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THE THERMAL DECOMPOSITION OF PHOSPHORUS IODIDES

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The thermal decomposition of crystalline PI_3 and P_2I_4 in nitrogen and oxygen is reported. The oxidation of PI_3 leads mainly to the formation of phosphorus pentoxide and iodine together with P_xI polymeric species as a minor product. The decomposition of the polymeric species $P_3I_2O_6$ in oxygen and nitrogen follows a two-stage route which precludes its involvement in the oxidation of P_2I_4.

Several investigations of the phosphorus iodides, PI_3 and P_2I_4, have centred on detailed measurement of I.R. and Raman spectra [1–3]. X-ray measurements on crystalline P_2I_4 give P–P bond length as 2.21 Å and the configurations of the iodine atoms are such that the lone pairs on the two phosphorus atoms are trans to each other [4]. Little attention has been paid to the thermal stability of either PI_3 or P_2I_4 although it has been suggested that a solid phase disproportionation of the diodide leads to formation of a polymeric phosphorus iodide [1]:

$$P_2I_4 \rightarrow PI_3 + 1/n\,(PI)_n$$

A recent investigation reported the formation of polymeric phosphorus iodides when P_2I_4 is dissolved in cyclohexane [5]

$$P_2I_4 \rightarrow 1.17\,PI_3 + 1/6\,n\,(P_5I_3)_n$$

while PI_3 yields a polymer range from $P_{10}I_9$ to P_5I_3 under photolysis conditions. When P_2I_4 is dissolved in carbon disulphide a slow decomposition occurs [6]

$$1.5\,P_2I_4 \rightleftharpoons 2\,PI_3 + 0.25\,P_4$$

Very recently new values have been obtained for the standard heats of formation of PI_3 and P_2I_4 [7].

This paper reports a systematic investigation of the thermal decomposition of PI_3 and P_2I_4 in nitrogen and oxygen and considers the possible involvement of the polymeric species $P_3I_2O_6$ in the oxidation reaction.

Experimental

The phosphorus iodides studied were very sensitive to air and moisture and all manipulations were carried out in a glove-box under dry nitrogen. All materials were stored in the dark to prevent photochemical breakdown.

The preparation and purification of PI_3 and P_2I_4 have been described in a previous paper [5]. Polymeric $P_3I_2O_6$ was prepared by passing rigorously dried oxygen gas into a solution of P_2I_4 in carbon disulphide until the solution darkened [8]. The polymeric $P_3I_2O_6$ precipitated as a yellow-white solid which was filtered under vacuum and freed of solvent on a high vacuum line. The product was exceedingly sensitive to moisture and rapidly turned orange on exposure to air. The methods of analysis have been previously described [5]. Typical results were:

	Found %		Required %	
	P	I	P	I
PI_3	7.5	91.5	7.5	92.5
P_2I_4	10.9	88.5	10.9	89.1
$P_3I_2O_6$	20.5	55.9	21.0	57.3

TG studies were carried out on a Stanton HT—M thermobalance, at a heating rate of 2° min^{-1}, under dry nitrogen or oxygen at flow rates not less than 2 litre min^{-1} which was found necessary to prevent hydrolysis. Samples, 50—200 mg, were contained in recrystallized alumina crucibles. Melting point and related studies were carried out on a Perkin—Elmer differential scanning calorimeter, model DSC 1B, under dry nitrogen or oxygen. Reproducible calorimetric measurements of the various reactions which ensued after sample melting proved unsuccessful due to attack by the products of reaction on the aluminium sample containers. Samples, 10—15 mg, were encapsulated in aluminium sample pans and scanned at 8° min^{-1} at a sensitivity of 8 millicalories sec^{-1}. Heats of fusion were obtained from the appropriate peak areas calibrated against 99.999% indium.

I.R. measurements were made either as nujol mulls on a Perkin—Elmer 457 spectrophotometer or as polythene discs on a RIIC Fourier spectrophotometer FS.720. The P—I absorption peaks found were:

	This paper (nm)	Ref. [2] (nm)
PI_3	297,310	297,310
P_2I_4	302,330	301,330
$P_3I_2O_6$	299,315,330	—

Diffuse reflectance spectra were obtained from samples diluted with magnesium oxide and measured on a Unicam SP.500 spectrophotometer fitted with a diffuse reflectance attachment.

Results

A preliminary investigation showed that when P_2I_4 was heated to 190°, the volatile phase, trapped in a sodium hydroxide solution containing hydrogen peroxide, gave on analysis the atomic ratio I/P = 2.97 indicating PI_3 as the only volatile. A decomposing melt of P_2I_4, frozen by plunging into liquid air, gave I.R. peaks corresponding to both PI_3 and P_2I_4. The results of thermobalance runs are given in Table 1 and Figures 1 and 2.

