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

Conversion of Liquid White Phosphorus to Red Phosphorus. I. Kinetics of the Reaction[1]

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In an investigation of the possibility that red phosphorus can be produced in a form sufficiently stable for bulk shipment, the TVA has made extensive laboratory-scale studies of the preparation and properties of red phosphorus. As a result, a continuous process for the preparation of red phosphorus has been projected to a scale sufficiently large to provide engineering data. In principle, the process comprises the partial conversion of liquid white phosphorus at, or near, its boiling point, and the subsequent distillation and recycling of the unconverted white phosphorus to leave the pulverulent red product. The more important results of fundamental studies pertaining to the process are being presented in a series of papers, of which the present paper is the first.

Vvedenskii and Frost[3] studied the conversion of pure liquid phosphorus to red phosphorus in the temperature range 176 to 373°. They considered the reaction to be of the first order and treated their data accordingly, despite the fact that, at temperatures below 263°, the definite upward trend of their constants with increasing percentage conversion indicated that the conversion was autocatalytic. A reinvestigation of the kinetics of the conversion therefore seemed desirable.

The accelerative effect of iodine on the conversion is generally known. Preliminary work indicated that sulfur has a similar effect. As quantitative work on conversion in the presence of accelerators has not been reported in the literature, a study of the effect of iodine, and of sulfur, on the conversion was included in this work.

Procedure

The phosphorus was purified by distillation in high vacuum at about 150°. The water-white product was collected directly in 0.25-cc. ampules, which were sealed under vacuum when nearly full. For study of the accelerative effect of iodine, and of sulfur, on the conversion, the apparatus shown in Fig. 1 was used to obtain at one time 42 ampoules of phosphorus containing the same concentration of accelerator. Sections D were immersed in a water-bath, maintained at about 50°, to prevent condensation of phosphorus in that part of the system during distillation. The tubing connecting flask G and receiver E was heated electrically to about 60°. After flushing the apparatus with oxygen-free nitrogen, molten phosphorus was added to flask G. The flask then was sealed; the apparatus was evacuated and phosphorus distilled into receiver E to a calibration mark. By-pass C was sealed and oxygen-free nitrogen was introduced carefully into the system and bubbled through the molten phosphorus in receiver E. When the nitrogen pressure became slightly greater than atmospheric, flask G was removed by cutting the tube at F. While nitrogen was being passed slowly through the phosphorus in receiver E, a weighed quantity of iodine was introduced through F. To ensure homogeneity of the solution of accelerator in phosphorus, nitrogen was bubbled through the solution for several minutes. Then the system was sealed at F, breakoff A was opened, and nitrogen was passed through the breakoff and the water seal. By-pass B was sealed, breakoff C was opened, and the nitrogen pressure was increased sufficiently to force the liquid phosphorus up the inner tube of receiver E and into sections D. Each section was thus filled and the excess phosphorus passed into the flask at the end of the train. After the tube below breakoff A was sealed and the nitrogen flow stopped, breakoff B was opened and the system evacuated. Sections D were sealed off individually from the rest of the train and placed in a water-bath at about 60°. By tilting each unit, sufficient phosphorus was flowed into a side arm to fill an ampoule, which then was sealed off. This procedure was repeated on alternate sides until all the ampoules had been filled.

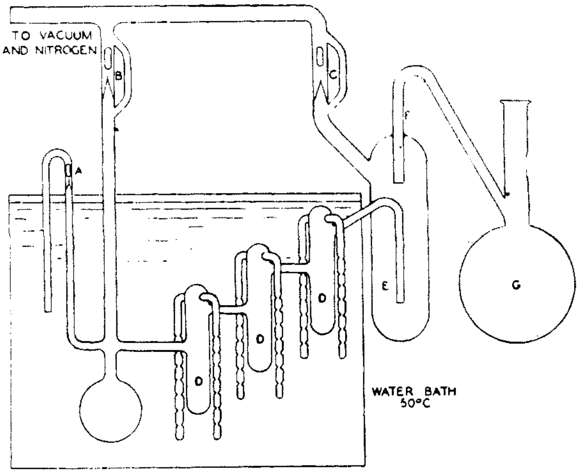

Fig. 1.—Apparatus for filling ampoules with phosphorus containing accelerator.

