289. *The Oxidation of Triethylphosphine.*

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The measurements to be described are a continuation of others recently published (this vol., pp. 746, 756) in which the oxidation of substances containing alkyl radicals was described. The objects of such investigations were discussed in the earlier papers.

No systematic work has been reported upon the oxidation of triethylphosphine. Cahours and Hofmann (*Annalen*, 1857, **104**, 9) noticed that the vapour was oxidised in air, forming a white cloud. In the presence of water the product of oxidation was regarded as the oxide $P(C_2H_5)_3O$, but it was also possible that the peroxide $P(C_2H_5)_3O_2$ was formed. Jorissen (*Z. physikal. Chem.*, 1897, **22**, 35), Engler (*Ber.*, 1897, **30**, 1670), and Engler and Weissberg (*Ber.*, 1898, **31**, 3055) observed an explosive oxidation in which a colourless oil was formed, having weakly peroxidic properties, and later affording crystals indicated by analysis to be a mixture of the oxide and ethoxydiethylphosphine oxide, $PEt_2O(OEt)$. The reactions suggested were: $PEt_3 + O_2 \longrightarrow PEt_3O_2$; $PEt_3 + PEt_3O_2 \longrightarrow 2PEt_3O$; $PEt_3O_2 + PEt_3O \longrightarrow 2PEt_2O(OEt)$ or $PEt_3O_2 \longrightarrow PEt_2O(OEt)$.

Measurements have recently revealed that the oxidation of phosphine occurs only between definite critical pressures of the reacting gases, and then explosively. Outside this region the interaction is negligible. The details of the process have been examined by Dalton and Hinshelwood (*Proc. Roy. Soc.*, 1929, **125**, *A*, 294; 1930, **128**, *A*, 263), by Dalton and by Melville and Ludlam (*ibid.*, 1931, **132**, *A*, 108); the results are summarised as follows.

The abrupt transitions from low rate to explosion at the pressure limits can be interpreted satisfactorily in terms of the theory of branching chains, the lower limiting pressure being that at which the chains begin to multiply more rapidly than they are broken on the vessel walls. A simple theory leads to the following relationship at the lower limit:

$$p_{O_2}p_{PH_3}[1 + p_{\text{inert gas}}/(p_{O_2} + p_{PH_3})]d^2 = K$$

where d is the diameter of the cylindrical reaction vessel. This expression, which ignores specific action of inert gases, was modified by Melville (*Trans. Faraday Soc.*, 1932, **28**, 308, 814) to

$$p_{O_2}p_{PH_3}[1 + D^{-1}\, p_{\text{inert gas}}/(p_{O_2} + p_{PH_3})]d^2 = K$$

which applies at any temperature, D being a measure of the diffusion coefficient of active centres through the particular inert gas employed, and subsequently to an expression in which D^{-1} is replaced by μ, a measure of the mass and size of the active centres. The experiments with different inert gases indicate clearly that the chains are being broken on the vessel walls.

There are, however, complications in the process which make the simple theory incomplete. For example, in the absence of inert gases the product $p_{O_2}p_{PH_3}$ is not strictly constant; nor is the influence of vessel diameter exactly as the equations would suggest. These subsidiary deviations are probably to be explained by the facts that reaction chains are also in some measure terminated in the gas, and that it is difficult to maintain a uniform surface.

Essentially similar phenomena have now been observed in the oxidation of triethylphosphine, though again there are complications. There is a critical region of pressure for explosion, and the lower limiting pressure is affected by the presence of inert gases and by the vessel dimensions qualitatively, at least, as would be expected. With pressures outside the critical region there is in general no appreciable pressure change over long periods, but occasionally a reaction with pressure decrease can be followed. This is not reproducible and appears to be largely dependent upon the surface. There is reason to believe that the active centres required for the propagation of the chains originate on the vessel walls, and whilst inert gases affect the explosion pressures in such a way as to imply breakage of the chains on the walls, there is nevertheless indication that gaseous deactivation is also important.

