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ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE RESEARCH BRANCH, DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY]

Synthesis of Phosphorus Nitrides[1]

BY E. O. HUFFMAN, GRADY TARBUTTON, KELLY L. ELMORE, W. E. CATE, H. K. WALTERS, JR., AND G. V. ELMORE

RECEIVED JULY 12, 1954

The measured concentration of phosphorus mononitride vapor in equilibrium with an equiatomic mixture of phosphorus and nitrogen at 900°, together with the value 9.756 e.v. for the dissociation energy of nitrogen, leads to a value of 7.1 ± 0.05 e.v. for the dissociation energy of phosphorus mononitride. The calculated equilibrium constants range from 1×10^{-2} at 900° to 2×10^{-1} at 2000°. The apparent energy of activation for the homogeneous synthesis is about 31 kcal. per mole of PN. The observed rates of synthesis in the presence of tungsten (hot-wire method) show that the reaction at temperatures above 1800° is catalyzed by tungsten and is $^1/_2$-order with respect to concentration of P_2. The activation energy is 59 kcal. The formation of phosphorus atoms at the tungsten surface is advanced as the rate-controlling step in the synthesis mechanism.

The synthesis of phosphorus nitrides directly from the elements in the presence of a heated tungsten filament or an electrical discharge was reported by several investigators.[2-5] When Moureu and Wetroff[5] brought a gaseous mixture of phosphorus and nitrogen into contact with a tungsten filament at 1500 to 1800°, solid phosphorus nitride condensed on an adjacent glass wall at 500°. Since phosphorus vapor is predominantly in the diatomic form at 1500 to 1800°, they concluded that the process could be represented by the equilibria

$$nP_2(g) + nN_2(g) \rightleftharpoons 2nPN(g) \rightleftharpoons 2(PN)_n(s) \qquad (1)$$

Moureu and co-workers[6] later reported that phosphorus mononitride vapor (PN) heated at 800° "completely decomposes into its elements."

Equilibrium constants for the reaction

$$P_2(g) + N_2(g) = 2PN(g) \qquad (2)$$

as calculated by McCallum and Leifer,[7] indicated that the equilibrium is favorable for the synthesis in the temperature range 800 to 1000°. McCallum and Leifer observed that a difference of a few tenths of an electron volt in the dissociation energy of phosphorus mononitride could account for the inconsistency of their calculation with the experimental[6] results. Gaydon[8] concluded that the dissociation energy of phosphorus mononitride is not known more precisely than 6.0 ± 0.8 e.v.

Perhaps an even greater uncertainty clouded the dissociation energy of nitrogen until Douglas[9] recently reported measurements from which he concluded that the spectroscopic evidence strongly supports the value 9.756 e.v. Herzberg[10] agrees.

To aid in an evaluation of phosphorus nitrides as potential intermediates in the production of fertilizers, the controlling factors in the phosphorus–nitrogen reactions were studied in the laboratory. This paper describes a measurement of the concentration of phosphorus mononitride vapor in equilibrium with an equiatomic mixture of phosphorus and nitrogen at 900°, measurements of the rate of decomposition of phosphorus mononitride vapor, and a kinetic study of the synthesis of phosphorus nitrides from the elements in the presence of tungsten. A new value is given for the dissociation energy of PN.

Equilibrium Concentration of PN at 900°.—Respective sealed quartz tubes containing equiatomic mixtures of nitrogen and phosphorus were heated at 900° for 42 hours and at 950° for 44 hours. The tubes were quenched to 500° in about one minute. Although phosphorus nitrides will condense to the solid state at 500°, neither of the condensed products contained a significant amount of fixed nitrogen. This result indicated either that the equilibrium concentration of phosphorus mononitride is negligible at 900 to 950° or that the condensed products did not represent the equilibrium composition, possibly because of an inadequate rate of quenching.

The composition of the gas at equilibrium was evaluated *at the equilibrium temperature* by a static method in a quartz apparatus. The method was based upon a pressure–composition relation, and pressures were measured with a contact-making Bourdon gage as a null-point instrument. The volume of the apparatus, 288 ml., was determined with mercury.