The same procedure was used for filling the ampoules with phosphorus containing sulfur, except that the sulfur was placed in the receiver prior to the introduction of the phosphorus.

For the conversion, the ampoules of phosphorus were placed in iron tubes filled with molten Wood's metal and immersed in a thermostat containing a lead-tin eutectic mixture at the desired temperature. The temperature of the bath was maintained constant to ±0.5°. At intervals the samples were removed from the bath and analyzed for red and white phosphorus.

The percentage conversion was determined by the following technique: The ampules were cleaned in nitric acid, dried, weighed, and then crushed under benzene. The unconverted white phosphorus was extracted with boiling benzene; the residue of red phosphorus and glass was re-

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moved by filtration and washed with benzene. The combined extract and washings were analyzed for phosphorus by standard methods. The red phosphorus and glass were treated with perchloric acid to oxidize the red phosphorus to orthophosphate, which was determined in the filtered solution. The glass residue was weighed, and the total weight of phosphorus was obtained by subtracting the weight of glass from the original weight of the ampoule plus sample. This value was used to check the sum of the values obtained for red and white phosphorus by the analytical procedures.

Results and Discussion

There are several qualitative aspects of the conversion of liquid white phosphorus to red phosphorus that are informative. The reaction mixture remains fluid until about 50% conversion is reached. On further reaction the mixture rapidly becomes viscous, passes through a plastic or mud-like stage, and finally solidifies. Below 50% conversion the reaction mixture contains suspended particles of red phosphorus large enough to settle rather rapidly on standing. Even at 6 to 10% conversion, many of the particles have diameters of 20 to 30 microns. Apparently these particles of red phosphorus grow both in size and number until, in the region of 50% conversion, they begin to touch one another and grow together, to form an interlocking mass. When it is considered that uniform touching spheres with cubic packing have about 50% free volume and that the density of red phosphorus is only about 20% greater than that of white phosphorus, it is quite understandable that, in the neighborhood of 50% conversion, further growth of the particles requires that they grow into one another to form a more or less rigid structure. The appearance of large particles, even in the early stages of the reaction, is an important fact for which any postulated mechanism must account.

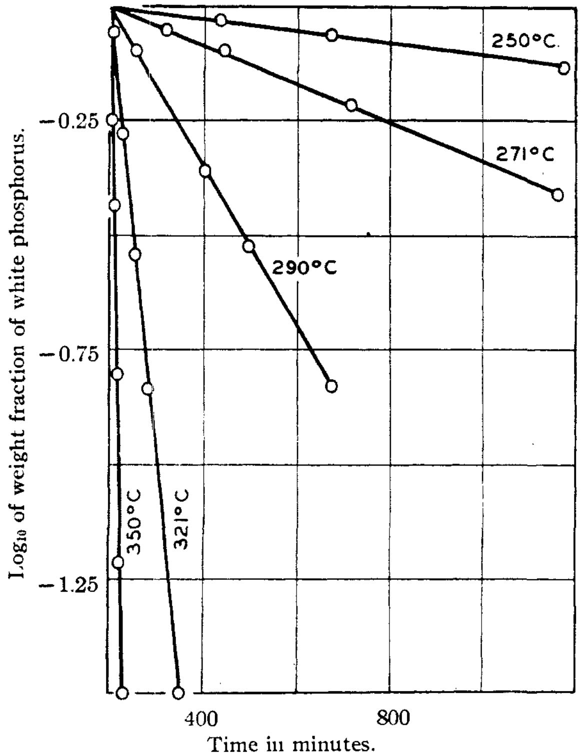

Fig. 2.—Rates of conversion of white phosphorus to red phosphorus.