EXPERIMENTAL.

Triethylphosphine, supplied by Schuchardt and by Kahlbaum in sealed tubes, was transferred by pouring in an atmosphere of nitrogen into the vessel required, frozen by solid carbon dioxide–acetone, the vessel sealed, and the nitrogen pumped off.

The experimental procedure was similar to that employed in the oxidation of diethylzinc (*loc. cit.*), the pressure changes being followed on a mercury manometer, and the apparatus wired and electrically heated so as to be about 60°. The reaction vessel was again suspended in an oil-bath maintained at the desired temperature.

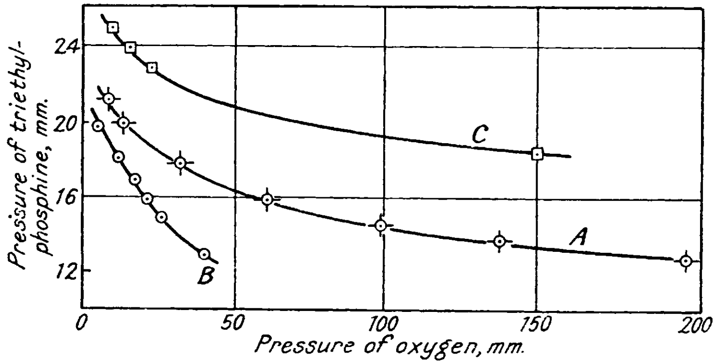
As in the previous experiments with the zinc alkyls, the reactivity of a sample increased as the early fractions were removed, but redistillation of the " pure " triethylphosphine gave no indication of a recognisable impurity. The significance of this inertness of the early fractions is not clear. It is quite certain that the phenomena noticed are due to some property of the triethylphosphine and not, *e.g.*, to variable surface effects. Reproducible and uniform results were obtained only with the second half of the samples, and the consequent waste of material has hindered the progress of the work. Sufficient evidence has, however, been obtained to indicate the general features of the phenomena.

Results.

The Explosive Reaction.—Provided that the pressure of triethylphosphine exceed a certain minimum value, there exists for a given concentration of this reactant at a given temperature a critical pressure of oxygen above which explosion occurs. There is conversely a critical pressure of the phosphine for any given oxygen pressure. Of the two reactants, the phosphine is apparently far more effective in promoting explosion, since a small decrease in concentration of this substance is only compensated by a large increase in the oxygen concentration.

FIG. 1.

Influence of temperature and vessel dimensions upon explosion pressures.



The similarity of this explosion " limit " to that observed in " branching-chain " explosions is indicated by experiments in which, with pressures of the reactants just lower than the critical values, no pressure change is observed over long periods; a small increase in the triethylphosphine concentration leads to immediate explosion. The critical pressures are decreased by rise of temperature or by increase in the vessel diameter.

The critical pressures were compared at two temperatures, 50° and 60°, in a reaction vessel 2·5 cm. in diameter, and were also determined in a vessel 3·4 cm. in diameter at 60°. The results are shown in Table I and plotted in Fig. 1. Values of $p_{\mathrm{PEt}_3}p_{\mathrm{O}_2}$ are also given; they

TABLE I.

