

Free Radical Chemistry of White Phosphorus: γ -Irradiation of P_4 in Bromoform

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$CHBr_2PBr_2$ and $(CHBr_2)_2PBr$ are formed in high yields and in preparatively useful amounts when solutions of white phosphorus in bromoform are exposed to γ -radiation. In the first stages of irradiation, a red phosphorus containing many groups from the solvent is the only reaction product. About 1000 molecules of P_4 are consumed per 100 eV of energy absorbed. In the later stages of irradiation, free radicals from the solvent attack this red phosphorus and lead to the formation of bromophosphines in high yield. Chain reactions are formulated for the formation of both the red phosphorus and the bromophosphines.

Increasing interest has been shown in the synthesis of organophosphorus compounds directly from white phosphorus over the past few years¹. γ -irradiation has been successfully used to initiate free radical reactions of white phosphorus dissolved in organic² or inorganic solvents³. The advantage of this method of initiation is that the radicals are produced in the solvent at a known rate, and hence the chain character of some of the subsequent reactions can be recognized from the measured radiation chemical yields of the final products. Furthermore, the γ -irradiation makes possible the initiation of the reaction over a wide temperature range. For example, CCl_3PCL_2 is formed on irradiation of a solution of P_4 in carbon tetrachloride^{2a}. Since the yield is greater than 40 molecules/100 eV above 130 °C, a chain mechanism is involved. At lower temperatures an interesting kind of red phosphorus is formed as a consequence of free radical attack on the white phosphorus. This red phosphorus contains a large number of radical groups from the solvent and can be used for chemical synthesis. In a similar investigation high yields of $C_6H_{11}PCL_2$ and other products were observed when solutions of P_4 in a mixture of carbon tetrachloride and cyclohexane were exposed to γ -irradiation^{2b}.

In these and related kinetic studies⁴ it has been proposed that the radical R, formed during the

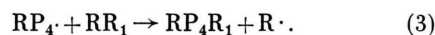
radiolysis of the solvent reacts rapidly with the white phosphorus to yield a phosphenyl type radical.



This radical may either dimerize



or abstract an atom or group R_1 from a solvent molecule RR_1



Since a new radical $R \cdot$ is formed in this process, a chain reaction is possible. At room temperature molecules of the type RP_4R_1 will mainly react among themselves to form a polymeric red phosphorus containing many solvent groups. At high temperatures they tend to abstract R_1 from the solvent. This leads through a stepwise degradation of the phosphorus skeleton to the formation of low molecular weight products.

In this paper, certain aspects of the mechanism will be described which had not been clearly recognized in the previous work. An advantage of using bromoform as a solvent is that a time delay occurs between the formation of the red phosphorus and that of the low molecular weight products. Thus evidence could be obtained that red phosphorus is a precursor of organophosphorus compounds such as

¹ a M. HALMANN, Topics in Phosphorus Chemistry **4**, 49. Interscience Publishers, N. Y. 1967. b M. M. RAUHUT, Topics in Phosphorus Chemistry, **1**, 1. Interscience Publishers, N. Y. 1964. c M. GRAYSON, IUPAC Symposium Organophosphorus Compounds, Heidelberg 1964, p. 193, Butterworth, London.

² a D. PERNER u. A. HENGLEIN, Z. Naturforschg. **17 b**, 703 [1962]. b K.-D. ASMUS, A. HENGLEIN, G. MEISSNER u. D. PERNER, Z. Naturforschg. **19 b**, 549 [1964].

³ a D. PERNER u. A. HENGLEIN, Radiochim. Acta **1**, 62 [1963]. b W. WAWRYCZEK, H. MAYAWSKA u. J. SOBOCZYNSKA, Naturwissenschaften **14**, 409 [1961].

⁴ H. DRAWE u. A. HENGLEIN, Makromolekulare Chem. **84**, 203 [1965].

$CHBr_2PBr_2$ (dibromomethylphosphonous dibromide) and not just a side product. In addition, that $(CHBr_2)_2PBr$ (di-dibromomethylphosphinous bromide) could also be isolated as a reaction product, is not only of preparative interest but also important for an understanding of the mechanism. In earlier work, products containing two organic groups from the solvent [e. g. $(CCl_3)_2PCl$] have never been found.

The radiation induced reaction was studied at temperatures between 25 °C and 140 °C. At higher temperatures, a thermal reaction takes place in which the same products are formed. White phosphorus has also been irradiated in PBr_3 in order to obtain a reactive red phosphorus for the purpose of making certain comparisons with the red phosphorus obtained from bromoform solutions.