Kinetics of the Conversion in the Absence of Accelerators.—The conversion of pure liquid white phosphorus to red phosphorus was studied in the temperature range 250 to 350°. The logarithm of the weight fraction of white phosphorus remaining at time *t* is plotted against time in Fig. 2. The reaction obeys a first-order rate equation within the limits of experimental error. Evidence of the autocatalytic effect mentioned by Vvedenskii and Frost[3] is lacking. The first-order constants obtained from these plots are listed in Table I.

Table I

Velocity Constants of the Conversion in the Absence of Accelerators

Temp., °C.	Velocity const., min.$^{-1}$
350	1.25×10^{-1}
321	2.49×10^{-2}
290	3.98×10^{-3}
271	9.74×10^{-4}
250	2.88×10^{-4}

Application of the Arrhenius equation to these constants (Fig. 3) leads to an energy of activation of 38,700 calories per mole for the reaction. Evaluation of the frequency factor, A, in

$$k = Ae^{-E/RT} \qquad (1)$$

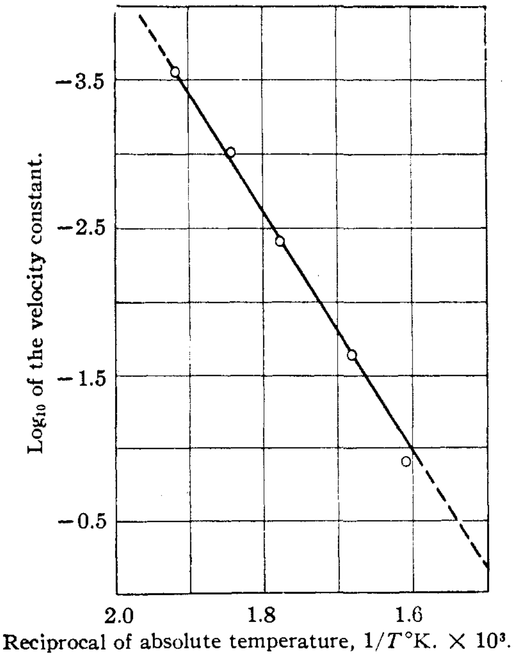

Fig. 3.—Relationship between velocity constant and temperature.

gives a value of 4.17 × 10^{12}. This value compares reasonably well with the theoretical ($k'T/h$) value of 1.2 × 10^{13} for unimolecular reactions at 280°. The relatively normal value of the frequency factor makes the presence of extensive chain reactions rather improbable. The straight first-order kinetics of the reaction and the absence of autocatalytic effects are evidence against any predominant surface reaction on the particles of red phosphorus. Therefore, a first-order production of nuclei of red phosphorus followed by agglomeration of these nuclei to form larger particles is favored as a qualitative picture of the course of the reaction.

Kinetics of the Conversion in the Presence of Accelerators.—Data for the conversion of white phosphorus to red phorphorus were obtained in the presence of 0.01 to 0.1% by weight of iodine and of 0.5 to 1.5% by weight of sulfur. Typical curves obtained by plotting the logarithm of the concentration of white phosphorus, expressed as weight fraction, against time are presented in Figs. 4 and 5.[4] In the presence of iodine or sulfur the reaction does not obey a first-order rate equation; the observed reaction rate is fast initially, then rapidly decreases and approaches values comparable to the rate of the conversion in the absence of accelerators. This suggests the occurrence of two simultaneous reactions: a first-order reaction and another reaction in which red phosphorus is formed rapidly owing to the action of the iodine or sulfur. Since the over-all rate soon approaches that of the reaction in the absence of accelerators, it is evident that the iodine and sulfur are consumed during the reaction.

The rate curves in Figs. 4 and 5 can be represented by an equation of the form

$$-\mathrm{d}m/\mathrm{d}t = Am + Bme^{-Ct} \qquad (2)$$

where m is the amount of white phosphorus present at time t, and A, B, and C are constants. Evaluation of the constants requires that some picture of the mechanism of the conversion be formulated, and the postulation that the conversion involves two simultaneous reactions is a reasonable starting point.