A. Vessel, 2·5 cm. diameter. Temp., 60°.				B. Vessel, 3·4 cm. diameter. Temp., 60°.				C. Vessel, 2·5 cm. diameter. Temp., 50°.			
p_{PEt_3}, mm.	p_{O_2}, mm.	$p_{\mathrm{PEt}_3} \times p_{\mathrm{O}_2}$.	$p_{\mathrm{PEt}_3} \times \sqrt[6]{p_{\mathrm{O}_2}}$.	p_{PEt_3}, mm.	p_{O_2}, mm.	$p_{\mathrm{PEt}_3} \times p_{\mathrm{O}_2}$.	$p_{\mathrm{PEt}_3} \times \sqrt[6]{p_{\mathrm{O}_2}}$.	p_{PEt_3}, mm.	p_{O_2}, mm.	$p_{\mathrm{PEt}_3} \times p_{\mathrm{O}_2}$.	$p_{\mathrm{PEt}_3} \times \sqrt[6]{p_{\mathrm{O}_2}}$.
21	6	126	28·3	20	3	60	24·0	25	7	175	34·7
20	14	280	31·0	18	12	216	27·2	24	13	312	36·7
18	36	648	32·7	17	16	272	27·0	23	25	575	39·3
16	64	1024	32·0	16	20	320	26·4	19	150	2850	43·7
15	98	1470	32·2	15	25	375	25·7				
14	140	1960	31·4	13	45	585	30·9				
13	200	2600	31·9								

are not constant as might have been expected on theoretical grounds. The function of the pressures which is most nearly constant is $p^6_{\mathrm{PEt}_3}p_{\mathrm{O}_2}$.

Another series indicates how the total critical pressure at the lower limit for an equal-volume mixture of triethylphosphine and oxygen varies with temperature :

Temp.	100°	90°	80°	60°	50°	42°
PEt_3, mm.	12	13	16	20	24	27
$\mathrm{PEt}_3 + \mathrm{O}_2$, mm. ...	24	26	32	40	48	54

The products of the explosion vary : broadly speaking, according as the oxygen pressure is greater or less than half that of the phosphine there results either an increase or a decrease in pressure, and this change is roughly equal to the initial oxygen pressure if this is not too relatively high. A flash accompanies the explosion only when there is an increase in pressure. The gaseous products probably consisted of carbon monoxide and hydrocarbons. A colourless oil was also formed, which later became yellow, owing presumably either to a decomposition or to the accumulation of a yellow product formed in the explosion. After long standing, colourless needle-shaped crystals separated from the oil. Typical data are given in Table II, where the pressure change is recorded in mm. and also as a percentage of the oxygen pressure.

FIG. 2.

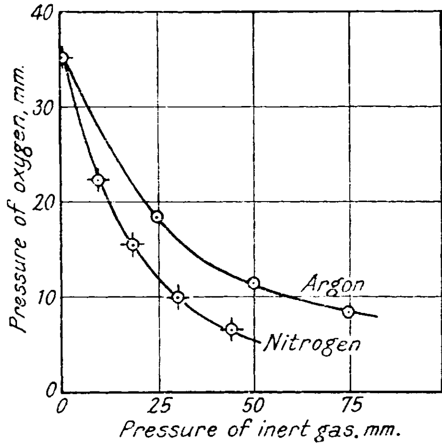


FIG. 3.

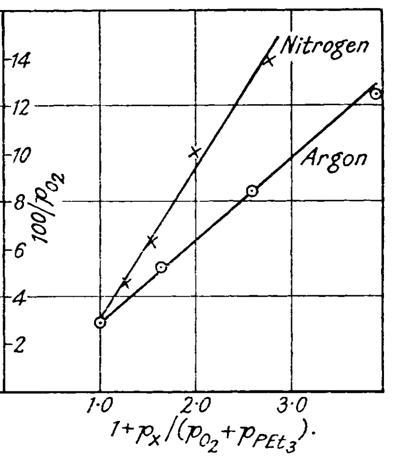


FIG. 2.—*Effect of inert gas upon explosion limits.* $p_{\mathrm{PEt}_3} = 18$ mm.

TABLE II.