Experimental

In this investigation bromoform was purified as recommended by SMYTH and ROGERS⁵, and white phosphorus (Merck, Darmstadt) was used without further purification.

Saturated solutions of P_4 in bromoform which were shown by elementary analysis to contain 0.99 moles of P_4 per litre were regularly prepared. Care was needed to prevent thermal or photochemical conversion of the P_4 to red phosphorus, or its oxidation to insoluble P_2O_5 . Less concentrated solutions were prepared by dilution of the saturated solution.

In the kinetic investigations, 2 cm³ of the solution were rapidly pipetted into a glass ampoule of 1 cm diameter, degassed by several freeze thaw cycles and sealed. The samples were irradiated with ⁶⁰Co- γ -rays at temperatures ranging from 25 °C to 140 °C. The dose rate was varied between 6.6×10^3 and 2.5×10^5 rad/hr. That a considerable reduction in the volume of the solution occurred during irradiation was obvious following separation of the red phosphorus. Quantitative determination of the products $(CHBr_2)PBr_2$ and $(CHBr_2)_2PBr$ and of unconsumed P_4 was carried out gas-chromatographically. Red phosphorus was separated by filtration, washed several times with n-hexane and dried under vacuum. A solid containing phosphorus, denoted in figure 1 as "colloidal red P", was recovered by evaporation of the filtrate.

In the preparative work, glass ampoules containing 50–100 ml of solution were irradiated at room temperature (7×10^6 rad). The red phosphorus was filtered off and the liquid compounds separated by fractional distillation at reduced pressure.

Results

a) Nature of the products

The gas chromatogram of an irradiated solution of P_4 in bromoform contains two major peaks which are attributed to reaction products. The two major products were synthesized in gram amounts by irradiating 100 ml of the solution and subsequently distilling.

The lower boiling point product is a colorless liquid with a density of 2.91 (23 °C) and a refractive index n_D of 1.622 (25.0 °C). Its boiling point is 65 °C at 0.3 Torr and is estimated from the gas chromatography retention time to be 260 ± 5 °C at atmospheric pressure. The elementary analysis is consistent with the formula $CHBr_2PBr_2$ [H = 0.35 (theoretical 0.28), C = 3.64 (3.34), P = 8.57 (8.52), Br = 86.7 (87.6)]. This structure is confirmed by the IR spectrum. Strong absorptions at 2940 cm⁻¹, 1250 cm⁻¹ and in the 650 cm⁻¹ region are assigned to C–H, C–P⁶ and C–Br₂ absorptions, respectively. The proton magnetic resonance spectrum simply shows a doublet (splitting 15 Hz) with $\tau = 4.0$. This is good evidence for the grouping H–CBr₂–P.

The higher boiling point substance is very easily hydrolyzed and oxidized and was therefore handled under a dry nitrogen atmosphere in a glove box. It is a colorless liquid with a density of 2.95 (22 °C) and a refractive index n_d of 1.682 (25.0 °C). The boiling point is 95 °C at 0.2 Torr and is estimated from the gas chromatography retention time to be 305 ± 5 °C at atmospheric pressure. The elementary analysis and proton magnetic resonance spectrum are consistent with the formula $(CHBr_2)_2PBr$. This is confirmed by the IR spectrum which shows stronger C–H (2950 cm⁻¹) and C–P (1260 cm⁻¹) absorptions than that of $CHBr_2PBr_2$.

The red phosphorus formed on irradiation of solutions of P_4 in bromoform contains a large number of foreign atoms and radicals bound to the phosphorus skeleton. A typical sample contained 40.4 P, 43.5 Br, 5.05 C, and 1.0 H. The remainder which was presumably oxygen amounted to 7 per cent. This corresponds to an approximate empirical formula of $CHBr_2P_3$ if it is assumed that inclusion of oxygen into this reactive hygroscopic material oc-

⁵ C. P. SMYTH U. H. E. ROGERS, J. Amer. chem. Soc. **52**, 2227 [1930].

⁶ L. C. THOMAS U. R. A. CHITTENDEN, Spectrochim. Acta [London] **21**, 1905 [1965].

curs on separation and subsequent analysis. With increasing dose, the color of the "red" phosphorus changes from red through yellow to cream. The cream colored "red" phosphorus which is formed in large quantities above 10^8 rad is water soluble (with decomposition) and has a pungent odor. As can be seen in Table 1, the number of foreign atoms in the red phosphorus increases rapidly above 5×10^7 rad, when the irradiation is carried out at room temperature.

