[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, DEPARTMENT OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Conversion of Liquid White Phosphorus to Red Phosphorus. II. Particle Size and Surface Area of Red Phosphorus as Functions of the Percentage Conversion[1]

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The results of a kinetic study[4] showed that the conversion of liquid white phosphorus to red phosphorus, in the absence of an accelerator, is a first-order reaction. It was observed, however, that the particles of red phosphorus become large enough to settle in the molten white phosphorus when as little as 6% of the phosphorus has been converted. A rapid increase in the total surface of the solid, corresponding to the formation of large particles, could not be reconciled with any reasonable reaction mechanism that agreed with a first-order rate equation. To elucidate further the mechanism of the reaction, therefore, the particle size and surface area of the red phosphorus were measured and correlated with the percentage conversion of the parent white phosphorus. The particle size and surface area of red phosphorus, in addition to their theoretical significance, markedly influence its stability toward atmospheric oxidation.

In the present paper, data are presented for the particle-size distribution and surface area of red phosphorus prepared by the partial (6 to 60%) conversion of white phosphorus at its boiling point (280°). This temperature and range of conversion are within the practical limits for a commercial process. The particle-size distribution was determined by a sedimentation method, and the surface area was measured by a gas-adsorption method.

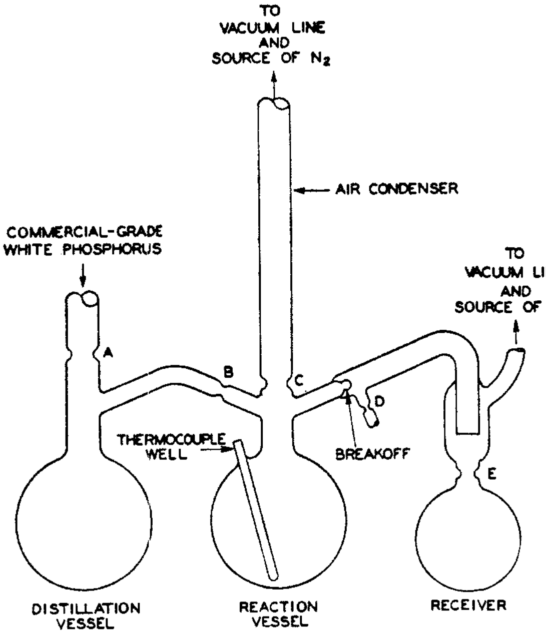

Fig. 1.—Apparatus for the preparation of red phosphorus from distilled white phosphorus.

Measurements

Red phosphorus was prepared in the glass apparatus shown in Fig. 1. The apparatus was flushed with nitrogen, and commercial-grade liquid phosphorus was transferred from a separatory funnel into the distillation vessel. The distillation vessel, sealed at A and evacuated, was heated at 125 to 200° to distil the phosphorus into the reaction vessel. The reaction vessel then was sealed at B, and nitrogen was introduced into the system.

Conversion of the distilled phosphorus at 280° was accomplished by boiling the phosphorus in an atmosphere of nitrogen at 760 mm. pressure for the time computed, from kinetic data,[4] to yield the desired percentage conversion. The reaction vessel then was cooled, the breakoff to the receiver was opened, and the openings to the breakoff and the condenser were sealed at D and C, respectively. The unconverted white phosphorus was distilled into the evacuated receiver. The red phosphorus was removed from the reaction vessel under water and was heated in boiling water to dissolve oxides that might be present and to ensure removal, by steam distillation, of the last trace of white phosphorus. The product was filtered and washed on fritted glass and was dried in a vacuum at 65°. The percentage conversion, as determined from the final weights of red and white phosphorus, generally was within 2% of that computed from the kinetic data.[4]

Particle-Size Distribution.—Since microscopic examination of the red phosphorus indicated that the particle diameters (1 to 150 microns) were in the range for which the sedimentation pipet is applicable, this device was used for the determination of the particle-size distribution. The apparatus and general procedure have been described by Schweyer.[5,6]

The suspending medium was a 50% solution of glycerol in water. With this solution at 30°, Stokes' law could be applied to particles up to 200 microns in diameter; with water alone, the corresponding diameter is 76 microns.[7] The density

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[4] T. W. DeWitt and S. Skolnik, THIS JOURNAL, **68**, 2305 (1946).