PEt_3, mm.	O_2, mm.	Press. change, mm.	Press. change, % of O_2.	PEt_3, mm.	O_2, mm.	Press. change, mm.	Press. change, % of O_2.
19	43	+50	+116	22	9	−10	−110
15	35	+34	+ 97	19	8·5	− 8·5	−100
35	31	+30	+ 97	30	6	− 6	−100
28	30	+31	+103				
18	22	+20	+ 91	26	16	− 6	− 38
20	14	+ 3	+ 21	26	12	− 4	− 33
28	11	−11	−100	22	10	− 4	− 40
21	10	−12	−120				

In the presence of inert gases the critical pressures of triethylphosphine and oxygen are lowered. The effect was studied with argon and nitrogen (from cylinders) in a vessel 2·5 cm. in diameter and at 60°. With a fixed pressure of triethylphosphine, the manner in which the required oxygen pressure was lowered on adding the inert gas was examined. The data are summarised in Table III and also in Fig. 2. In Fig. 3 the graph of $1/p_{\mathrm{O}_2}$ against $[1 + p_{\text{inert gas}}/(p_{\mathrm{O}_2} + p_{\mathrm{PEt}_3})]$ is seen to be nearly linear.

The explosion is, in general, preceded by an induction period, which may extend over 1—2 mins. For a given triethylphosphine pressure, the induction period is shortened by increase in the pressure of oxygen.

The Non-explosive Reaction.—With initial pressures lower than those leading to explosion there is usually no measurable reaction. It might be argued that the occurrence of a very long

TABLE III.

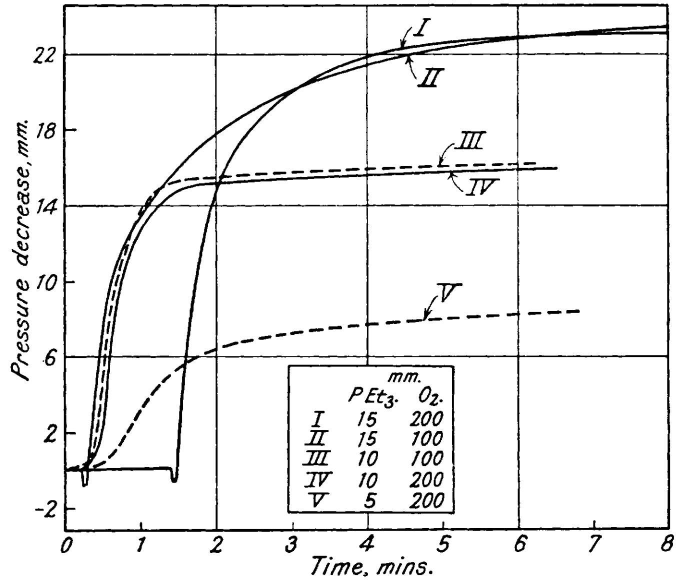
Temperature 60°. Pressure of triethylphosphine, 18 mm.

Argon.				Nitrogen.			
p_A.	p_{O_2}.	$1/p_{O_2}$.	$1 + \frac{p_A}{p_{O_2} + p_{PEt_3}}$.	p_{N_2}.	p_{O_2}.	$1/p_{O_2}$.	$1 + \frac{p_{N_2}}{p_{O_2} + p_{PEt_3}}$.
0	35	0·028	1·0	0	36	0·028	1·0
25	19	0·0525	1·7	10	22	0·045	1·25
50	12	0·083	2·67	20	16	0·0625	1·59
75	8	0·125	3·9	28	10	0·10	2·0
				45	7	0·14	2·8

induction period masks the detection of a reaction, but this is extremely unlikely, for the reaction mixtures were observed over long periods.

If the partial pressure of oxygen in the mixture is high, however, it is sometimes possible to observe a measurable reaction at pressures below the explosion limits. This reaction is not reproducible either in occurrence or in general course. Usually when it occurs at all, it is fairly fast and proceeds to a definite end-point. At first it was thought that this reaction could only be observed within a narrow range of pressures just below the lower critical limit; subsequently, however, exceptions were noted.

FIG. 4.



The results suggest that the course of the reaction is primarily determined by the state of the vessel walls; the estimated order is zero, but it is doubtful whether this has any significance. In one respect the reaction is reproducible, for the pressure decrease, Δp, is usually 150% of the initial pressure of triethylphosphine (Table IV). Some typical runs are shown in Fig. 4. The product of the measurable reaction is a colourless oil.