The starting material was a laboratory preparation of phosphorus nitride containing 67.60% P, 31.36% N and 0.32% acid-insoluble material. It was degassed thoroughly at the beginning of each experiment. Three equilibria were involved.

$$(PN)_n(s) = nPN(g) \qquad (3)$$

$$2PN(g) = P_2(g) + N_2(g) \qquad (2)$$

$$P_4(g) = 2P_2(g) \qquad (4)$$

In a preliminary experiment, the phosphorus mononitride was vaporized into the system at 900° to a pressure of 391 mm. The capillary connecting the vaporizer to the equilibration flask was sealed, and the pressure was measured at intervals for 5 hours. A constancy of pressure showed that the vapor reached equilibrium forthwith. After the gas was pumped from the system at the end of the experiment, a check of the gage constant showed that it had drifted < 1 mm.

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[1] Presented before the Southwide Chemical Conference, October 1951, at Wilson Dam, Ala. Article not copyrighted.

[2] R. J. Strutt, *Proc. Roy. Soc. (London)*, **A85**, 219 (1911).

[3] V. Kohlschütter and A. Frumkin, *Z. Elektrochem.*, **20**, 110 (1914).

[4] W. Moldenhauer and H. Dörsam, *Ber.*, **59B**, 926 (1926).

[5] H. Moureu and G. Wetroff, *Compt. rend.*, **207**, 915 (1938).

[6] H. Moureu, B. Rosen and G. Wetroff, *ibid.*, **209**, 207 (1939).

[7] K. J. McCallum and E. Leifer, *J. Chem. Phys.*, **8**, 505 (1940).

[8] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 212.

[9] A. E. Douglas, *Can. J. Phys.*, **30**, 302 (1952).

[10] G. Herzberg, letter, November 12, 1952.

A 0.1353-g. charge of the phosphorus mononitride then was vaporized in the apparatus at a nominal temperature of 900°, and the vaporizer was again sealed off. Temperatures measured along the vertical axis of the equilibration flask were 900 ± 3°. The temperature range of the vapor was well within the limits 900 ± 5°. The second column of Table I shows the pressure that the charge of nitride would have developed in this range of temperature had the vapor consisted entirely of PN molecules. The third column shows the pressure corresponding to complete dissociation of the nitride into P_4, P_2 and N_2 molecules.

TABLE I

EQUILIBRIUM CONCENTRATION OF PN AT 900 ± 5° AS FOUND BY STATIC METHOD

Temp., °C.	Theor. pressure, mm., for vapor in combination shown PN	P_4, P_2 and N_2	Concn. of PN, % by vol.[a]
895	757	578.5	2.6
900	760	581	
905	763	583.5	1.7

[a] Calculated on basis of 593.5 mm. pressure.

The observed pressure was 591 mm. after 95 hours, 593 mm. after 110 hours and 593.5 mm. after 120 hours. A comparison of the final pressure with the pressures in Table I shows that dissociation of the mononitride was incomplete. The last column of Table I indicates the extent of the dissociation. Had the dissociation been complete, the measured pressure of 593.5 mm. would have required an average temperature of 925°. The average was not this high. It is concluded, therefore, that the equilibrium concentration of phosphorus mononitride vapor at 900° and 0.7 to 1 atmosphere is within the limits 1 to 3%.

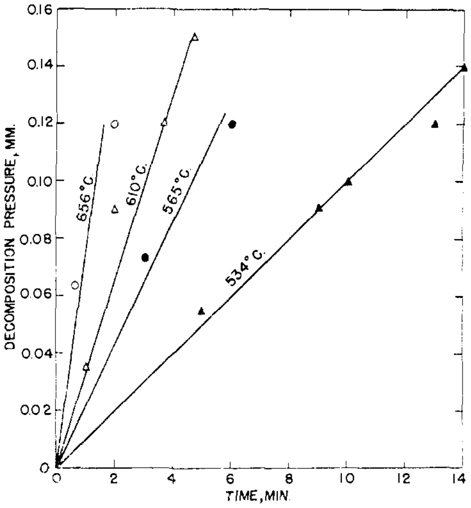

Fig. 1.—Rate of decomposition of PN vapor.