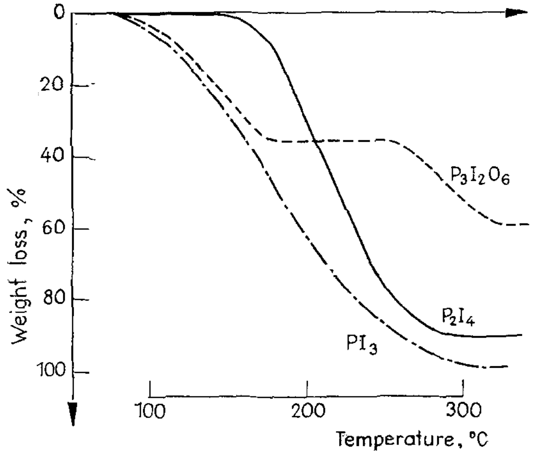


Fig. 1. TG curves of PI_3, P_2I_4 and $P_3I_2O_6$ in nitrogen

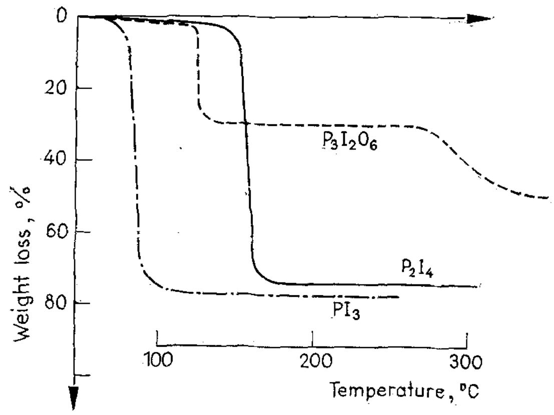


Fig. 2. TG curves of PI_3, P_2I_4 and $P_3I_2O_6$ in oxygen

Heating PI_3 in nitrogen results in simple volatilisation. A trace of phosphorus found in the residue is probably the result of phosphorus impurity in the sample.

Table 1

TG results in nitrogen and oxygen

Reaction in nitrogen			
	PI_3	P_2I_4	$P_3I_2O_6$
Initiation temp. °C	65	130	70, 270
Loss %	98.9	95.0	37.5, 23.2
Residual P %	0.1	3.7	16.9
Residual I %	0.0	0.0	0.0
Reaction in oxygen			
	PI_3	P_2I_4	$P_3I_2O_6$
Initiation temp. °C	70	130	125, 270
Loss %	77.5	73.9	32.6, 21.4
Residual P %	7.3	10.7	20.5
Residual I %	9.8	0.2—0.9	0.0

The oxidation reaction is complex; the results can be interpreted as a two path reaction:

$$PI_3 + 5/4\, O_2 \rightarrow 1/2\, P_2O_5 + 3/2\, I_2 \tag{1}$$

and

$$xPI_3 \rightarrow 1/n\,(P_xI)_n + (3x - 1)/2\, I_2 \tag{2}$$

(1) represents the expected oxidation path while (2) results in the formation of a polymeric phosphorus-iodine species. Both the extent to which each path is followed and the value of x are influenced by furnace temperature as shown in Table 2.

Table 2

The influence of furnace temperature on the formation of P_xI from PI_3 in oxygen

Furnace temp. °C	70*	175	250	300
Loss %	77.5	79.3	82.6	82.4
Moles % via (1)	53.2	56.0	73.0	62.6
Value of x	1.5	2.2	2.7	2.8

* normal initiation temperature

The P_xI species appears to be resistant to oxidation and only at temperatures in excess of 350° did a further slow loss of iodine occur. The reaction (2) is apparently not due to oxygen starvation as increased oxygen flow did not significantly alter the results. Decomposition of P_2I_4 in nitrogen follows the path:

$$P_2I_4 \rightarrow 4/3\, PI_3 + 2/3\, n\, P_n \tag{3}$$

required for (3) loss % 96.3, residual P% 3.6. The oxidation reaction follows the conversion to free iodine and phosphorus pentoxide:

$$P_2I_4 + 5/2O_2 \rightarrow P_2O_5 + 2\,I_2 \tag{4}$$

required for (4) loss % 75.3, residual P% 10.9. A small and variable amount of iodine, 0.2–0.9%, was detected in the residue.