[5] H. E. Schweyer, *Rock Products*, **45**, No. 11, 56, 94–96 (1942).

[6] H. E. Schweyer, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 622–632 (1942).

[7] W. C. Krumbein and F. J. Pettijohn, "Manual of Sedimentary Petrography," D. Appleton-Century Co., New York, N. Y., 1938, pp. 95–102.

TABLE I

PARTICLE-SIZE DISTRIBUTION OF RED PHOSPHORUS PREPARED BY PARTIAL CONVERSION OF LIQUID WHITE PHOSPHORUS AT 280°

Wt. % of white phosphorus converted	Cumulative wt. % of red phosphorus less than indicated particle size in microns											Av. particle size,[9] microns
	10	20	30	40	50	60	70	80	90	100	110	
6	8	21	82	97	98							26.5
15	4	5	37	91	97	98						31.5
22	<1	3	17	78	92	97	98					37
28	<1	...	6	67	87	94	96	98				37.5
37	<1	<1	3	19	67	83	90	92	95			46.5
40	<1	<1	2	26	67	85	92	95	98	99		44
60[a]	<1	<1	<1	<1	10	29	52	68	77	81	83	60
60[a]	<1	...	2	6	16	32	46	56	67	76	81	61

[a] These samples contained particles as large as 150 microns in diameter.

and viscosity of the glycerol solution agreed with published data.[8]

The red phosphorus was dispersed by vigorous stirring for thirty minutes. Completeness of the dispersion was confirmed microscopically within the limits of the instrument. The sedimentation measurements were made in a constant-temperature bath at 30°. The samples from the sedimentation pipet were washed free of glycerol on weighed glass filters, dried in a vacuum at 65°, and weighed.

The data obtained for particle sizes of red phosphorus prepared by partial liquid-phase conversion of white phosphorus at 280° are shown in Table I and are plotted as integral distribution curves in Fig. 2. Except for the product representing 60% conversion, which contained particles up to 150 microns in diameter, the particle sizes fall in the range of 1 to 100 microns, with only small percentages less than 10 microns in diameter (Table I). The average particle size[9] increases from 26.5 microns at 6% conversion to about 60 microns at 60% conversion.

A logarithmic probability plot of the particle-size distribution of the red phosphorus (Fig. 3) shows that the straight line representing symmetrical distribution is approached at about 60% conversion. The product obtained at 60% conversion was a friable mass that crushed readily to a powder. As the conversion proceeded beyond 60%, the product became firmer and finally set in a hard lump that required severe grinding for reduction to a powder. The particle sizes of such products obviously would not be related to the mechanism of the reaction; data therefore were not obtained for conversions in excess of 60%.

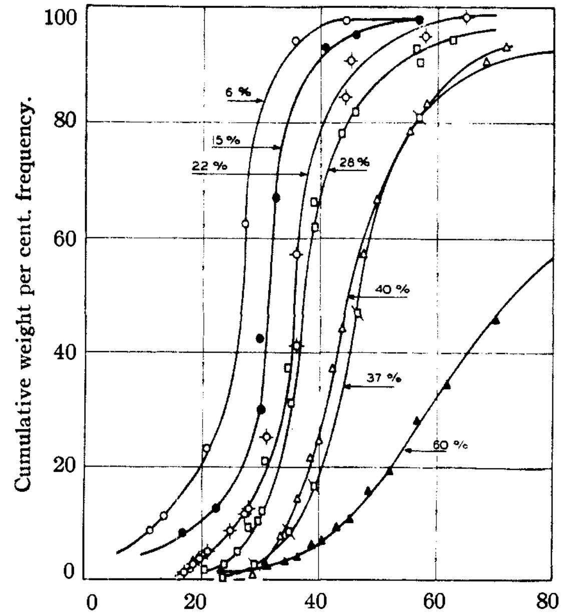

Fig. 2.—Integral distribution of particle sizes of red phosphorus from different percentages of conversion at 280°.