Empirical formula of the red phosphorus *	Temp. [°C]	Dose [rad]
$\text{PC}_{0.31}\text{Br}_{1.0}$	25	3.9×10^6
$\text{PC}_{0.30}\text{Br}_{1.1}$	25	1.0×10^7
$\text{PC}_{0.30}\text{Br}_{1.1}$	25	4.5×10^7
$\text{PC}_{1.8}\text{Br}_{4.0}$	25	1.3×10^8
$\text{PC}_{0.20}\text{Br}_{1.1}$	80	2.0×10^5
$\text{PC}_{0.33}\text{Br}_{0.1}$	180	1.0×10^4

Table 1. Composition of the red phosphorus formed at different doses and temperatures. * The hydrogen content was always about 1 per cent.

b) Yields of the products and P_4 disappearance

The dependence of the concentration of white phosphorus, $\text{CHBr}_2\text{PBr}_2$, $(\text{CHBr}_2)_2\text{PBr}$ and of precipitated and colloidal red phosphorus on dose is shown in Figure 1. The initial radiation chemical yield of the disappearance of white phosphorus amounts to 1000 P_4 molecules/100 eV at 25 °C and increases by more than a factor of 10 as the temperature is raised above 100 °C. These high yields clearly indicate that the consumption of phosphorus occurs by a chain mechanism. $G(-\text{P}_4)$ also depends on the initial concentration of white phosphorus. It is found to decrease from 1000 to 300 at 25 °C as the P_4 concentration is reduced from 0.99 M to 0.33 M. During the disappearance of white phosphorus, red phosphorus is formed in increasing amount. It is practically the only reaction product as long as white phosphorus is still present in the solution. After the consumption of the white phosphorus, $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ are formed. Their concentrations increase with dose to a maximum, and then decrease due to the radiation induced decomposition of the products. The amount of red phosphorus (i.e. the sum of colloidal and precipitated phosphorus) also increases with increasing dose to a maximum, although it should be remembered from Table 1 that the composition changes. The dashed line in Fig. 1 shows a material

balance for the phosphorus (i.e. the sum of the phosphorus in the reactant P_4 , the red polymer and the low molecular weight products) at various doses. The straight line obtained indicates that the analysis accounts for all the products.

The delay between the white phosphorus disappearance and the appearance of $\text{CHBr}_2\text{PBr}_2$ can be clearly seen in Figure 1. At 25 °C for instance, the

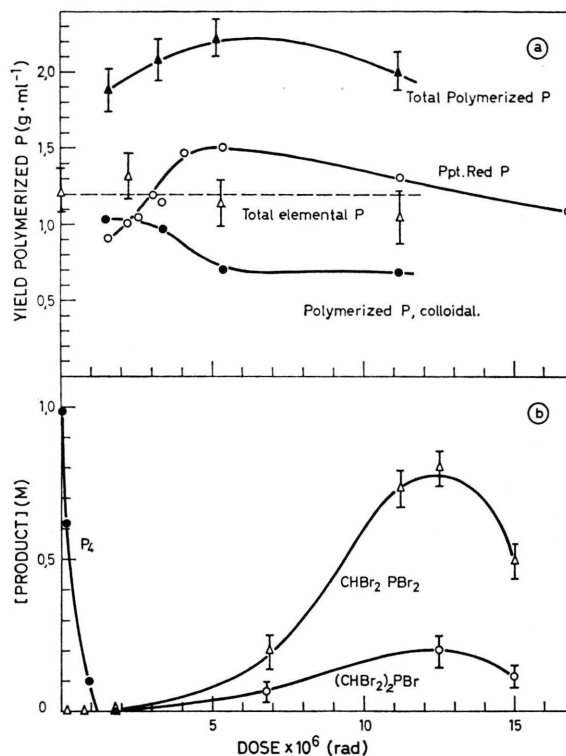


Fig. 1. a) The dependence on dose of the total polymerized phosphorus (\blacktriangle), that part of it precipitated (\bigcirc), and that in colloidal suspension (\bullet). The dashed line indicates the total recovered elementary phosphorus, i.e. that in the red phosphorus and in the low molecular weight products. b) The variation of $[\text{P}_4]$, $[\text{CHBr}_2\text{PBr}_2]$ and $[(\text{CHBr}_2)_2\text{PBr}]$ with dose. (Dose rate = 2.62×10^5 rad/hr.; Temperature = 25 °C).