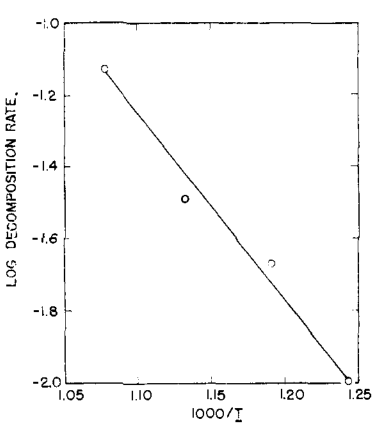

Fig. 2.—Effect of temperature on the rate of decomposition of PN vapor.

This approximate experimental value for the equilibrium concentration of PN at 900°, along with fundamental constants for phosphorus,[11-15] phosphorus mononitride,[16] and nitrogen,[9,17] leads to 7.1 ± 0.05 e.v. for the dissociation energy of PN—a value 0.3 e.v. higher than the highest value previously considered probable.[8] The values D_0 PN (g) = 7.1 e.v. and D_0 N_2(g) = 9.756 e.v. lead to equilibrium constants, $K_{\text{atm.}}$, ranging from 1×10^{-2} at 900° to 2×10^{-1} at 2000°, and an average ΔH of 14.2 kcal. for the homogeneous synthesis according to equation 2.

Rate of Decomposition of PN Vapor.—Although phosphorus mononitride vapor decomposes rapidly and almost completely at 900°, the nitride can be distilled in a vacuum at lower temperatures with only partial decomposition. Measurement of the rate of decomposition of the vapor therefore was possible.

Solid phosphorus mononitride was placed in a porcelain tube that was sealed to a vacuum system containing a cold trap and a McLeod gage. The trap was cooled with solid carbon dioxide in acetone to collect elemental phosphorus resulting from the decomposition. The nitride was degassed for several hours at 400° and a pressure of 1×10^{-5} mm. The rate of decomposition at a given temperature then was measured by closing the system from the pump and reading the McLeod gage at intervals. The system was exhausted again, and similar measurements were made at another temperature. The weight ratio of solid to vapor was so large that the surface area of the solid was not a significant variable.

The rates of decomposition at four temperatures are plotted in Fig. 1, and the logarithms of the rates are plotted against $1/T$ in Fig. 2. The slope of the line in Fig. 2 indicates that the activation energy for the decomposition is 24 kcal. per mole. When the energy of activation for the synthesis process is approximated by adding the ΔH for the synthesis reaction—7 kcal. per mole—to the activation energy of decomposition, the result is 31 kcal. per mole of PN. Upon assumption that the reaction is second order and is "normal" in that the steric factor deviates from 1 by a factor no greater than 10, a range frequently applicable in reactions of diatomic molecules,[18] an energy of activation of 31 kcal. indicates that the velocity of reaction is not the factor responsible for the scant yields in the synthesis experiments.

The magnitude of the energy of activation shows that neither free atoms of phosphorus nor free atoms of nitrogen represent the activated state or enter into its formation in the over-all reaction 2. The energy required for the formation of atomic phosphorus is 58 kcal. g.-atom^{-1}, and that for atomic nitrogen is 112 kcal. g.-atom^{-1}.

Synthesis in the Presence of Tungsten.—The reported synthesis of phosphorus nitride in the presence of tungsten,[5] together with a report[19] that incandescent tungsten in a phosphorus atmosphere produces atomic phosphorus, suggested that atoms of phosphorus may play an important part in the synthesis under these conditions. The kinetics of the synthesis in the presence of tungsten therefore was investigated.

Apparatus and Procedure.—The rate of formation of solid phosphorus nitride from phosphorus vapor and nitrogen was measured in both constant-volume and constant-pressure systems. The condensing surfaces in both systems were kept at 500°—a temperature high enough to prevent the

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(11) L. R. Maxwell, S. B. Hendricks and V. M. Mosley, *J. Chem. Phys.*, **3**, 699 (1935).