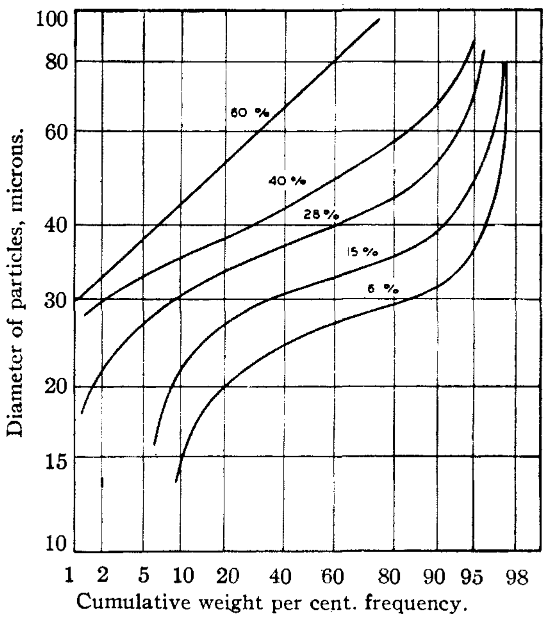

Fig. 3.—Logarithmic probability plot of cumulative distribution curves for different percentages of conversion at 280°.

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[8] M. L. Sheeley, *Ind. Eng. Chem.*, **24**, 1060–1064 (1932).

[9] The average particle size is the mode determined by graphical differentiation of the integral distribution curves shown in Fig. 2.

Surface Area.—The relative surface area of the red phosphorus was obtained from gas-adsorption isotherms. The apparatus and procedure were similar to those described by Emmett.[10] The pressure measurements were simplified by replacing the usual constant-volume manometer with a glass Bourdon gage that was operated as a null-point instrument in conjunction with a mercury manometer. The null point was indicated by an electronic relay that operated when platinum points in the gage made contact as the pressures on both sides of the elastic element were balanced. A precision of ± 0.2 mm. was obtained with this arrangement. The relative error in low-pressure measurements was minimized by closing the stopcock in the line leading to the sample bulb and using the gas buret as a McLeod gage. The low pressures then were computed by means of the standard gas equation.

Preliminary measurements at -196° with nitrogen (average cross-sectional area of molecules, 16.2 sq. Å.[11,12]) as the adsorbate indicated that the specific surface of most samples of the red phosphorus was less than the accepted lower limit of 10,000 sq. cm.[11] for precise measurement with this adsorbate. Propane exhibited the relatively small saturation pressure of 110 $\pm$ 3 mm. at -78.6°, a temperature conveniently obtained with a mixture of Dry Ice and acetone, and hence was selected as an adsorbate that would yield more precise measurements than nitrogen. The average area of the propane molecule as computed from the density[13] of liquid propane at -78.6° and the equation[10] for hexagonal close packing of the molecules is 26 sq. Å.

To determine whether the specific surfaces indicated by the adsorption of propane were significantly smaller than the absolute values, comparative tests were made of the adsorption of propane and nitrogen on a silica gel of large specific surface and a sample of red phosphorus that had a specific surface of about 6,000 sq. cm. The adsorption of nitrogen on the silica gel indicated a specific surface 40% greater than that indicated by the adsorption of propane. A similar difference betwen the adsorption of nitrogen and butane (molecular area, 32 sq. Å.) on silica gel was reported by Brunauer, Emmett and Teller.[14] Differences of this type have been attributed to the inability of large molecules, such as those of butane, to enter the extremely small pores that are penetrated by the nitrogen molecules. In the tests with red phosphorus the surface area indicated by the adsorption of nitrogen was only 10% greater than that indicated by the adsorption of propane. Since 10% probably is about the limit of precision for the measurement of small specific surfaces with nitrogen, the red phosphorus apparently had a structure that permitted the approximate measurement of its absolute surface by the adsorption of propane. The measurements with propane generally checked within $\pm 2\%$.

