reaction. The phosphine fraction showed that two substances were present. Oxidation of this fraction yielded carbon dioxide thus confirming the presence of ethane as a product. The amount of ethane was about 2% - 6% by volume of the phosphine fraction.

Methyl phosphine, distilled at -150° C gave only one peak thus indicating a pure substance. The third fraction, which contained all the remaining volatile products, indicated that at least two and possibly three individual substances were present.

In an attempt to produce enough products for positive identification both methane and phosphorus were passed through the discharge with argon as a carrier gas. Under these circumstances phosphine was still the major product but considerably more product was obtained. The phosphorus reservoir temperature was kept at 25° C and the methane flow rate was approximately  $3 \times 10^{-5}$  moles/min. Relative amounts of product obtained in a five-hour experiment were

(1) Phosphine	$19.5 \times 10^{-4}$ moles
(2) Methylphosphine	$4.16 \times 10^{-5}$ moles

- |   |                             |
|---|-----------------------------|
| (3) Product corresponding to vapour pressure of dimethyl phosphine          | $3.5 \times 10^{-5}$ moles  |
| (4) Unknown product with vapour pressure of $10^{-3}$ mm at $-90^{\circ}$ C | $4.87 \times 10^{-5}$ moles |

An infra red absorption spectrum of product (3) supported the possibility that dimethyl phosphine was a product. The spectrum of the unknown product exhibited methyl groups and methyl-phosphorus bonds along with phosphorus-hydrogen bonds. From this and vapour pressure considerations the product may be explained on the basis of a hydrazine type structure;  $\text{CH}_3\text{PH}\cdot\text{PHCH}_3$ . This product is identical, by vapour pressure, with the unknown product obtained in the phosphorus-methane reaction conducted with the temperature of the phosphorus reservoir at  $60^{\circ}$  C. It is not identical with the liquid product obtained from the experiments where the temperature of the phosphorus reservoir was  $80^{\circ}$  C.

In the reaction of active phosphorus with acetylene the only volatile product was again phosphine. This reaction produced a blue reaction flame unlike the violet one observed with most other hydrocarbon-phosphorus reactions. The temperature of the phosphorus reservoir was  $25^{\circ}$  C, the flow rate of acetylene was  $1.0 \times 10^{-5}$  moles/min., and the phosphine was produced at the rate of  $2 \times 10^{-7}$  moles/min. When methylene chloride was used as reactant at a flow rate of  $9 \times 10^{-6}$  moles/min.,  $1.5 \times 10^{-7}$  moles of phosphine were produced per minute of reaction.

The next reactant gas used was ammonia. This was done with the view of finding a parallel to the active nitrogen-phosphine reaction. As before, phosphine was produced along with a less volatile product. In this system ammonia seemed to be absorbed by the wall contaminants.

When ammonia was simply passed through the reaction vessel and then measured in the analytical line more than half seemed to "disappear". When the experiments were conducted in a clean-walled apparatus a considerable amount of solid was seen to deposit in the reaction vessel. With the phosphorus reservoir at 70° C and flow rate of ammonia at  $1.9 \times 10^{-5}$  moles/min., phosphine was produced at  $2 \times 10^{-7}$  moles/min. and the other volatile product was formed at  $7 \times 10^{-7}$  moles/min. However, the volatile products accounted for only about 10% of the reacted ammonia. It would seem likely then that the solid produced would be either a (PN) polymer similar to that reported in the nitrogen-phosphine reaction or the (PN) polymer which results when ammonia and white phosphorus are mixed in a discharge. A positive identification of this was hindered by the large amounts of red phosphorus and solid phosphorus hydrides which also deposit on the walls. No identification was attempted on the trace amounts of low volatile products but from vapour pressure considerations a compound of the type  $\text{H}_2\text{P-NH}_2$  does not seem unlikely.

In the reaction of phosphorus and hydrazine only phosphine and ammonia were obtained as volatile products;  $4.4 \times 10^{-6}$  moles of phosphine were formed as against  $5.65 \times 10^{-5}$  moles of ammonia. From the relatively large amount of ammonia found one would have doubts as to whether the ammonia was formed as a result of a reaction with phosphorus or as a result of decomposition in the activated argon stream.