(12) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 299.

(13) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 561.

(14) G. Herzberg, L. Herzberg and G. G. Milne, *Can. J. Research*, **18**, *A*, 139 (1940).

(15) A. Stock, G. E. Gibson and E. Stamm, *Ber.*, **45**, 3527 (1912).

(16) Reference 13, p. 564.

(17) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series III, Vol. I, Table 18, Washington, D. C., March 31, 1947, and June 30, 1948.

(18) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 6.

(19) O. S. Duffendack and H. Huthsteiner, *Phys. Rev.*, **25**, 501 (1925).

deposition of red phosphorus and yet low enough to prevent the generation of a significant vapor pressure of phosphorus nitride.

The rate of synthesis in the constant-volume system was determined from the pressure–time relation in a borosilicate glass reaction cell. The cell was 7.4 cm. i.d. by 19 cm. long with a 0.091- by 12.7-cm. tungsten wire along its vertical axis and with a short radial arm containing an optical window. The junction of a Pt–Pt–10% Rh thermocouple was imbedded in the cell wall. Pressures were measured with a null-point Bourdon gage, which gave reproducible measurements at 500° when kept free of strain. The gage was kept in balance and at constant temperature.

The cell was connected to a vacuum system, a source of nitrogen, and a phosphorus vaporizer. The connection to the vacuum and the nitrogen was through a bank of parallel breakoff valves. The connection to the vaporizer bypassed the valves. Cell, gage and breakoff valves were heated at 500 ± 2° in a muffle furnace. The vaporizer was heated in an adjacent furnace, and the interconnecting line was heated independently.

The temperature of the tungsten wire was measured by means of a Leeds & Northrup No. 8622 optical pyrometer. The radiation standard was a lamp calibrated by the National Bureau of Standards. To ensure clear visibility of the wire, the optical window was held at a temperature 100° above that of the main wall of the cell. Observed wire temperatures were corrected[20] for the radiation characteristics of tungsten and for light absorption by the window. The readings were reproducible to within ±3°.

The reaction cell was evacuated to a pressure of 1×10^{-5} mm. at the beginning of an experiment, and the constant for the Bourdon gage was determined. The vaporizer then was charged with red phosphorus in an amount that would yield a partial pressure of $^1/_3$ atmosphere in the system at 500°. The red phosphorus was degassed for several hours at 300° and 1×10^{-5} mm. The system was sealed, and the vaporizer was brought to 500°, where it was held for the period of the experiment. Dry, oxygen-free nitrogen was introduced through a breakoff valve to bring the total pressure in the system to 1 atmosphere.

The phosphorus vapor and nitrogen were held at 500° for several hours to ensure mixing. The tungsten wire then was energized, and the pressure in the system was measured as a function of time.

At the end of the run, the pressure of the residual gas was measured at 500° with the tungsten wire "off." A breakoff was opened, and the gas was pumped from the system through hot copper wool, which absorbed the phosphorus vapor. The N:P ratio in the residual gas was calculated from the total pressure and the amount of phosphorus absorbed by the copper.

The drift in the gage constant during a run was always <1 mm. The absence of measurable pressure from the condensed phosphorus nitride in the evacuated system within 8 hours at 500° showed that no decomposition or vaporization of the nitride occurred in the system.

The reaction cell in the constant-pressure or flow system was similar to the one in the constant-volume system and was heated likewise at 500 ± 2°. Mixtures of phosphorus and nitrogen containing from 5.2 to 17.6% P_4 by volume entered the cell near the bottom, and the unreacted gas left near the top.

The difference between the rates of flow of nitrogen into and out of the system was a measure of the nitrogen consumed in the synthesis of phosphorus nitride. These flows (<3 ml. per min.) were measured with capillary flowmeters in a constant-temperature bath.