Weighed samples of the red phosphorus were degassed in the adsorption bulb for several hours at temperatures of 150 to 200° and a pressure of 10^{-5} mm. of mercury or less. The exact temperature within this range and the period of evacuation were not critical; samples heated for various periods of time had identical specific surfaces. Also, since the original material was prepared at 280°, degassing for a few hours at temperatures up to 200° would not be expected to alter the surface area. At temperatures above 200° red phosphorus slowly vaporizes. All the samples for which data are reported exhibited reversible adsorption at low relative pressures ($p/p_0 = 0.05$ to 0.35), thus indicating the absence of chemisorption.

A plot of the adsorption data in accordance with the Brunauer–Emmett–Teller equation,[15] as shown in Fig. 4, yields straight lines over the range of relative pressures (0.05 to 0.35) for which the equation is valid. The specific surfaces of the respective samples, as calculated by use of the same equation, are shown in Table II.

TABLE II

SPECIFIC SURFACE OF RED PHOSPHORUS PREPARED BY PARTIAL CONVERSION OF LIQUID WHITE PHOSPHORUS AT 280° AS DETERMINED FROM THE ADSORPTION ISOTHERM WITH PROPANE GAS AT -78.6°

Wt. % of white phosphorus converted	Specific surface, sq. cm.	Wt. % of white phosphorus converted	Specific surface, sq. cm.
6	19,700	37	3470
10	12,100	40	2120
15	5,980	42	2980
22	4,760	45	3320
27	3,400	55	2550
36	2,830	60	1720

Adsorption measurements with two samples of the red phosphorus at relative pressures (p/p_0) greater than 0.5 yielded reversible hysteresis loops. One of the isotherms is presented in Fig. 5. This isotherm was obtained with a sample of red phosphorus representing 60% conversion. A sample representing 13% conversion yielded a similar loop that extended to a somewhat lower relative pressure (about 0.5). In view of the generally accepted theory[16] that hysteresis results from the lowering of the vapor pressure of the adsorbate in pores in accordance with the Kelvin equation, the porous structure of the red phosphorus appears to be established.

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(10) P. H. Emmett in E. O. Kraemer's "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, pp. 1–36.

(11) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1553–1564 (1937).

(12) P. H. Emmett, *Ind. Eng. Chem.*, **37**, 639–644 (1945).

(13) "International Critical Tables," Vol. III, p. 28.

(14) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309–319 (1938), as corrected by P. H. Emmett and T. DeWitt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28–73 (1941), footnote p. 30.

(15) Equation A of ref. 14.

(16) S. Brunauer, "The Adsorption of Gases and Vapors," Vol. I Princeton University Press, Princeton, N. J., 1943, Chapt. XI.

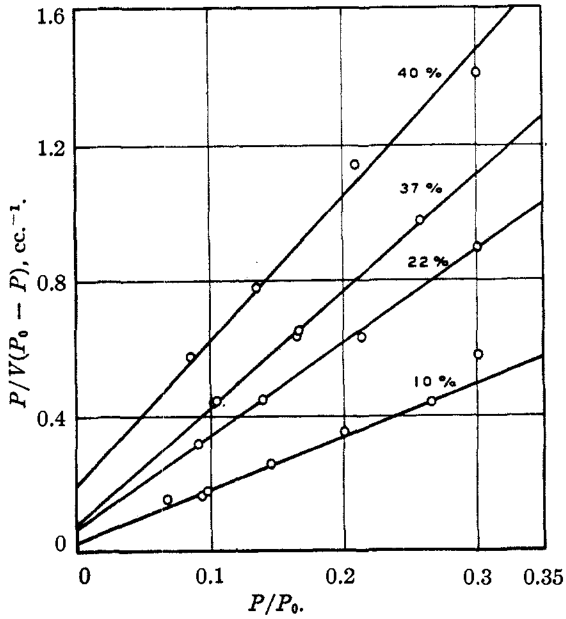

Fig. 4.—Isotherms for the adsorption of propane by red phosphorus from different percentages of conversion at 280°.

