Free Radical Chemistry of White Phosphorus: \(\gamma\)-Irradiation of \(P_4\) in Bromoform

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CHBr\(_2\)PBr\(_2\) and (CHBr\(_2\))\(_2\)PBr are formed in high yields and in preparatively useful amounts when solutions of white phosphorus in bromoform are exposed to \(\gamma\)-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 years. \(\gamma\)-Irradiation has been successfully used to initiate free radical reactions of white phosphorus dissolved in organic or inorganic solvents. 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 yields of the final products. Furthermore, the \(\gamma\)-irradiation makes possible the initiation of the reaction over a wide temperature range. For example, CCl\(_4\)PCL\(_2\) is formed on irradiation of a solution of \(P_4\) in carbon tetrachloride. Since the yield is greater than 40 molecules/100 eV above 130 \(^\circ\)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\(_6\)H\(_{11}\)PCL\(_2\) and other products were observed when solutions of \(P_4\) in a mixture of carbon tetrachloride and cyclohexane were exposed to \(\gamma\)-irradiation.

In these and related kinetic studies it has been proposed that the radical \(R^\cdot\) formed during the radiolysis of the solvent reacts rapidly with the white phosphorus to yield a phenyl type radical.

\[
R^\cdot + P_4 \rightarrow R P_4^\cdot .
\]

This radical may either dimerize

\[
2 R P_4^\cdot \rightarrow R_2 P_8
\]

or abstract an atom or group \(R\) from a solvent molecule \(R R_1\)

\[
R P_4^\cdot + R R_1 \rightarrow R_2 P_4 R_1 + R^\cdot .
\]

Since a new radical \(R^\cdot\) is formed in this process, a chain reaction is possible. At room temperature molecules of the type \(R R_1\) 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

\[\text{(1)}\]

\[\text{(2)}\]

\[\text{(3)}\]
CHBr₂PBr₂ (dibromomethylphosphonous dibromide) and not just a side product. In addition, that (CHBr₂)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. (CCl₄)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 PBr₃ 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 P₄ in bromoform which were shown by elementary analysis to contain 0.99 moles of P₄ per litre were regularly prepared. Care was needed to prevent thermal or photochemical conversion of the P₄ to red phosphorus, or its oxidation to insoluble P₂O₅. 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 x 10⁹ and 2.5 x 10⁹ 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 (CHBr₂PBr₂ and (CHBr₂)₂PBr) and of unconsumed P₄ 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 x 10⁴ 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 P₄ 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 nD 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 CHBr₂PBr₂ [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—P and C—Br absorptions, respectively. The proton magnetic resonance spectrum simply shows a doublet (splitting 15 Hz) with τ = 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 nD 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 (CHBr₂)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 CHBr₂PBr₂.

The red phosphorus formed on irradiation of solutions of P₄ 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 CHBr₂P₃ if it is assumed that inclusion of oxygen into this reactive hydroscopic material oc-

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⁵ C. P. Smyth u. H. E. Rogers, J. Amer. chem. Soc. 52, 2227 (1930).

The empirical formula of the red phosphorus is given in Table 1. 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. 2. The dependence of the concentration of CHBr₂PBr₂ (b), and of the precipitated red phosphorus (a) on the dose at various indicated temperatures ([P₄] initial = 0.99 M; dose rate 1.66 x 10⁵ 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 CHBr₂PBr₂ and (CHBr₂)₂PBr are formed via an efficient chain mechanism.

Fig. 3. The variation of G_max(CHBr₂PBr₂) and G_max((CHBr₂)₂PBr) with temperature ([P₄] initial = 0.99 M; dose rate 1.66 x 10⁵ 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 x 10⁶ 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 x 10⁵ rad/hr.). The yields increase markedly as the dose rate is decreased.

Fig. 4. The variation of the concentrations of CHBr₂PBr₂ and (CHBr₂)₂PBr with dose rate (total dose = 3.2 x 10⁶ rad; [P₄] initial 0.99 M; Temp. 25 °C).

The ratio of the yields of CHBr₂PBr₂ to (CHBr₂)₂PBr is practically independent of the temperature of irradiation, as can be seen from Table 2.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>25</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>G(CHBr₂PBr₂)/G((CHBr₂)₂PBr)</td>
<td>4.0 ± 0.5</td>
<td>4.8</td>
<td>4.5</td>
<td>5.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Table 2. Ratio of the 100 eV yields of CHBr₂PBr₂ to (CHBr₂)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 CHBr₂PBr₂ and (CHBr₂)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,
Table 3. G-values of CHBr₂PBr₂ and (CHBr₂)₂PBr formed on γ-irradiation of suspension of red phosphorus in bromoform (the red phosphorus was obtained by irradiating a solution of P₄ in PBr₃).