## DISCUSSION

The original purpose of this work was to determine if a system of active phosphorus reactions analogous to the active nitrogen reactions existed and if it did, to identify what seemed to be the major products. Since the system was so arranged that the hydrocarbon did not undergo initial decomposition and that white phosphorus itself did not react with the hydrocarbon it seems that the reactions were indeed due to some activated form of phosphorus. The products obtained, however, were not directly analogous to the nitrogen system and for the most part were either unknown or poorly characterized.

In view of the fast nitrogen reaction with ethylene and propylene these gases were chosen as our first reactants. When separation difficulties presented themselves with ethylene, propylene was used. After it was proved that phosphine was a product of the reaction it seemed to be advantageous to use propane in order to determine the role of the double bond in the reaction mechanism. The rate of formation of phosphine from propane was found to be somewhat greater than that from propylene at similar flow rate of reactant gas. This indicates that the double bond has little or no influence on the reaction mechanism and that the rate of production of phosphine may be dependent on the number of hydrogen atoms in the reactant molecule. The rate of production of phosphine from

methane and acetylene in experiments done under identical conditions (i.e. flow rate of reactant and phosphorus reservoir temperature identical) was  $8.3 \times 10^{-7}$  moles/min. and  $2 \times 10^{-7}$  moles/min. respectively. This of course supports the supposition that the rate of production of phosphine is dependent to some degree on the number of hydrogen atoms in the reactant molecule.

The methane experiments bring to light at least two more factors which influence the rate of production of phosphine. Firstly, considering the temperature of the phosphorus reservoir which is an indirect measure of the phosphorus concentration in the argon stream it is observed that, under similar conditions of flow rate of methane etc., the production of phosphine with phosphorus reservoir temperatures at  $25^{\circ}\text{C}$  and at  $65^{\circ}\text{C}$  is quite nearly the same being of the order of  $8.3 \times 10^{-7}$  moles/min. On successive experiments with identical conditions with the phosphorus reservoir at  $80^{\circ}\text{C}$ , the rate of production of phosphine varied considerably. The results given in Table II lead to the conclusion that the concentration of the phosphorus in the argon stream certainly plays a part in the reaction. Since the only difference in the experiments mentioned in Table II was that the extent of wall deposits ranged from none at the beginning of the first experiment of the series to a great deal for the second and third, one must also recognize the complications of wall reactions. It is possible that with an increase in concentration these wall reactions and effects become more prevalent and so reduce the amount of activated phosphorus available for reaction with the reactant gases. It is also possible that with the different degrees of concentration different degrees

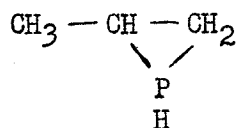
of activation will be attained. In any case it is evident that temperature and therefore concentration, and wall reactions influence the rate of production of phosphine. This may be explained in part by the fact that with increase in concentration of  $P_4$  the probability for the reaction,  $P + P_4 \longrightarrow P_{red} \text{ (wall)}$ , increases. This reaction would account for the apparently reduced concentration of active phosphorus at higher phosphorus concentrations.

From the results given in Table I it is evident that kinetic studies of active phosphorus reactions with hydrocarbons are possible. In plotting rate of production of products versus flow rate of methane, graphs of the same general shape as obtained in nitrogen studies are the result. Interpretation of these plots in the manner used in nitrogen discussions is of course possible but this requires a definite knowledge of all main products. This will be discussed shortly.

The secondary objective, that is the identification of the products, did not enjoy total success. The products of high volatility, such as phosphine, ethane, methyl phosphine, and dimethylphosphine were identified with relative certainty. However, it was the products of low volatility that presented difficulties. In all there were four of these; two produced in methane reactions and one each from propylene and ammonia. The product obtained in the ammonia reaction exhibited a vapour pressure between that of biphosphine and hydrazine. Since the only volatile products that one could obtain in this system are hydrides, a mixed hydride would seem a reasonable product. Therefore a structure of the type  $PH_2 \cdot NH_2$  might conceivably be the answer, however, not enough of this substance was produced

to be able to identify it with certainty.