Discussion

In Fig. 6 the specific surface, S, is plotted against the reciprocal of the percentage, P, of conversion. Treatment of the data in Fig. 6 by the method of least squares yields the equation, S (sq. cm.) = $111{,}700/P$. The coefficient of correlation of this equation with the data is 0.95, which indicates that the linear relationship between the specific surface and the percentage conversion is real. This means that although the specific surface decreases with increase in percentage conversion, the total surface of the red phosphorus produced by the conversion of a given mass of white phosphorus does not change greatly over the range studied.[17] The mechanism of the conversion therefore could involve, among other reactions, a reaction on the surface of the red phosphorus without a consequent autocatalytic effect.

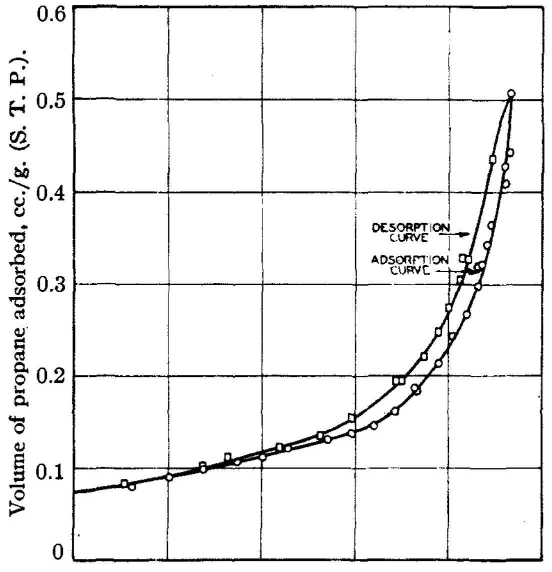

Fig. 5.—Reversible hysteresis in the adsorption of propane on red phosphorus prepared by 60 per cent. conversion at 280°.

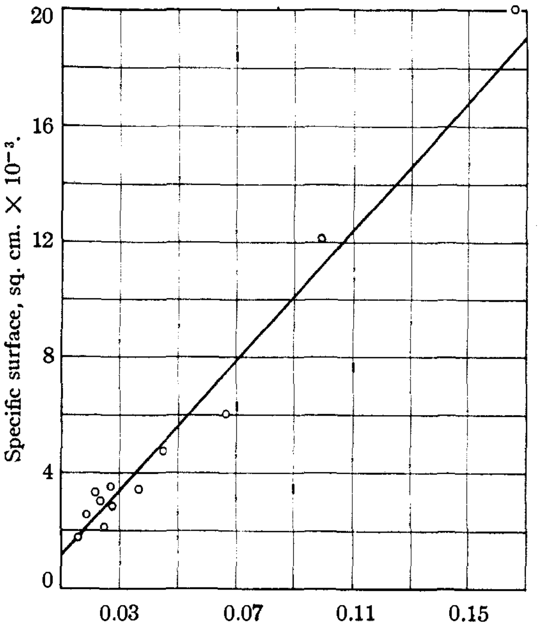

Fig. 6.—Specific surface of red phosphorus as a function of the reciprocal of percentage conversion.

If the red phosphorus is assumed to exist as uniform, non-porous spherical particles of known density,[18] specific surface and particle size become interconvertible. On the basis of this assumption, however, particle sizes computed from the sedimentation data are 4 to 18 times as large as those derived from the adsorption data (Fig. 7), and the reverse relationship applies to specific surfaces. The particle sizes representing the sedimentation data extrapolate to a size of 22 microns, and those representing the adsorption data extrapolate to zero size at zero per cent. converion. Even with due recognition of the fact that the average sizes obtained from the sedimentation data are based on weight percentage, whereas the calculation based on the adsorption data gives a value more closely related to a number average, the discrepancies resulting from interconversion of the two types of data are consistent with the hypothesis that the particles are porous.

(17) In the present measurements the average deviation from the arithmetic mean of the total surface of red phosphorus produced by 6 to 60% conversion of a given mass of white phosphorus was only ±15.3%, whereas the specific surface decreased by a factor of 11.4 in the same range.

(18) The density of red phosphorus was measured in unpublished work and found to be 2.16. Nitrogen at 34.5° was used as the densimetric fluid.

