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## The Photochemical Oxidation of Phosphine above the Upper Explosion Limit

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An investigation has been made of the kinetics of the photochemical oxidation of phosphine above the upper explosion limit. The results are summarized by the equations

Mercury sensitized reaction  $-d[\text{PH}_3]/dt$   
 $= \text{const. } [\text{PH}_3]/[\text{O}_2]^2 \text{ intensity.}$

Direct photo-reaction  $-d[\text{PH}_3]/dt = \text{const. } [\text{PH}_3]^2/[\text{O}_2]^2.$

The reactions are shown to be of the chain type and inhibited by oxygen. On the basis of previous knowledge of the propagation of the chains, the question of termination was examined and it is shown that out of six possible cases, only one is in agreement with the experimental facts. This is that the chain carrier, which normally reacts with phosphine, is destroyed in a ternary collision with two oxygen molecules or with one oxygen and one nitrogen

molecule (or an argon atom). The efficiency of the collision is about 0.5. In view of these results, it is highly probable that this carrier is an oxygen atom. In the photosensitized reaction one-fifth of the collisions between oxygen molecules and excited mercury atoms results in the initiation of a chain. These results are shown to be quantitatively consistent with the shape and also the position of the upper limiting explosion curve, except that the limiting pressure is a little higher than that calculated by a strict application of the theory of branched chains. The upper limit is displaced to higher pressures by illumination of the mixture, a phenomenon not predicted by theory. The effect is of short duration, <2 sec. and it is not exhibited at the lower limit. The significance of this result is discussed in relation to the theory of the reaction.

THE introduction of the conception of branching chains and of the diffusion of chain carriers to the walls into the theory of thermal chain reactions has provided an acceptable picture of the mechanism of many oxidation reactions. While much experimental work has revealed the essential similarity underlying these reactions there are many corollaries to the theory which have yet to be explored in detail. The difficulty, in many cases, is experimental; in others, it is not at present quite certain whether factors not at all included in the chain theory prevent to some extent its rigorous application. For example, there is a possibility that sharp explosion limits may be due to causes other than simple branching of the reaction chains.

One of the corollaries is the following: It is postulated that the condition for explosion is that the product of the probabilities of branching and termination be equal to unity. The limits should consequently be independent of the rate of starting of the chains, provided that there is actually some reaction taking place.

A second is concerned with the mechanism of the reaction outside the explosion limits. In the quantitative application of the theory, expressions are derived which give the stationary

concentration of the carriers for any pressure. It happens, however, that in the thermal reaction, the rate of starting is often so small that a stable reaction is never observed. Sometimes, the stable is masked by a relatively fast heterogeneous reaction.

The reaction between phosphine and oxygen is particularly well suited to answer some of these questions. Its mechanism is undoubtedly complicated, but the general chain features which it exhibits are in very good agreement with the theory. Moreover, it has the further advantage that the propagation collisions are nearly one hundred percent efficient and thus do not require any energy of activation.<sup>1</sup> The correlation between the kinetics below and at the lower limit has been fairly fully established.<sup>1, 2</sup> No experiments have, however, been carried out above the upper limit except a preliminary set<sup>3</sup> where a complete analysis was not attempted. Such an analysis was necessary in order to establish a relationship between the two conditions.

In this connection, curious results have been obtained by Grant and Hinshelwood<sup>4</sup> at the upper limit in the hydrogen-oxygen reaction.

<sup>1</sup> Melville, Proc. Roy. Soc. **A139**, 555 (1933).

<sup>2</sup> Dalton and Hinshelwood, Proc. Roy. Soc. **A125**, 294 (1929); Melville, *ibid.* **A138**, 374 (1932).

<sup>3</sup> Melville and Roxburgh, Nature **131**, 690 (1933).

<sup>4</sup> Grant and Hinshelwood, Proc. Roy. Soc. **A141**, 29 (1933).

\* Senior Student, Exhibition of 1851.

The limit is apparently governed by some form of gas phase inhibition, for argon and helium lower the upper explosion pressure. Above the limit, however, there is a stable reaction in which the same gases accelerate the reaction rate showing that the chains now end on the walls. It was thought at first that two entirely different mechanisms were in operation, for obviously, one of the conditions for the appearance of an upper limit is that the chain length should increase with decreasing pressure, whereas the kinetics of the stable reaction indicated that the chain length probably increased with pressure. The explanation apparently is that the decrease in chain length is more than compensated for by the increase in the probability of branching as the pressure is reduced.

It was thought that instead of employing photochemical means of artificially increasing the rate of starting, the introduction of a hot filament might prove just as suitable and at the same time provide detailed information about the heterogeneous starting of chain reactions. Unfortunately, the reaction is almost wholly heterogeneous<sup>5</sup> and so photo-initiation had to be employed.