The rate of consumption of phosphorus in the synthesis reaction was found from the rate of consumption of nitrogen and the composition of the nitride that was formed.

Although the measurements made in the two systems generally were in good agreement, those made in the constant-volume system were somewhat more precise and were used more extensively in the kinetic evaluation of the rate of synthesis.

Kinetic Evaluation.—Eleven experiments were made in the constant-volume system at seven temperatures ranging from 1720 to 2127°. The falling pressure was measured at intervals—generally until it reached 100 mm. The rate measurements gave smooth curves when plotted as temperature–pressure–time isograms. Although the N:P ratio in the synthesis gas was 1.00, the ratio in the condensed products ranged from 1.03 to 1.19.

The constant-pressure experiments covered about the same range of temperature. The experimental data for the two sets of measurements are available.[21]

The concentration of phosphorus at the hot wire at a given time was calculated from the observed pressure and the composition of the gas mixture as found from the N:P ratios in the gas and in the nitride product. The dissociation constants for phosphorus were calculated from data[11–15] pertinent to the equilibrium $P_4 = 2P_2$. At temperatures of 1500 to 2127° and a pressure of 1 atmosphere, from 87 to 99.5% of the phosphorus vapor is in the diatomic form.

The dimensions of the apparatus and the occurrence of reaction between the phosphorus and nitrogen impeded separation of the gases through thermal diffusion and convection.[22,23] An absence of significant separation of the gases was evidenced by (1) the agreement between the rate data obtained with the closed system and with the flow system, (2) the apparent uniformity of reaction mechanism over a wide range of pressures, and (3) the absence along the tungsten wire of the type of temperature gradient that is associated with stratification of the surrounding gases.

A direct proportionality between the rate of synthesis and the concentration of phosphorus in the synthesis gas is shown by the data in Table II. The rate data from the constant-volume experiments conform to the $^1/_2$-order rate equation

$$-\mathrm{d}C_{P_2}/\mathrm{d}t = kC_{P_2}^{1/2} \qquad (5)$$

where C_{P_2} is the concentration of P_2 in molecules per cc. The plots in Fig. 3 indicate the change

TABLE II

EFFECT OF CONCENTRATIONS OF PHOSPHORUS AND NITROGEN ON THE RATE AT ATMOSPHERIC PRESSURE

System	Composition of gas, % P_4	N_2	Temp., °C.	k^a
Constant pressure	7.16	92.84	2080	1.9×10^4
Constant pressure	7.18	92.82	2097	1.9×10^4
Constant pressure	11.54	88.46	2097	2.1×10^4
Constant pressure	11.0	89.0	2165	3.5×10^4
Constant volume	33.3	66.7	2127	4.2×10^4
Constant pressure	7.18	92.82	2227	2.2×10^4
Constant pressure	11.5	88.5	2212	3.8×10^4
Constant volume	33.3	66.7	2127	4.2×10^4

[a] From equation 5, where the $^1/_2$-order rate constant, k, is in (molecules $P_2)^{1/2}$ cc.$^{1/2}$ sec.$^{-1}$ cm.$^{-2}$.

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[20] P. D. Foote, C. O. Fairchild and T. R. Harrison, Natl. Bur. Standards Tech. Paper No. 170, p. 105 (1921).

[21] Tables showing (a) the temperature-pressure-time relationship in the constant-volume system and (b) the rate of nitrogen fixation as a function of phosphorus concentration and temperature in the constant-pressure system have been deposited as Document number 4339 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[22] K. Clusius and G. Dickel, *Naturwissenschaften*, **26**, 546 (1938).

[23] K. Clusius and G. Dickel, *ibid.*, **27**, 148 (1939).

in concentration of P_2 with time in accordance with the foregoing equation.