The unaccelerated reaction, as shown in the preceding section, follows a simple first-order rate equation

$$-\mathrm{d}m/\mathrm{d}t = k_1m \qquad (3)$$

where k_1 is the first-order velocity constant. In the simultaneous accelerated reaction, the rate of consumption of the accelerator, presumably through reaction with the large excess of phosphorus, probably follows an apparent first-order law with respect to the accelerator. If, for simplification, the accelerator is assumed to react with both red and white phosphorus at the same rate, the rate of disappearance of the accelerator is independent of the extent of conversion of white to red phosphorus and may be expressed as

$$w = w_0e^{-k_3t} \qquad (4)$$

where w is the amount of accelerator present at time t, k_3 is the velocity constant, and w_0 is the initial amount of accelerator. The accelerator, by reaction with red phosphorus, simply becomes deactivated, whereas, by reaction with white phosphorus, it produces additional red phosphorus. The rate of the accelerated formation of red phosphorus hence is proportional to the rate at which the accelerator reacts with white phosphorus or to the total rate of disappearance of accelerator, $-\mathrm{d}w/\mathrm{d}t$, times the fractional amount of white phosphorus present, m/m_0. The ap-

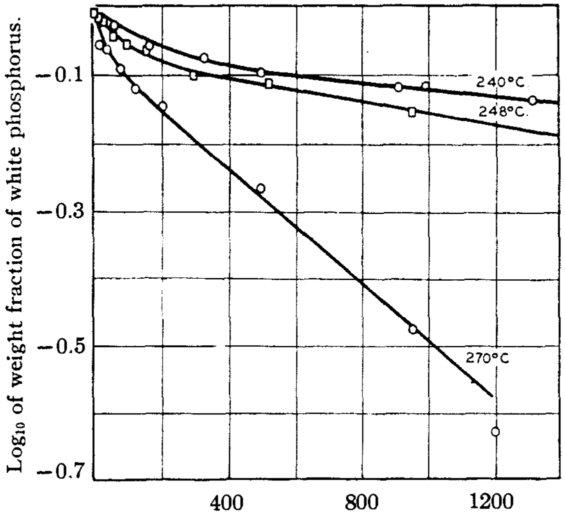

Fig. 4.—Rates of conversion in the presence of 0.05% iodine.

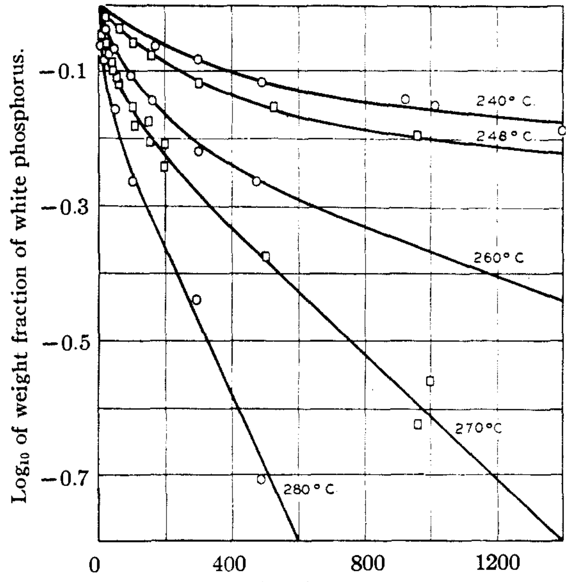

Fig. 5.—Rates of conversion in the presence of 1.0% sulfur.