The same was true of the product, which is just volatile at  $-120^{\circ}\text{C}$ , obtained in the reaction of propylene and phosphorus. Again very little was obtained and copper oxide combustion showed the presence of one carbon and one hydrogen per molecule. In view of the fact that combustions of phosphorus compounds give a variety of oxides this result is undoubtedly not entirely correct. If we assume that PH radicals are formed a compound of the imine type would seem reasonable. Therefore the propylene-phosphorus compound may have the structure



Compounds of the type  $\text{CH}_2=\text{CH}-\text{CH}_2\text{PH}_2$  may also form but these would be much more difficult to account for with the use of PH radicals.

In the methane reaction with the phosphorus reservoir temperature at  $80^{\circ}\text{C}$  the liquid which formed was not identical to the product which was volatile at  $-90^{\circ}\text{C}$ , formed in all other methane reactions. After the walls became contaminated the liquid was no longer produced and the product of slightly higher volatility was produced. This latter product, as discussed in the results may be explained by a structure of the type  $\text{CH}_3-\text{PH}-\text{PH}-\text{CH}_3$ . This again is not a positive identification but a probable indication of the structure of the compound.

The liquid product showed as odd behaviour as were the conditions of formation. It is slightly less volatile than the other product mentioned above and slightly more volatile than water. From the evidence



discussed in the results a compound of the type H-C P is indicated but is far from a certainty. It is without a doubt the most peculiar and interesting compound found among the products of the reactions studied.

### The Mechanism

Since phosphine was found as a product in all cases a hydrogen abstraction by some activated form of phosphorus is undoubtedly the first step in any reaction mechanism one might propose. In the case of methane a reaction of the form

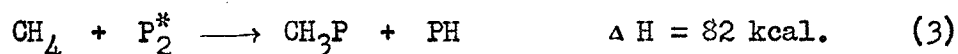


must occur, assuming that the active phosphorus is atomic phosphorus. The bond dissociation energy  $D(\text{CH}_3\text{-H})$  has a value of 103 kcal. as compared to about 77 kcal. for the  $E(\text{P-H})$  (56). Winkler (34), estimates the value for  $D(\text{P-H})$  bond at 72 kcal. The energy necessary for  $\text{CH}_4$  and P to react so the C-H bond would be broken and a P-H bond would be formed is at least the endothermic heat of reaction. Therefore 26 kcal., or using Winkler's value, 31 kcal. would be an approximate value for the activation energy of the proposed reaction. A reaction with such a high activation energy would not normally proceed with measureable speed at room temperature. To explain the occurrence of the above reaction we must therefore consider excited atoms. The phosphorus atom in the first excited state  $^2\text{D}$ , has an energy in excess of the ground state of  $\approx 32.5$  kcal. (57). Therefore excited phosphorus atoms may very well be the reactive species since it has more than the necessary energy requirements for the reaction to proceed. Therefore equation (1) can now be written



The exothermicity of reaction (2) would permit a very low activation energy for the reaction and would also account for the fact that the rate of formation of phosphine is somewhat dependent on the availability of hydrogen in the reactant.

Diatomic phosphorus molecules may also react with methane to form PH radicals.



Here  $D(\text{P}=\text{P})$  which has a value of 116.7 kcal. must be broken along with a  $D(\text{CH}_3-\text{H})$  bond of 103 kcal. to form a  $E(\text{P}-\text{H})$  bond of  $\approx 77$  kcal. and a  $E(\text{CH}_3-\text{P})$  bond which has a value of the order of 63 kcal. (58). Here then the difference in bond dissociation energies between the reactants and products is of the order of 82 kcal., or using Winkler's value for  $D(\text{P}-\text{H})$ , 87 kcal. Again, such a reaction would have activation energy of at least 82 kcal. and would not proceed with measureable rate at low temperatures. However metastable  $\text{P}_2^*$  molecules have energies in excess of the ground state of 90 kcal. or greater (59). Hence the reaction



is possible.