Although equation 5 does not reflect the complete mechanism, the conformance of the data to the $^1/_2$-order equation suggests that the concentration of phosphorus is closely associated with the rate-controlling step. Furthermore, the $^1/_2$-order rate of consumption of the phosphorus indicates that the synthesis reaction is catalyzed by the hot tungsten. The catalytic dissociation of hydrogen, oxygen, nitrogen, sulfur dioxide and carbon monoxide in the presence of heated metals has been shown also to follow $^1/_2$-order processes, the activated complexes being atoms or radicals adsorbed upon the surface of the metal.[24]

The relatively high catalytic activity of tungsten in the synthesis was demonstrated in a run where a carbon filament was substituted for the tungsten wire. As shown in Fig. 3, the rate of reaction in the presence of carbon at 1868° was about one-tenth of that in the presence of tungsten at 1875°—a much greater difference in rate than can be attributed to the small difference in temperature.

The condition of the surface of the tungsten affected the rate of synthesis markedly. One of the three wires used in the constant-volume system (wire C) was pretreated by alternate oxidation and reduction to roughen its surface. The rate of synthesis at 1927° with the treated wire was about twice as fast as with an untreated wire.

Temperatures above 2000° adversely affected the activity of the tungsten. At 2127° the effect of the pretreatment of wire C was almost nullified, and a later microscopic examination showed that the wire had lost much of the surface roughness imparted by the pretreatment. The adverse effect of temperatures above 2000° was evident in other experiments. Wire A promoted the synthesis at a somewhat greater rate at 1875° than wire B at 1927°. The highest temperature at which wire A had been operated in earlier runs was 1963°, whereas wire B had been operated at 2127°.

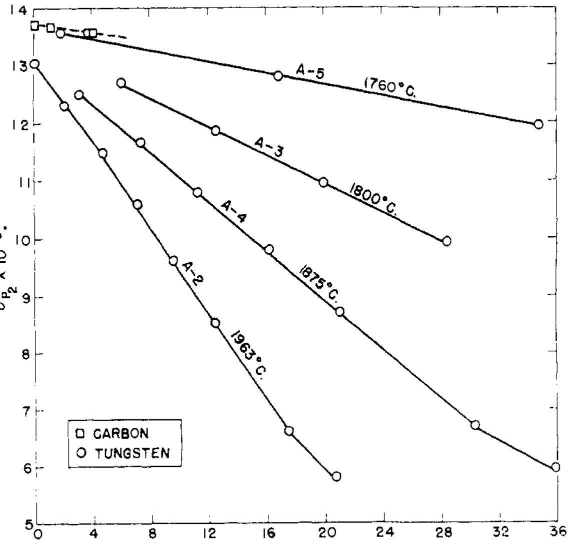

Fig. 3.—Rate of conversion of phosphorus to phosphorus nitride in the presence of tungsten and of carbon—constant-volume system. A-5 is the fifth run with tungsten wire A, and so on.

Catalysts with similar histories, and consequently similar surfaces, yielded $^1/_2$-order rate constants that were in good agreement for the two systems. To reduce the constants to the basis of an arbitrary area of tungsten surface, the wire was assumed to be a smooth cylinder. The values of the constants, in (molecules $P_2)^{1/2}$ cc.$^{1/2}$ sec.$^{-1}$ cm.$^{-2}$, ranged from 6.7×10^3 at 1800° to 4.5×10^4 at 2127°.

The logarithms of the rate constants are plotted against reciprocal temperature in Fig. 4. This plot again illustrates the adverse effect of temperatures above 2000° on the activity of the tungsten. The temperature dependence of the rate for a given catalyst surface at temperatures above 1800° is uniform, however, and indicates uniformity in mechanism of reaction. The apparent decrease in temperature dependence with increase in temperature above 2000° is attributed to a decrease in the surface area of the tungsten. The deviation of the rate constants for temperatures above 2000° from values obtained by extrapolation of the curve for wire A probably is a measure of the change in surface area.