Under nitrogen, the TG curve of $P_3I_2O_6$ showed two distinct weight loss regions with elemental iodine observed in the second stage only. The final iodine-free residue was phosphorus pentoxide, found P% 42.9, required P% 43.6. Analysis (Table 1) showed that 0.20 g atom of phosphorus per g atom initially present in $P_3I_2O_6$ was lost from the system. This observation together with the total weight loss of 60.7% defines the overall reaction as:

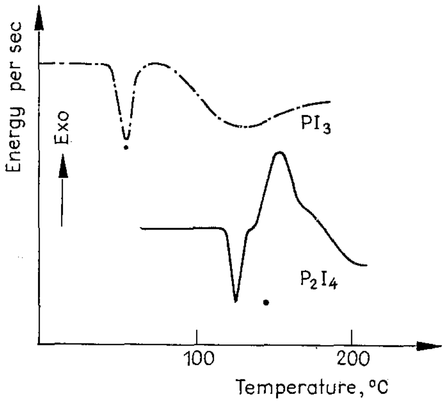


Fig. 3. DSC of PI_3 and P_2I_4 in nitrogen

$$5/n\,(P_3I_2O_6)_n \rightarrow 3\,PI_3 + 1/2\,I_2 + 6\,P_2O_5 \tag{5}$$

required for (5), loss % 61.5. The separate stages are interpreted as initial loss of 2 PI_3, required loss 38.3%, and subsequent loss of PI_3 and 1/2 I_2, required loss 24.4%. The oxidation reaction also showed a two stage reaction corresponding to the oxidation of the PI_3 proposed in (5), thus:

$$PI_3 + 5/4\,O_2 \rightarrow 1/2\,P_2O_5 + 3/2\,I_2$$

The overall reaction follows the route:

$$5/n\,(P_3I_2O_6)_n + 25/4\,O_2 \rightarrow 5\,I_2 + 6\,P_2O_5 \tag{6}$$

required for (6) loss % 51.9, residual P% 21.0. The residue contained 44.6% P. The nature of the intermediate in both nitrogen and oxygen remains unknown as it reacted instantly with moisture of the atmosphere on being withdrawn from the thermobalance.

The DSC results are shown in Figures 3 and 4. PI_3 in nitrogen gives a simple endothermic melt transition followed by endothermic removal of PI_3. The oxidation also proceeds via an initial melt followed by endothermic removal of some PI_3 before a strongly exothermic oxidation to iodine and phosphorus pentoxide [reaction (2)] occurs. In nitrogen P_2I_4 also shows an initial melt endotherm followed by exothermic rupture of the phosphorus–phosphorus bond [reaction (3)]. In oxygen the initial melt endotherm is drastically curtailed by the large exothermic conversion to phosphorus pentoxide and iodine. The polymeric $P_3I_2O_6$ proved to be too spontaneously reactive to afford a consistent DSC pattern. Measurement of the melt endotherms gave the following values for heats of fusion:

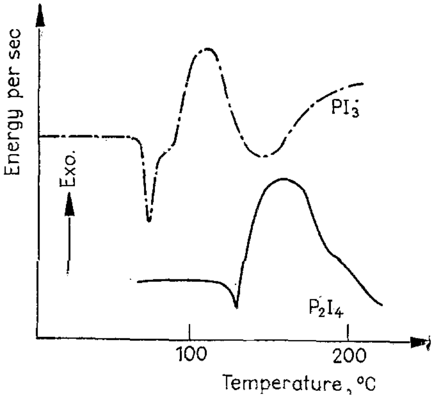


Fig. 4. DSC of PI_3 and P_2I_4 in oxygen

	PI_3	P_2I_4
$\Delta H_{(fusion)}$ (KJ mol^{-1})	10.9	17.2

Discussion

It is noteworthy that the reactions of PI_3 and P_2I_4 in both nitrogen and oxygen become significant at a temperature close to the corresponding melting-points (61° and 127°). The oxidation of P_2I_4 results from direct attack on the P–P bond rather than its initial rupture

$$P_2I_4 \rightarrow 4/3\ PI_3 + 2/3\ n\ P_n \qquad (3)$$

and subsequent oxidation of the product PI_3. This view is supported by the absence of iodine in the residue of oxidised P_2I_4 comparable with that found in PI_3 oxidation and the observation that red phosphorus does not undergo oxidation on the thermobalance until a temperature of >350° is reached. However, the small and variable iodine content of the residue may indicate a very small contribution from reaction (3) which, on the basis of the results given in Table 2, amounts to approximately four per cent. The oxidation of P_2I_4 in carbon disulphide has been reported [8] as:

$$7\,P_2I_4 + 6\,O_2 \rightarrow 2/n\,(P_3I_2O_6)_n + 8\,PI_3$$

It is possible that in the solid phase, there is initial oxidation of P_2I_4 to produce $P_3I_2O_6$ and loss of PI_3. The initially formed $P_3I_2O_6$ then undergoes further oxidation by route (6). However, since $P_3I_2O_6$ shows two weight-loss regions in oxygen which did not occur in the oxidation of P_2I_4, this decomposition route is rejected.