Reactions (2) and (5) would proceed with evolution of heat since there is a slight energy excess in the activated states of phosphorus considered. Experimentally, temperatures in the reaction zone were slightly ( $5^\circ \text{C}$ ) above room temperature. This slight increase in temperature may be taken as an indication of heat of reaction as well as the

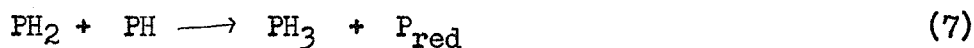
heat liberated by the recombination of phosphorus atoms and radicals.

It would seem necessary that excited atoms and molecules be the reactive species, and it seems unlikely that only one activated species is obtained. However, in view of the results, the various excited species must initiate similar reactions or perhaps one activated form of phosphorus is predominant thus allowing the formation of P-H radicals to be the predominant reaction.

Assuming the formation of (P-H) radicals the production of the phosphorus hydrides is then readily explained by disproportionation reactions having the end result



One possible sequence is :



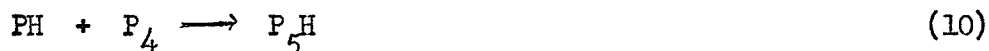
According to Winkler (34) the reaction



occurs in the atomic hydrogen-phosphine reaction. Reaction (8) is more exothermic than reaction (6) which is just a hydrogen exchange and is therefore more likely to occur than (6). Then



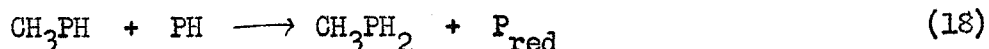
would be the sequence necessary for the formation of phosphine. The solid hydrides would be the result of reactions of the type :



The existence of ethane as a product confirms the existence of methyl radicals. Then



are reactions which may occur. Similarly,



are also possible.

Striking differences are at once evident between the reactions of active nitrogen and active phosphorus with hydrocarbons. Active nitrogen reactions with hydrocarbons invariably give hydrogen cyanide as a major product, whereas in the case of active phosphorus reactions phosphine is the major gaseous product. In the case of the nitrogen the active species are acknowledged to be ground state nitrogen atoms and excited nitrogen molecules. However, neither of these appear to take the course of hydrogen abstraction which the phosphorus active species must. If one could get similar active states of phosphorus and nitrogen one might then obtain analogous products. For example, if we assume that the  $^2\text{D}$  state of the phosphorus atom is the reactive species giving reaction (2) then the  $^2\text{D}$

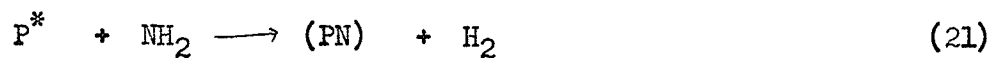
state of the nitrogen atom might be expected to give this type of reaction yielding N-H radicals. The  $^2D$  state has been found to exist in active nitrogen by spectroscopic methods. It comprises only about 1% of the active form, however, and one would need a greater percentage than this in order to detect a reaction different from the general one which gives hydrogen cyanide. Considering the phosphorus experiments a method for doing this presents itself. All one need do is work with low concentrations of nitrogen in an excited atmosphere of helium or argon. This would lessen the probability that atoms would lose their energies by mutual collisions and enhance the possibility of obtaining the atoms in excited states. This then would be analogous to the observed concentration effects in the phosphorus reactions. Having obtained the  $^2D$  atom of nitrogen in a relatively large percentage of the active constituent one might then expect ammonia and its derivatives as products. This is indicated by the very recent experiments of Dewhurst (60) who found small amounts of ammonia as product along with hydrogen cyanide in the active nitrogen reactions with primary amines, neopentane and hexane.

If one now considers the reactions of active nitrogen and phosphine and active phosphorus and ammonia, differences are once again evident. In the active nitrogen-phosphine reaction, (PN) polymer with red phosphorus, hydrogen and nitrogen were reported as products. For the active phosphorus-ammonia reaction, phosphine, quite likely hydrazine and possibly some mixed phosphorus-nitrogen hydrides were formed.

The analogue to equation (2) must occur thus



and



may also occur. Mixed hydrides might form from the reaction



Now if the nitrogen reactive species had the same order of reactive power one could then easily imagine an identical scheme with the role of phosphorus and nitrogen interchanged.

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