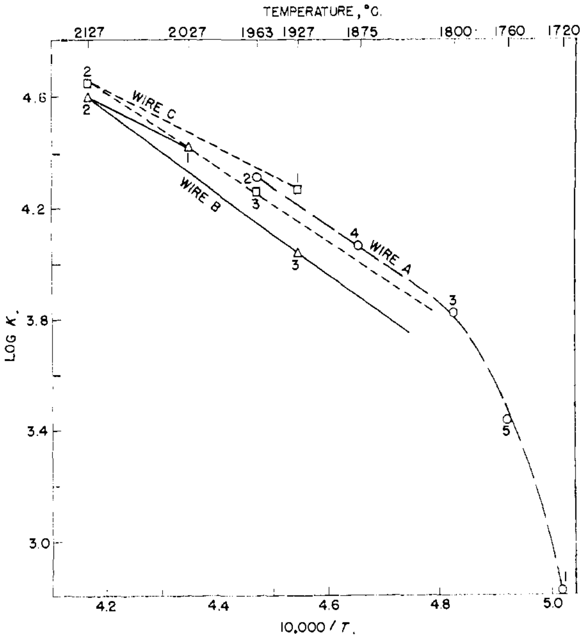

Fig. 4.—Temperature dependence of the rate of tungsten-catalyzed conversion of phosphorus to phosphorus nitride. Numbered points show sequence of runs with each wire.

The much higher temperature dependence of the reaction rate at temperatures below 1800° indicates that the catalyst was covered, or poisoned, to a high degree in this region of temperature. The condition of the tungsten surface apparently was changing rapidly in the runs at temperatures below 1800°.

The energy of activation of the catalytic process at temperatures above 1800° is 59 kcal. The energy of dissociation of diatomic phosphorus into normal atoms at absolute zero is 58 kcal. per g.-atom,[25] whereas the corresponding value for nitrogen probably is 112 kcal.[9]

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[24] K. J. Laidler, *J. Phys. Colloid Chem.*, **53**, 712 (1949).

[25] Reference 13, p. 448.

The process controlling the rate of formation of phosphorus nitride from phosphorus and nitrogen at temperatures above 1800°, therefore, is viewed as the catalyzed dissociation of diatomic phosphorus into atoms. The process probably involves adsorption of diatomic phosphorus on the tungsten, release of phosphorus atoms from the surface and reaction of the phosphorus atoms with nitrogen in the gas phase.

The ratio N:P in the phosphorus nitride products was always greater than unity. This occurrence could result from the presence of phosphorus atoms in accordance with the mechanism postulated below.

Phosphorus atoms—produced at the tungsten surface—react with nitrogen molecules to form the complex PNN, which then reacts with another phosphorus atom. The resultant groupings may combine to yield the polymer $(\mathrm{PN})_n$. Or they may continue to grow through alternate collisions with nitrogen molecules and phosphorus atoms until the reaction ends at an N:P ratio in the range from unity, as in $(\mathrm{PN})_n$, to 5:3, as in the polymer $(\mathrm{P_3N_5})_n$, which has the highest nitrogen content of the known phosphorus nitrides.

Other mechanisms were considered: (a) the atom chain reaction

$$\mathrm{P + N_2 \longrightarrow PN + N}$$
$$\mathrm{N + P_2 \longrightarrow PN + P}$$

leading into a polymerization reaction, and (b) reaction of the diatomic molecules

$$\mathrm{P_2 + N_2 \longrightarrow P_2N_2^{\ddagger} \longrightarrow 2PN}$$

also leading into a polymerization reaction. Calculations based upon the dissociation energies of $\mathrm{N_2}$ and PN and the probable energy of polymerization[26] of PN indicate that the energy level of mechanism (a) is nearly twice as high as the experimental activation energy. The chain reaction might proceed, however, in the vicinity of an electric arc. The magnitude of the experimental activation energy, 59 kcal., is inconsistent also with mechanism (b), because the formation of $\mathrm{P_2}$ molecules requires only 26.8 kcal. mole^{-1}, and the estimated energy level of a $\mathrm{P_2N_2}$ complex is considerably below that of phosphorus atoms.