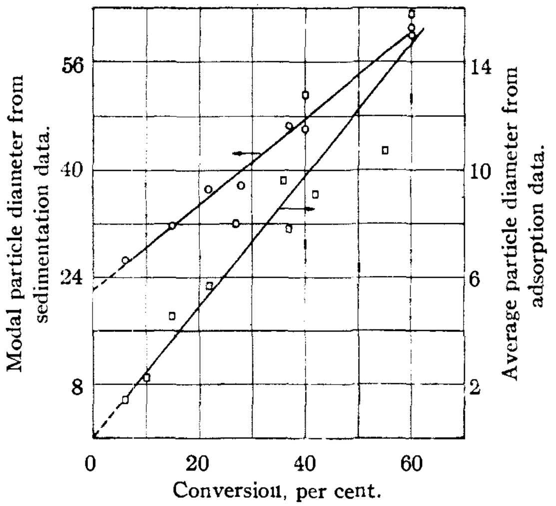

Fig. 7.—Relationship of percentage conversion at 280° to particle diameter as computed from adsorption data and from sedimentation data.

Also, this hypothesis is consistent with the observations on the character of the reaction mixture during the conversion of liquid white phosphorus to red phosphorus.[4]

Since particle size increases with percentage conversion, whereas the total surface remains essentially constant, the spongelike particles must grow not only by the formation of red phosphorus on their surfaces but also by their becoming strongly bonded to each other. To attribute the increase in particle size with increase in percentage conversion to depositional growth alone is inconsistent with the constancy of surface and with both the sedimentation and adsorption data. These data show, respectively, 2.3- and 6-fold increase in particle size as the conversion proceeds from 10 to 60%. Even if it is assumed that the formation of new particles has ceased at 10% conversion, depositional growth during the 6-fold increase in percentage conversion could account for only a 1.8-fold increase in particle size.

The presence of relatively large particles of red phosphorus at low percentages of conversion and the rapid and uniform increase in the size of these particles with further conversion indicate, as do the kinetic data,[4] that the mechanism of the conversion involves a polymerization reaction. The general approach to the kinetics of polymerization reactions[19] involves an initiation reaction (nuclei formation), a growth reaction, and a chain termination reaction. Since reactions by which nuclei are formed generally involve high energies of activation, the rate of formation of nuclei appears to be the rate-controlling factor in the conversion and to account for the fact that the kinetic data[4] for the unaccelerated conversion fit a first-order rate equation. The polymerization of nuclei into red phosphorus would require a small energy of activation and would result in a three-dimensional network of porous structure, even for particles of very small diameter. The kinetic data[4] indicated the absence of a chain reaction.

The particles apparently are composed of large numbers of fundamental units that are strongly bonded into porous structures. The increase in particle size during the conversion is ascribed primarily to the chemical combination of nuclei and the agglomeration of larger units. The decrease in the specific surface of the agglomerates is ascribed to the formation and deposition of red phosphorus within the pores. Deposition on the outer surface of the particles probably occurs simultaneously and accounts in part for both particle growth and decrease in specific surface.

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Summary

In connection with the preparation of red phosphorus by the partial conversion of liquid white phosphorus at its boiling point, the particle-size distribution and specific surface of the red phosphorus have been studied as functions of the degree of conversion in the range 6 to 60%.

The particle sizes, as determined by a sedimentation method, were from 1 to 150 microns, and the modal diameter increased from 26.5 microns at 6% conversion to about 60 microns at 60% conversion.

The specific surface, as measured by the gas-adsorption method with propane at −78.6° as the adsorbate, was a linear function of the reciprocal of the percentage conversion. Application of the adsorption data to calculation of particle sizes yielded values significantly smaller than those measured by sedimentation. Both this observation and the existence of well-defined hysteresis loops in the adsorption data at high relative pressures are consistent with the hypothesis that the particles of red phosphorus are porous.

A postulated mechanism for the conversion involves the formation of nuclei that agglomerate to form porous aggregates.

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[19] H. Mark, "Chemistry of High Polymers," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1941.