TABLE IV.

Temperature, 60°.

Vessel diameter, 2·5 cm.					Vessel diameter, 3·5 cm.				
p_{PEt_3}. mm.	p_{O_2}, mm.	Induction period, secs.	Δp, mm.	Δp, as % of p_{PEt_3}.	p_{PEt_3}, mm.	p_{O_2}, mm.	Induction period, secs.	Δp, mm.	Δp, as % of p_{PEt_3}.
15	200	15	23	153	10	97	12	15·8	158
15	100	90	23	153	10	81	10	17	170
10	200	21	15·5	155	10	45	19	15	150
10·5	100	18	15·5	148	10	43	10	16	160
5	200	30	7·5	150					

DISCUSSION.

It is clear that limit phenomena are involved in the oxidation of triethylphosphine ; the lower critical pressure for explosion is well established. That a measurable reaction at lower pressures is occasionally observed is not contrary to this result, since it appears to be a surface rather than a gaseous reaction. It seems, however, that the relationships are more involved than in the oxidation of phosphine or in other reactions which exhibit explosion limits.

The influence of inert gases reveals that they may primarily function by decreasing the possibility of deactivation on the vessel walls. That the product $p_{PEt_3}p_{O_2}$ is not constant at any given temperature in a given vessel in the absence of inert gas, may be due to the fact that there is also gaseous deactivation of some kind, or alternatively, the much larger size of the triethylphosphine molecule may lead to abnormal effects.

It seems likely that oxygenated products are concerned in the reaction chains, but there is no direct proof of this. Melville (*Trans. Faraday Soc.*, 1932, **28**, 814) has attempted to calculate μ (see p. **1231**) in the various reactions from the data on the inert-gas effect. The results for argon and nitrogen in several cases are given below :

Calculated values of μ.

	H_2–O_2.	PH_3–O_2.	CS_2–O_2.	P_4–O_2.	CO–O_2.
A	1·5 or 1·16	0·9	0·64	0·46	1·2
N_2	1·9 or 2·35	0·3	0·42	0·37	0·6

It is questionable whether the general theory should be applied to a calculation of μ in the oxidation of triethylphosphine because, in the absence of inert gases, the product $p_{PEt_3}p_{O_2}$ is not constant. In spite of this it might be legitimate to plot the lines in Fig. 3 since the pressure of triethylphosphine was constant. Assuming the validity of the equation

$$\frac{1}{p_{PEt_3}'p_{O_2}'} = \frac{1}{p_{Et_3}p_{O_2}}\left(1 + \frac{\mu p_X}{p_{PEt_3} + p_{O_2}}\right)$$

one obtains the following values: $\mu_A = 1{\cdot}2$; $\mu_{N2} = 2{\cdot}4$. These are noticeably higher than those calculated for other reactions, and it would be logical to infer that in this reaction the active centres have a relatively high mass, *i.e.*, may consist of oxygenated products of a peroxidic character. It is, however, not certain how much importance should be attached to this result, for a later series of experiments using carbon dioxide as inert gas gave an apparently low slope for the graph, and $\mu = 0{\cdot}64$. The data are given below :

Temperature 60°. Pressure of triethylphosphine 18 mm.

p_{CO_2}, mm.	0	20	43
p_{O_2}, mm.	36	29	20

The anomalies may, however, arise in consequence of gaseous deactivation processes. Originally the remarkable agreement between theory and experiment was discovered in reactions, such as the oxidation of phosphine, where much smaller total pressures are involved than in the present case. The extent to which surface deactivation, and hence diffusion effects, will be important should decrease as the pressure increases, and it is reasonable to assume that at the higher pressures some gaseous collisions will lead to deactivation. In particular, inert gases such as nitrogen and argon may therefore be deactivators as well as agents which retard diffusion, and the above approximation to linearity may be somewhat fortuitous.