The reaction velocities found experimentally were compared with those calculated according to the absolute rate equation[27] which applies to the postulated mechanism

$$v_{\mathrm{x}} = C_{\mathrm{P_2}}{}^{1/2}c_{\mathrm{S}}\,\frac{kT}{h} \times \frac{f^{\ddagger}}{F_{\mathrm{P_2}}{}^{1/2}f_{\mathrm{S}}}\,e^{-E_0/RT}$$

The number of active sites per square centimeter of catalyst surface, c_{s}, is a function of the composition of the catalyst and the degree of covering by the adsorbate. From the adsorption isotherm[27] applicable to the mechanism suggested here, the degree of covering is estimated to be 1 to 10%. An assumption that the phosphorus–tungsten complexes are the active sites leads to absolute reaction rates five to ten times as great as the experimental values—a fairly good agreement in view of the uncertainties as to the surface area of the catalyst and the efficiency of condensation of the nitride.

Acknowledgment.—Henry Eyring, Consultant to TVA, gave helpful advice concerning the study. Mary Griffin Rountree and A. J. Smith assisted with the experimental measurements. J. A. Brabson, O. W. Edwards and Inez Jenkins Murphy dealt with the problems of chemical analysis. Thad D. Farr made useful suggestions about the manuscript.

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[26] National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series I, Vol. I, Table 19-10, Washington, D. C., December 31, 1947, and March 31, 1949.

[27] Reference 18, p. 358.

WILSON DAM, ALABAMA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

Interaction of Nitrous Acid with Hydrogen Peroxide and with Water

BY MICHAEL ANBAR[1] AND HENRY TAUBE

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The rate law for the exchange of oxygen between nitrite and water in the *p*H range 4–6 is $k(\mathrm{H^+})^2(\mathrm{NO_2^-})$; at $\mu = 1.00$ and 25°, $k = 2.6 \times 10^8$ l.^{2} mole^{-2} min.$^{-1}$. The rate is unaffected by phosphate buffer at low concentration. The form of the rate law, the inhibition by $\mathrm{H_2O_2}$ of the exchange, and the kinetics of the reaction of $\mathrm{NO_2^-}$ and $\mathrm{H_2O_2}$ are explained by the formation from the activated complex of an intermediate (possibly $\mathrm{NO^+}$), and competition of $\mathrm{H_2O}$ and $\mathrm{H_2O_2}$ for reaction with the intermediate. At low nitrite concentrations, two oxygen atoms are transferred from peroxide for each mole nitrate formed, corresponding to decomposition of an intermediate pernitrate ($\mathrm{ON\overset{*}{O}\overset{*}{O}H}$) by internal rearrangement. At high nitrite and low peroxide one atom of peroxide oxygen appears in each nitrate formed, a result which corresponds to the process: $\mathrm{ON\overset{*}{O}\overset{*}{O}H + NO_2^- \rightarrow ONO^{*-} + {}^{*}ONO_2^- + H^+}$. When nitrite and peroxide are high, peroxide oxygen appears in the nitrite (but nitrite oxygen does not appear in the peroxide). The exchange results are applied in testing mechanisms which have been proposed for the reaction of amines and nitrites.

The reaction

$$\mathrm{NO_2^- + H_2O_2 = NO_3^- + H_2O} \qquad (1)$$

takes place very rapidly in acid solution, but the rate decreases markedly as the acidity is reduced. The rate law for the reaction has been shown to be[2] $-\mathrm{d(peroxide)}/\mathrm{d}t = k(\mathrm{H^+})(\mathrm{HNO_2})(\mathrm{H_2O_2})$ with $k = 8.3 \times 10^3$ l.^{2} mole^{-2} min.$^{-1}$ at 19°. It also has been shown[3] that in acid solution pernitrite (presumably ONOOH) is formed in equivalent amounts. This was done by making the solution containing $\mathrm{NO_2^-}$, $\mathrm{H_2O_2}$ and acid alkaline soon after mixing. In some experiments as much as 0.7 of the nitrite

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[1] UNESCO Fellow on leave from Weizmann Institute, Rehovoth, Israel.

[2] E. Halfpenny and P. L. Robinson, *J. Chem. Soc.*, 928 (1952).

[3] K. Gleu and R. Hubold, *Z. anorg. Chem.*, **223**, 305 (1935).