#### THE THEORY OF THE STABLE REACTIONS

The theory has been worked out for the kinetics at the explosion limits<sup>6</sup> but to apply it to the stable reactions requires some modification. Before deriving the equations for a number of assumptions, it is necessary to examine the simplifications which were made in the original theory. It was assumed that both carriers  $X_o$  and  $X_p$  are equally well removed by collision with the walls and that the rates of reaction with phosphine and with oxygen, respectively, are the same. There is a considerable amount of evidence that these assumptions are sufficiently exact for the purposes of calculation. For example, the theoretical and observed chain lengths below the lower limit are in good agreement, and the second postulate must be nearly true. If one carrier were more easily destroyed than the other, then it can easily be shown that the lower explosion limit equation would be

$$[PH_3]\{[PH_3]+[O_2]\} = \text{const.} \quad (1)$$

or

$$[O_2]\{[PH_3]+[O_2]\} = \text{const.}, \quad (2)$$

which is not in so good accordance with experiment as the equation  $[PH_3][O_2] = \text{const.}$  Below the lower limit, the stationary concentrations of the carriers are given by

$$\begin{aligned} d[X_o]/dt &= I + k[X_p][O_2] + k[X_o][PH_3] \\ &\quad - K[X_o] = 0, \end{aligned} \quad (3)$$

$$\begin{aligned} d[X_p]/dt &= k[X_o][PH_3] - k[X_p][O_2] \\ &\quad - K[X_p] = 0 \end{aligned} \quad (4)$$

and therefore

$$-d[PH_3]/dt = (k[PH_3][O_2]/K') \cdot I, \quad (5)$$

where  $K = K'/([PH_3] + [O_2])$ ,  $K$  being a constant and  $I$  the rate of starting.

Above the upper limit, there are a number of ways in which  $X_o$  and  $X_p$  may be destroyed. One of the objects of this investigation is to determine the kinetics of the reaction in order that an unequivocal choice may be made from among the possible mechanisms, and further to see whether the mechanism so chosen is consistent simultaneously with the position and shape of the upper limit curve.

There are six possible ways whereby the carriers could be destroyed

- |                    |            |                    |            |
|--------------------|------------|--------------------|------------|
| 1. $X_o + X$       | ( $k_4$ ), | 4. $X_p + X$       | ( $k_7$ ), |
| 2. $X_o + X_o + X$ | ( $k_5$ ), | 5. $X_p + X_p + X$ | ( $k_8$ ), |
| 3. $X_o + X + X$   | ( $k_6$ ), | 6. $X_p + X + X$   | ( $k_9$ ). |

$k$  is the velocity coefficient and  $X$  is either  $PH_3$  or  $O_2$  or any other molecule which may have been added to the gas mixture. Three examples of each case will be worked out *viz.*, (a) mercury sensitized initiation; in addition to the dissociation of the  $PH_3$  by  $Hg(^3P_1)$ , it may also happen that oxygen is activated in such a manner as to start chains, and there are therefore two equations for this kind of initiation, (b) direct photo-dissociation of the  $PH_3$ .

This procedure of examining each possibility is adopted in order to meet a criticism which is often advanced against the interpretation of kinetic results, namely, that two or more mechanisms may lead to the same equation. This occurs, in fact, in the present analysis, but fortunately there are means by which an unambiguous choice can be made.

<sup>5</sup> Melville and Roxburgh, J. Chem. Soc. 586 (1933); 264 (1934).

<sup>6</sup> See, e.g., Hinshelwood, *Kinetics*, 3rd edition, p. 264.

**Case 1**

The equations for  $[X_O]$  and  $[X_P]$  are

$$d[X_O]/dt = I + k[X_P][O_2] - k[X_O][PH_3] - k_4[X_O][X] = 0, \quad (6)$$

$$d[X_P]/dt = k[X_O][PH_3] - k[X_P][O_2] = 0. \quad (7)$$

For the mercury sensitized reaction, phosphine being dissociated

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n[PH_3]}{[PH_3] + 0.5[O_2] + 0.37}. \quad (8)$$

The constant 0.37 (allowing for the radiation of resonance light) is calculated for the case where  $[PH_3]$  and  $[O_2]$  are expressed in mm of mercury, for a 2 cm tube and a mercury vapor pressure of 0.001 mm,<sup>7</sup>  $I_n$  is proportional to the intensity of the 253.7 m $\mu$  line from the mercury lamp. One important simplification can now be made. In the region above the upper limit where the phosphine pressure is low, that of the oxygen is so high that X in the above reaction scheme may be considered to be  $O_2$ . Eq. (8) can thus be simplified to

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2]^2) \cdot I_n. \quad (9)$$