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[4] The apparent extrapolation of some of the curves in Figs. 4 and 5 actually is based upon experimental data beyond the range of the figures.

plication of equation 4 and its differential form to the accelerated formation of red phosphorus (disappearance of white phosphorus) yields

$$-\frac{dm}{dt} = -k_2\frac{mdw}{m_0dt} = k_3k_2\frac{mw_0}{m_0}e^{-k_3t} = k_3k_2mC_0e^{-k_3t} \quad (5)$$

where C_0 is the initial concentration of accelerator. The sum of equations 5 and 3 represents the overall rate of disappearance of white phosphorus,

$$-dm/dt = k_1m + k_3k_2mC_0e^{-k_3t} \quad (6)$$

which, upon integration and introduction of the condition that $m = m_0$ when $t = t_0$, yields

$$-2.303 \log m/m_0 = k_1t + k_2C_0(1 - e^{-k_3t}) \quad (7)$$

If m_0 is chosen as unity, m becomes the fractional amount of white phosphorus remaining at time t. The constants k_1, k_2 and k_3 then can be evaluated from the graphs of the logarithm of the fractional amount of white phosphorus against time (using equations 6 in the form, $-d \ln m/dt = k_1 + k_3k_2C_0e^{-k_3t}$). From equation 6, when $t = 0$ the slope is equal to $(k_1 + k_3k_2C_0)/2.303$; from equation 7, when t is sufficiently large for the exponential in equation 7 to be negligible, the curve becomes linear with the slope equal to $k_1/2.303$ and the intercept equal to $k_2C_0/2.303$. Since C_0 is known, all the constants can be evaluated. These constants at several temperatures and for various concentrations of iodine and sulfur are listed in Tables II and III. Apparent energies of activation for constants k_1 and k_3 are shown in Table IV. Constant k_2 appears to be essentially independent of temperature. Because of the sparsity of the points used for their determination, the values for the activation energies probably are approximations only, but they are useful for estimating the effect of temperature on the overall reaction.

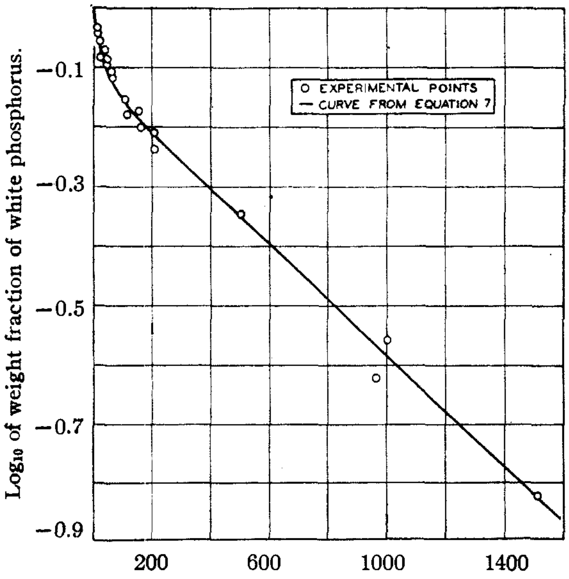

Fig. 6.—Test of equation 7 for the conversion at 270° in the presence of 1% sulfur.

Table II

Velocity Constants of the Iodine–Accelerated Conversion

Initial concn. of iodine, mole fraction[a] × 10^3	Velocity const. $k_1 \times 10^3$, min.$^{-1}$	k_2[b]	$k_3 \times 10^3$, min.$^{-1}$	k_1[c] $\times 10^3$, min.$^{-1}$
		270°		
0.489	1.08	545	64.8	1.00
.244	1.10	584	36.6	
		248°		
0.489	0.304	377	25.2	0.251
.244	.230	682	14.0	
.0489	.200	202	17.9	
		240°		
0.244	0.117	997	3.47	0.145
.0489	.143	145	7.81	

[a] Calculated on the basis of the molecular formulas P_4 and I_2. [b] Dimensionless. [c] Velocity constants of the reaction in the absence of accelerators as determined from Fig. 3.