white phosphorus has been practically consumed at a dose of 10^6 rad, while $\text{CHBr}_2\text{PBr}_2$ is first detected at a "critical dose" of 2×10^6 rad. The concentration of $\text{CHBr}_2\text{PBr}_2$ increases with increasing dose to a maximum at about 10^7 rad and then decreases again. The concentration of $(\text{CHBr}_2)_2\text{PBr}$ shows a similar dose dependence. At higher temperatures (Figure 2), both the "critical dose" and the maximum of the concentration dose curves shift to lower doses. G -values for the formation of $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ were calculated from the maximum

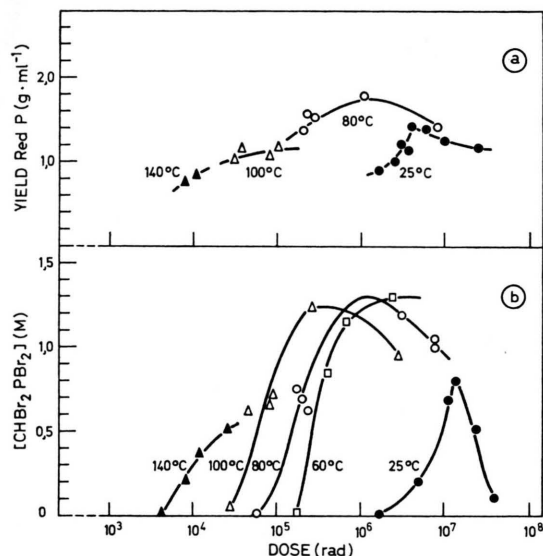


Fig. 2. The dependence of the concentration of $CHBr_2PBr_2$ (b), and of the precipitated red phosphorus (a) on the dose at various indicated temperatures ($[P_4]$ initial = 0.99 M; dose rate 1.66×10^5 rad/hr.).

concentrations and the corresponding doses. The dependence of these G -values on the temperature of irradiation is shown in Figure 3. The high values obtained indicate that $CHBr_2PBr_2$ and $(CHBr_2)_2PBr$ are formed via an efficient chain mechanism.

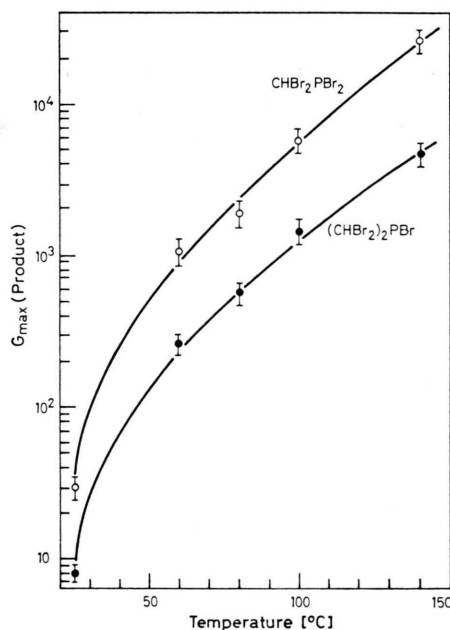


Fig. 3.

The variation of $G_{max}(CHBr_2PBr_2)$ and $G_{max}((CHBr_2)_2PBr)$ with temperature ($[P_4]$ initial = 0.99 M; dose rate 1.66×10^5 rad/hr.).

The dependence of the product concentrations on dose rate at 25 °C is shown in Fig. 4. A total dose of 3.2×10^6 rad was used throughout. This dose was chosen because the bromophosphines are formed in yields which are very low at the highest dose rate studied (7.1×10^5 rad/hr.). The yields increase markedly as the dose rate is decreased.

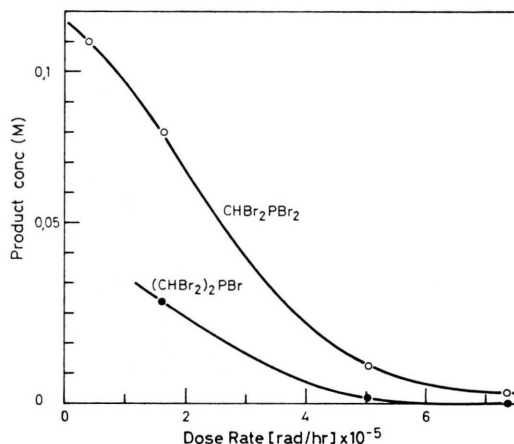


Fig. 4. The variation of the concentrations of $CHBr_2PBr_2$ and $(CHBr_2)_2PBr$ with dose rate (total dose = 3.2×10^6 rad; $[P_4]$ initial 0.99 M; Temp. 25 °C).