For mercury sensitization with initiation by oxygen,

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_4[O_2]} \cdot \frac{I_n \cdot \{A \cdot [O_2] \cdot 0.5 + [PH_3]\}}{[PH_3] + 0.5[O_2] + 0.37} = \frac{k[PH_3]}{k_4[O_2]} \cdot I_n, \quad (10)$$

where  $A$  is defined as the number of chains started per excited mercury atom which is deactivated by oxygen. For the direct dissociation,

$$-d[PH_3]/dt = (k[PH_3]^2/k_4[O_2]) I_n. \quad (11)$$

**Case 2**

The last term in the equation for  $X_O$  will now be  $-k_5[X_O]^2[X]$  and therefore

$$I = k_5[X_O]^2[X]. \quad (12)$$

Mercury sensitization ( $PH_3$ )

$$-\frac{d[PH_3]}{dt} = k[PH_3] \left\{ \frac{[PH_3] \cdot I_n}{k_5[X]([PH_3] + 0.5[O_2] + 0.37)} \right\}^{\frac{1}{2}} = \frac{k[PH_3]^{\frac{3}{2}}}{[O_2]} \left( \frac{I_n}{k_5} \right)^{\frac{1}{2}}. \quad (13)$$

Mercury sensitization ( $O_2$ )

$$-d[PH_3]/dt = k[PH_3](I_n \cdot A/k_5[O_2])^{\frac{1}{2}}, \quad (14)$$

and the direct reaction

$$-d[PH_3]/dt = k[PH_3]^{\frac{3}{2}}(I_n/k_5[O_2])^{\frac{1}{2}}. \quad (15)$$

**Case 3**

The last term in the equation for  $[X_O]$  is  $k_6[X_O][X]^2$ . Mercury sensitization ( $PH_3$ ),

$$-\frac{d[PH_3]}{dt} = \frac{k[PH_3]}{k_6[X]^2} \cdot \frac{[PH_3] \cdot I_n}{[PH_3] + 0.5[O_2] + 0.37} = \frac{k[PH_3]^2 \cdot I_n}{k_6[O_2]^3}. \quad (16)$$

Mercury sensitization ( $O_2$ ),

$$-d[PH_3]/dt = (k[PH_3]I_n \cdot A)/k_6[O_2]^2. \quad (17)$$

Direct reaction,

$$-d[PH_3]/dt = (k[PH_3]^2 \cdot I_n)/k_6[O_2]^2. \quad (18)$$

<sup>7</sup> Cf. Proc. Roy. Soc. A138, 385 (1932).

## Cases 4, 5 and 6

The corresponding cases for  $X_P$  are obtained in exactly the same way. The last term in the  $X_O$  equation is discarded, while an additional term is added to the  $X_P$  equation in order to express how this carrier is removed. This gives rise to the following nine equations.

<b>Case 4</b> $X_P + X$	$(k_7)$	$\left\{ \begin{array}{l} \text{Hg (PH}_3\text{)} \\ \text{Hg (O}_2\text{)} \\ \text{Direct} \end{array} \right.$	$\left\{ \begin{array}{l} -d[\text{PH}_3]/dt = kI_n/k_7, \\ -d[\text{PH}_3]/dt = k[\text{O}_2] \cdot A/k_7[\text{PH}_3], \\ -d[\text{PH}_3]/dt = k[\text{O}_2]/k_7. \end{array} \right.$	(19) (20) (21)
<b>Case 5</b> $X_P + X_P + X$	$(k_8)$	$\left\{ \begin{array}{l} \text{Hg (PH}_3\text{)} \\ \text{Hg (O}_2\text{)} \\ \text{Direct} \end{array} \right.$	$\left\{ \begin{array}{l} -d[\text{PH}_3]/dt = k([\text{PH}_3] \cdot I_n/k_8)^{1/2}, \\ -d[\text{PH}_3]/dt = k(I_n \cdot A/k_8[\text{O}_2])^{1/2}, \\ -d[\text{PH}_3]/dt = k([\text{O}_2][\text{PH}_3] \cdot I_n/k_8)^{1/2}. \end{array} \right.$	(22) (23) (24)
<b>Case 6</b> $X_P + X + X$	$(k_9)$	$\left\{ \begin{array}{l} \text{Hg (PH}_3\text{)} \\ \text{Hg (O}_2\text{)} \\ \text{Direct} \end{array} \right.$	$\left\{ \begin{array}{l} -d[\text{PH}_3]/dt = k[\text{PH}_3]I_n/k_9[\text{O}_2]^2, \\ -d[\text{PH}_3]/dt = k \cdot [\text{PH}_3] \cdot I_n/k_9[\text{O}_2], \\ -d[\text{PH}_3]/dt = k[\text{PH}_3]I_n/k_9[\text{O}_2]. \end{array} \right.$	(25) (26) (27)

A possible objection might be raised against case 6, for  $X = \text{O}_2$  and  $X_P + \text{O}_2$  is a propagating collision. In presence of a third molecule, however, it is quite conceivable that a redistribution of energy occurs in such a way as to prevent the emergence of an  $X_O$  molecule from the collision.