<table>
<thead>
<tr>
<th>Temperature of irradiation [°C]</th>
<th>Dose [rad]</th>
<th>G(CHBr₂PBr₂)</th>
<th>G((CHBr₂)₂PBr)</th>
<th>G(CHBr₂PBr₂)/G((CHBr₂)₂PBr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.7 × 10⁷</td>
<td>2.2</td>
<td>0.06</td>
<td>37 ± 20</td>
</tr>
<tr>
<td>120</td>
<td>1.9 × 10⁶</td>
<td>90</td>
<td>2.5</td>
<td>36 ± 5</td>
</tr>
</tbody>
</table>

The red phosphorus precipitated during the γ-irradiation of white phosphorus in phosphorus tribromide, 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 \( G((CHBr₂)₂PBr) \) is much higher than that found on irradiation of solutions of P₄ in bromoform (compare Tables 2 and 3).

d) Thermal reaction

Table 4 indicates the rate at which CHBr₂PBr₂ and (CHBr₂)₂PBr 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 CHBr₂PBr₂ to (CHBr₂)₂PBr 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 (CHBr₂)₂PBr is to be expected.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Time [hrs.]</th>
<th>CHBr₂PBr₂ conc (M)</th>
<th>(CHBr₂)₂PBr conc (M)</th>
<th>CHBr₂PBr₂ rate ([M^{-1}min^{-1}])</th>
<th>(CHBr₂)₂PBr rate ([M^{-1}min^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>29</td>
<td>no products detected</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>29</td>
<td>0.011</td>
<td>6.10⁻⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>1.5</td>
<td>no products detected</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>1.1</td>
<td>0.001</td>
<td>1.5 × 10⁻⁵</td>
<td>0.006</td>
<td>9 × 10⁻⁵</td>
</tr>
<tr>
<td>170</td>
<td>1.09</td>
<td>0.013</td>
<td>2.0 × 10⁻⁴</td>
<td>0.048</td>
<td>8 × 10⁻⁴</td>
</tr>
<tr>
<td>190</td>
<td>0.85</td>
<td>0.41</td>
<td>7.2 × 10⁻³</td>
<td>0.094</td>
<td>1.7 × 10⁻³</td>
</tr>
<tr>
<td>200</td>
<td>0.50</td>
<td>0.21</td>
<td>7.2 × 10⁻³</td>
<td>0.018</td>
<td>0.6 × 10⁻³</td>
</tr>
<tr>
<td>210</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The elemental composition of the red phosphorus corresponds approximately to the formula (CHBr₂PBr)₃. The structure at low dose may be approximately described by the following formula:

\[
\begin{array}{ccc}
\text{CHBr}_2 & \text{Br} & \text{CHBr}_2 \\
\vdots & \vdots & \vdots \\
\text{P} & \text{P} & \text{P} \\
\text{CHBr}_2 & \text{Br} & \text{P} \\
\end{array}
\]

b) Chain mechanism of formation of the bromophosphines

Since CHBr₂PBr₂ and (CHBr₂)₂PBr only start to be formed after all the P₄ has been converted into red phosphorus, it must be assumed that the red phosphorus are explained by the following chain reaction:

\[
\begin{align*}
\text{CHBr}_3 & \rightarrow \text{·CHBr}_2 + \text{Br} \cdot \quad (4) \\
\text{·CHBr}_2 + \text{P}_4 & \rightarrow \text{CHBr}_2\text{P}_4 \cdot \quad (5) \\
\text{CHBr}_2\text{P}_4 + \text{CHBr}_3 & \rightarrow \text{CHBr}_2\text{P}_4\text{Br} + \text{·CHBr}_2 \cdot \quad (6)
\end{align*}
\]

A free radical formed on the absorption of high energy radiation by the solvent (equation 4), reacts with a P₄ molecule (equation 5) to form a phosphoryl 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 bromoform. The red phosphorus is built up in subsequent reactions of intermediates of the type CHBr₂P₄Br. At high temperature CHBr₂P₄Br may react with a solvent molecule by bromine abstraction. This would lead to a branching of the chain.

**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:

\[
\begin{align*}
\text{CHBr}_3 & \rightarrow \text{·CHBr}_2 + \text{Br} \cdot \quad (4) \\
\text{·CHBr}_2 + \text{P}_4 & \rightarrow \text{CHBr}_2\text{P}_4 \cdot \quad (5) \\
\text{CHBr}_2\text{P}_4 + \text{CHBr}_3 & \rightarrow \text{CHBr}_2\text{P}_4\text{Br} + \text{·CHBr}_2 \cdot \quad (6)
\end{align*}
\]

F. Ramierez 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 CHBr₂PBr₂ and (CHBr₂)₂PBr on the dose rate.

In has previously been postulated that a radical attacks red phosphorus preferentially at a phosphorus atom which already carries a foreign group²ᵃ. 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 P₄ 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). (CHBr₂)₂PBr will be formed when the CHBr₂ radical adds to a phosphorus atom already carrying a CHBr₂ group. The very low yield of (CHBr₂)₂PBr (see Table 3) formed by the ·CHBr₂ radical attack on the red phosphorus prepared from the P₄–PBr₃ solution is simply explained by the absence of CHBr₂ 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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