The following cycle of changes is suggested as leading to equations and relationships closely similar to those found :

(1) $PEt_3 + O_2 \longrightarrow$ active centre A
(2) $A + O_2 \longrightarrow$ inactive molecules
(3) $A +$ wall $\longrightarrow$,, ,,
(4) $A + N_2 \longrightarrow$ inactive molecules
(5) $A + PEt_3 \longrightarrow$ products $\longrightarrow \alpha A$

(1) represents the formation of reaction centres in a reaction between triethylphosphine and oxygen: this may occur in the gas phase or on the vessel walls; (2) expresses a deactivation by oxygen, (3) by the wall, (4) by nitrogen; (5) leads to the final product and a cycle of changes as a result of which α fresh active centres arise from each original one.

Then, for a stationary state,

$$\frac{d[A]}{dt} = k_1[O_2][PEt_3] - k_2[O_2][A] - k_3[A] - k_4[A][N_2] - k_5[A][PEt_3] + \alpha k_5[A][PEt_3] = 0$$

whence
$$[A] = \frac{k_1[PEt_3][O_2]}{k_3 + k_2[O_2] + k_4[N_2] + (1 - \alpha)k_5[PEt_3]}$$

If the rate is determined primarily by (5),

$$\text{rate} = k_5[A][PEt_3] = \frac{k_1 k_5[PEt_3]^2[O_2]}{k_3 + k_2[O_2] + k_4[N_2] + (1 - \alpha)k_5[PEt_3]}$$

Hence, for a sudden transition to explosion, *i.e.*, at the "limit,"

$$k_3 + k_2[O_2] + k_4[N_2] + (1 - \alpha)k_5[PEt_3] = 0 \quad . \quad . \quad . \quad . \quad (6)$$

In the absence of inert gases, this becomes

$$k_3 + k_2[O_2] + (1 - \alpha)k_5[PEt_3] = 0$$

As already explained, the experiments show that in a given vessel at a given temperature $[PEt_3][O_2]^{1/6}$ is approximately constant. This result can be expressed in the form $[PEt_3][O_2]/(a + b[O_2]) = \lambda$ where a and b are suitable coefficients. Then

$$a\lambda + b\lambda[O_2] - [O_2][PEt_3] = 0.$$

This relationship is similar to that required by the theory, *viz.*,

$$k_3 + k_2[O_2] - (\alpha - 1)k_5[PEt_3] = 0.$$

Identity of the two equations would imply a proportionality between $(\alpha - 1)$ and $[O_2]$, *i.e.*, the efficiency of chain propagation should be proportional to the oxygen concentration. If deactivation by means of (2) were not operative, this proportionality might be easily understood; but if gaseous deactivation plays an important part (similarity of the terms $b\lambda[O_2]$ and $k_2[O_2]$) it is not so obviously explained. It seems probable that oxygen can act in both ways, but that the gaseous deactivating influence is the less important.

The above chain scheme and the resulting equation (6) give a qualitative interpretation of the depression of the oxygen concentration by increase in inert-gas concentration. With nitrogen as inert gas, the total pressure ($p_{N_2} + p_{O_2}$) at the limit is approximately constant. This may imply a rough equality of k_2 and k_4, the velocity coefficients of deactivation by oxygen and by nitrogen respectively, a result which might be expected.

Note.—In an attempt to use sulphur dioxide as an inert gas, it was found to react with triethylphosphine. The pressure decrease was 200% of the initial phosphine pressure when the dioxide was in excess, and the "order" about unity with respect to each reactant. This reaction was not examined further.

SUMMARY.

The oxidation of triethylphosphine vapour is a chain reaction. Explosion occurs within a critical range of pressure. Outside this critical region, reaction is slight and, when it occurs at all, is determined by surface conditions. The influence of vessel dimensions, temperature, and inert gases upon the critical pressures for explosion is qualitatively in accordance with that to be expected, but there are complications; *e.g.*, deactivation in the gaseous phase is probably important as well as that occurring on the vessel walls.

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