Phosphorus-iodine polymeric species have been reported in a previous photolysis study of P_2I_4 and PI_3 in cyclohexane in which PI_2 radicals play a controlling role [5]

$$PI_3 \xrightarrow{h\nu} PI_2 + I$$

$$PI_3 + I \rightarrow PI_2 + I$$

$$PI_2 + PI_3 \rightarrow P_2I + 2\,I_2$$

It is unlikely that this mechanism occurs in the liquid phase under oxygen. The polymeric species found in the normal oxidation of PI_3 approximates to the composition P_3I_2 which is similar to the range of compositions, P_5I_3 to $P_{10}I_9$, found in the photolysis study. The higher P/I compositions occurring at high furnace temperatures and approximating to P_3I may result from a higher degree of cross-linking in the phosphorus skeleton. A composition, P_3I, has been reported from the reaction between phosphonium iodide and phosphorus(V) chloride [8].

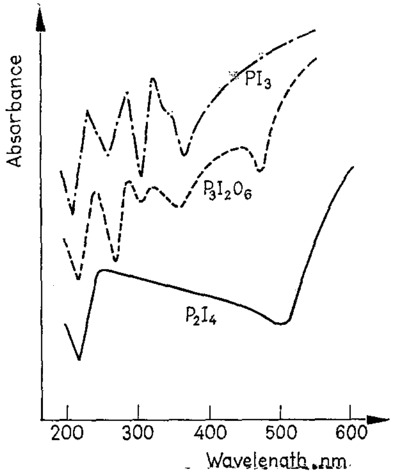
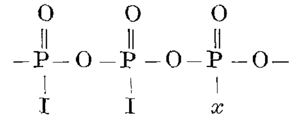


Fig. 5. Diffuse reflectance spectra of PI_3, P_2I_4 and $P_3I_2O_6$

The production of PI_3 from the decomposition of polymeric $P_3I_2O_6$ in nitrogen is difficult to reconcile with the proposed essential structural unit [9]:



$$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle I}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle I}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle x}{|}}{P}}-O-$$

The oxidation reaction can be explained if the PI_3 proposed as product in reaction (5) is fully oxidised but does not require its initial formation and subsequent oxidation; the absence of residual iodine supports this view. It is interesting that the composition $P_3I_2O_6$ approximates to $2\,P_2O_5 \cdot PI_3$ $(P_3I_{1.8}\,O_6)$. The diffuse reflectance spectra (Fig. 5) indicate certain similarities between $P_3I_2O_6$ and PI_3 although the far I.R. spectrum is inconclusive showing one peak, 299 nm, in common with PI_3, one peak, 330 nm, in common with P_2I_4 and a third, 315 nm, shown by neither.

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Résumé — On décrit la décomposition thermique, dans l'azote et dans l'oxygène, de PI_3 et de P_2I_4 cristallins. L'oxydation de PI_3 conduit principalement à la formation d'iode et de pentoxyde de phosphore, avec de petites quantités de P_xI de type polymère. La décomposition de l'espèce polymère $P_3I_2O_6$, dans l'oxygène et dans l'azote, s'effectue suivant un processus en deux étapes excluant sa participation à l'oxydation de P_2I_4.

Zusammenfassung — Es wurde die thermische Zersetzung von kristallinem PI_3 und P_2I_4 in Stickstoff und Sauerstoff untersucht. Die Oxydation von PI_3 führt zur Bildung von Phosphorpentoxyd und Jod mit wenig Polymeren der Zusammensetzung P_xI. Die Zersetzung der Polymeren $P_3I_2O_6$ in Sauerstoff und Stickstoff erfolgt in zwei Stufen, die eine Beteiligung in der Oxydation von P_2I_4 ausschließen.

Резюме — Описан термораспад кристаллических веществ PI_3 и P_2I_4 в атмосфере азота и кислорода. При окислении PI_3, главным образом, образуется пятиокись фосфора и йода, а также — в небольшом количестве — соединения P_xI полимерного типа. Распад полимерных видов $P_3I_2O_6$ в кислороде и азоте происходит по двухстадийному пути, что устраняет их помехи при окислении P_2I_4.