The ratio of the yields of $CHBr_2PBr_2$ to $(CHBr_2)_2PBr$ is practically independent of the temperature of irradiation, as can be seen from Table 2.

Temperature [°C]	25	60	80	100	140
$G(CHBr_2PBr_2)/G((CHBr_2)_2PBr)$	4.0 ± 0.5	4.8	4.5	5.0	6.0

Table 2. Ratio of the 100 eV yields of $CHBr_2PBr_2$ to $(CHBr_2)_2PBr$ at different temperatures.

c) Experiments with preformed red phosphorus

That the red phosphorus is formed during the first stage of irradiation, and the low molecular weight products only at higher doses, clearly indicates that the red phosphorus is a precursor of $CHBr_2PBr_2$ and $(CHBr_2)_2PBr$ and not just a side product. The red phosphorus, which largely precipitates is therefore highly reactive.

When commercial red phosphorus was suspended in bromoform and irradiated no bromophosphines could be detected. Similarly, red phosphorus, formed by γ -irradiation of benzene solutions of white phosphorus was found to be inactive when subsequently suspended in bromoform and irradiated. However,

Temperature of irradiation [°C]	Dose [rad]	$G(\text{CHBr}_2\text{PBr}_2)$	$G[(\text{CHBr}_2)_2\text{PBr}]$	$\frac{G(\text{CHBr}_2\text{PBr}_2)}{G[(\text{CHBr}_2)_2\text{PBr}]}$
25	1.7×10^7	2.2	0.06	37 ± 20
120	1.9×10^6	90	2.5	36 ± 5

Table 3. G -values of $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ formed on γ -irradiation of suspension of red phosphorus in bromoform (the red phosphorus was obtained by irradiating a solution of P_4 in PBr_3).

the red phosphorus precipitated during the γ -irradiation of white phosphorus in phosphorus tri-bromide, was found to produce both bromophosphines upon further irradiation of a suspension of it in bromoform. The G -values which are much lower than those in Fig. 2 are listed in Table 3. Furthermore, the ratio $\frac{G(\text{CHBr}_2\text{PBr}_2)}{G[(\text{CHBr}_2)_2\text{PBr}]}$ is much higher than that found on irradiation of solutions of P_4 in bromoform (compare Tables 2 and 3).

d) Thermal reaction

Table 4 indicates the rate at which $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ are formed thermally in solutions of white phosphorus (0.99 M) in bromoform at various temperatures. At the highest temperature used in the γ -irradiation (140 °C) the thermal reaction did not interfere with the radiation chemical reaction. The ratio of the yields of $\text{CHBr}_2\text{PBr}_2$ to $(\text{CHBr}_2)_2\text{PBr}$ is about the same in the thermal reaction at higher temperatures as in the γ induced reaction except at 200 °C where some thermal decomposition of the $(\text{CHBr}_2)_2\text{PBr}$ is to be expected.

Temperature	Time [hrs.]	$\text{CHBr}_2\text{PBr}_2$ conc (M)	$\text{CHBr}_2\text{PBr}_2$ rate [$\text{M}^{-1}\text{min}^{-1}$]	$(\text{CHBr}_2)_2\text{PBr}$ conc (M)	$(\text{CHBr}_2)_2\text{PBr}$ rate [$\text{M}^{-1}\text{min}^{-1}$]
61	29	0.011	no products detected		
100	29		6×10^{-6}		
120	4.5				
140	1.5	0.001	no products detected		
160	1.1		1.5×10^{-5}		
170	1.1		2.0×10^{-4}		
180	1.0	0.013	5.0×10^{-3}	0.006	9×10^{-5}
190	0.95	0.31	7.2×10^{-3}	0.048	8×10^{-4}
200	0.50	0.41	7.2×10^{-3}	0.094	1.7×10^{-3}
200	0.50	0.21	7.2×10^{-3}	0.018	0.6×10^{-3}
210	0.51	dar residue			

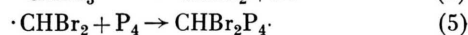
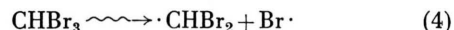
Table 4. Yields of $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ from the thermal reaction.