Table III

Velocity Constants of the Sulfur-Accelerated Conversion

Initial concn. of sulfur, mole fraction[a] × 10^3	Velocity const. $k_1 \times 10^3$, min.$^{-1}$	k_2[b]	$k_3 \times 10^3$, min.$^{-1}$	k_1[c] $\times 10^3$, min.$^{-1}$
		280°		
7.31	3.41	31.5	85.1	1.78
4.86	2.30	80.5	32.7	
		270°		
7.31	2.23	37.9	45.7	1.00
4.86	1.08	56.6	31.8	
2.42	0.99	22.7	20.9	
		260°		
7.31	.880	48.7	18.7	0.576
4.86	.432	83.0	9.35	
		248°		
4.86	.215	56.8	4.38	0.251
		240°		
4.86	.205	37.8	1.77	0.145
2.42	.105	47.8	0.850	

[a] Calculated on the basis of the molecular formulas P_4 and S_8. [b] Dimensionless. [c] Velocity constants of the reaction in the absence of accelerators as determined from Fig. 3.

Table IV

Apparent Activation Energy of Reactions Corresponding to the Velocity Constants k_1 and k_3 of Conversion in the Presence of Accelerators

Accelerator	Apparent activation energy, calories per mole Const. k_1	Const. k_3
Sulfur	42,000	49,000
Iodine	35,800	37,000

Although the test plot in Fig. 6 indicates that equation 7 reasonably describes the course of the reaction at a given temperature, the data in Tables II and III show that the equation may not be entirely adequate. The average values of k_1 compare favorably with those obtained in the study of the unaccelerated conversion, but they, as well as the values of k_3, show significant trends, particularly with initial concentrations of accelerator. Both the scattering of the data, due to analytical difficulties, and the inherently sensitive graphical methods used in evaluating the rate constants introduce an element of uncertainty in the accuracy of the constants. The contribution of these factors to the trends is unknown. It is possible that the trends are real and that they reflect an oversimplification in the picture used in arriving at equation 7. At least the main outlines of the reaction appear, however, to be fairly well established.

More detailed study of the effect of the initial concentration of accelerator, particularly in the first stages of the reaction, would provide most useful data for setting up a more satisfactory rate equation. Knowledge of the mechanism of the reaction also would be furthered by a study of the real identity of the accelerator, its final inactive form, and its distribution between the red and white phosphorus during the reaction. Some attempt was made in the direction of such a study, but analytical difficulties involved in the determination of a small amount of accelerator in a large excess of phosphorus led to abandonment of the work. Some evidence was obtained that the accelerative effect of sulfur is due to a phosphorus sulfide, rather than to elemental sulfur. A phosphorus sulfide was isolated from a mixture of sulfur and white phosphorus that had been heated to a temperature just below that at which red phosphorus begins to form. Progress in this direction could be made by studying the accelerative effect of added phosphorus sulfides or phosphorus iodides.

If the postulated mechanism leading to equation 7 is essentially correct, the dimensionless constant, k_2, is a direct measure of the number of moles of red phosphorus formed per mole of accelerator reacting with white phosphorus. The value of k_2 should indicate the relative effectiveness of the accelerator and also the length of chain, if any, involved in the accelerated conversion. The average values for this constant from Tables II and III are 500 and 50 for iodine and sulfur, respectively. Reduction of these values, which are based on the molecular formulas, I_2 and S_8, to the corresponding values per atom of iodine or sulfur, yields 250 and 6.25, respectively. A chain reaction thus is indicated, and iodine is 40 times as effective per atom as sulfur. Although the constants are scattered, the absence of a consistent trend with temperature lends reasonableness to the conclusion that the length of the chain has little, if any, dependency on the temperature.

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Summary

The kinetics of the thermal conversion of liquid white phosphorus to red phosphorus was studied experimentally. The reaction was found to be strictly first order in the temperature range 250 to 350° with an energy of activation of 37,800 calories per mole.

The addition of small amounts of iodine or sulfur to liquid white phosphorus markedly accelerated its thermal conversion to red phosphorus. The accelerative effect was pronounced in the initial stages of the conversion but soon disappeared, and the conversion continued at a rate comparable to that in the absence of accelerators. A rate law was derived for the reaction.

In the early stages of the conversion, the reaction mixture consisted of particles of red phosphorus suspended in white phosphorus. At about 50% conversion, these particles became numerous and large enough to make the reaction mixture semifluid. Further conversion yielded a solid mass of product.

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