Discussion

a) Chain mechanism of formation of red phosphorus

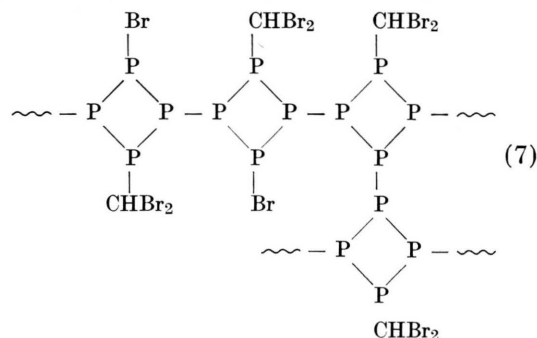
The high G -value observed for the disappearance of white phosphorus and for the appearance of red

phosphorus are explained by the following chain reaction:



A free radical formed on the absorption of high energy radiation by the solvent (equation 4), reacts with a P_4 molecule (equation 5) to form a phosphinyl type radical which subsequently abstracts a bromine atom from the solvent (equation 6). Such an abstraction has been postulated to explain the reactions between substituted phosphines and bromoform⁷. The red phosphorus is built up in subsequent reactions of intermediates of the type $\text{CHBr}_2\text{P}_4\text{Br}$. At high temperature $\text{CHBr}_2\text{P}_4\text{Br}$ may react with a solvent molecule by bromine abstraction. This would lead to a branching of the chain.

The elementary composition of the red phosphorus corresponds approximately to the formula $(\text{CHBr}_2\text{P}_x\text{Br})_n$. The structure at low dose may be approximately described by the following formula:



b) Chain mechanism of formation of the bromophosphines

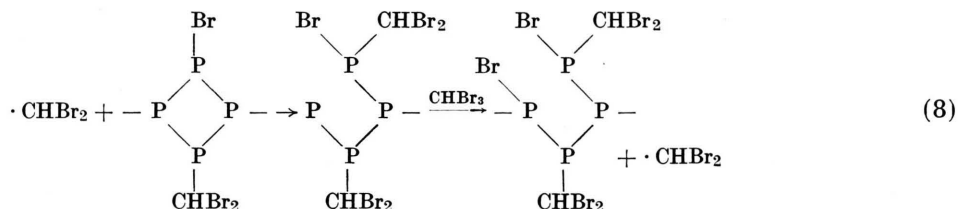
Since $\text{CHBr}_2\text{PBr}_2$ and $(\text{CHBr}_2)_2\text{PBr}$ only start to be formed after all the P_4 has been converted into red phosphorus, it must be assumed that the red

⁷ F. RAMIERZ u. N. MCKLEVIE, J. Amer. chem. Soc. **79**, 5289 [1957].

phosphorus is further attacked by solvent radicals, as a result of which many P—P bonds of the phosphorus skeleton are broken. As a consequence, the number of foreign groups attached to the phosphorus skeleton increases at high dose. It is important to note that in the free radical attack on the precipitated red phosphorus two phases are involved. Since only a small percentage of the radicals from the solvent can reach the red phosphorus under these circumstances, and the low molecular weight products are formed in high yield, a very efficient chain reaction must take place. That most of the

free radicals from the solvent are deactivated by mutual interaction, explains the observed dependence of the yields of $CHBr_2PBr_2$ and $(CHBr_2)_2PBr$ on the dose rate.

It has previously been postulated that a radical attacks red phosphorus preferentially at a phosphorus atom which already carries a foreign group^{2a}. A chain reaction will be propagated if the P radical, formed on addition of the solvent radical to the phosphorus skeleton, can also abstract a bromine atom from the solvent, and thus produce a new radical.



The open P_4 structure in the polymer formed in these reactions is probably stabilized by spontaneous breaking of the P—P bonds and subsequent abstraction of a Br atom from the solvent. This would lead to a branching of the chain, and explain the high yields at elevated temperature (Fig. 2). $(CHBr_2)_2PBr$ will be formed when the $CHBr_2$ radical adds to a phosphorus atom already carrying a $CHBr_2$ group. The very low yield of $(CHBr_2)_2PBr$ (see Table 3) formed by the $\cdot CHBr_2$ radical attack on the red phosphorus prepared from the $P_4 - PBr_3$ solution is simply explained by the absence of $CHBr_2$ substituents in this polymeric red phosphorus.

The elementary steps described above give only an outline of the mechanism for the formation of red phosphorus and of the low molecular weight compounds. A more detailed kinetic description cannot be given since the situation is complicated by the fact that the red phosphorus partly appears in a colloidal form partly as precipitated, and we are dealing with a heterogeneous system the nature of which changes with dose.

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