## EXPERIMENTAL

Fig. 1 illustrates the essential parts of the apparatus. The main difficulty was to measure a change in phosphine pressure in presence of a large excess of oxygen. The apparatus was so arranged that it could readily be used for experiments on the upper limit. The silica reaction tube was placed in a water bath at 20°C fitted with a silica window. The source of the mercury line was a tungsten anode lamp  $L$  with a water-cooled cathode. A filter was employed to vary the intensity of the light and consisted of a solution of carbon tetrachloride in pure hexane.<sup>8</sup> A condensed spark between zinc disks rotating at right angles served as a light source for the experiments on the direct reaction. The input to the spark was about 0.2 amp. at 5000 volts, the distance between spark and reaction tube being 15 cm. Large pressures were measured by a capillary mercury manometer, smaller pressures by the spring gauge  $M_2$  and low pressures by the oil manometer  $M_1$ , the position of the meniscus being read by a microscope. Apiezon oil  $A$ , thoroughly degassed, proved to be satisfactory. To increase the sensitivity, one of the limbs was

made much wider than the other. Since this manometer was used differentially, it was also placed in a water bath. For the experiments at the upper limit, a steel needle valve was attached to the apparatus to regulate the rate of exhaustion of the explosion tube.

The procedure for the experiments on the stable reaction above the upper limit and at low phosphine pressures was as follows: Phosphine was admitted to  $R$  and to  $M_1$ ,  $T$  being closed, and its pressure observed.  $T$  was opened and oxygen admitted, the pressure being now measured on

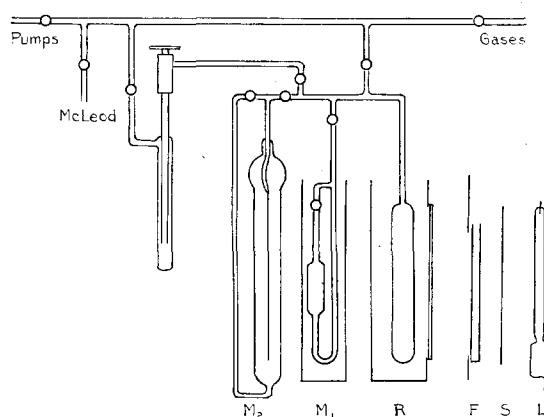


FIG. 1. Diagram showing essential parts of apparatus.

<sup>8</sup> Melville and Walls, Trans. Faraday Soc. 29, 1255 (1933).

$M_2$ ,  $T$  was closed again and the shutter removed for a given time, after which the oil manometer was again read. This procedure was repeated for a number of exposures. In this manner, changes of pressure of 0.1 mm could be measured in presence of 30 mm of oxygen. Several blank experiments were made with oxygen alone to ensure that no spurious effects occurred, for instance, oxygen does dissolve in the oil, but since it was present at the same pressure in both limbs of the manometer and the runs were not prolonged, no appreciable change of oil level could be detected. The deposition of the phosphoric acid on the walls of the reaction did not appear to cut down the reaction velocity, for no increase in rate resulted when the tube was cleaned out. With excess of oxygen, the phosphine is practically completely oxidized to  $H_3PO_4$ , since the pressure decrease after the reaction had gone to completion amounted to nearly three times the pressure of the phosphine.

The preparation of mixtures above the upper limit was carried out in the usual way. The water bath surrounding the reaction vessel was removed and a small annular cup was fixed to  $R$ . Phosphine was passed in, liquid air poured into the cup and then the oxygen was added. When the liquid air had evaporated, the water bath was replaced and the apparatus allowed to stand for a few minutes until the pressure became steady, after which exhaustion and exposure were commenced.

The gases were prepared as described in previous papers.

## RESULTS

### Photosensitized oxidation

It will be observed from an inspection of Eqs. (13)–(15) and (22)–(24) that the rate of oxidation for cases 2 and 5 should vary as the square root of the intensity, whereas in the other cases the relation is linear. Several possibilities can thus at once be eliminated if the intensity law is first of all investigated. Below the lower limit, the rate should, of course, be proportional to the intensity. The results (Table I) below the lower limit are in accordance with expectation and above the upper limit, there is no doubt that the rate is proportional to the first power of the

TABLE I.

Lower limit, $p_{PH_3}=0.254$ mm, $p_{O_2}=0.584$ mm			
Intensity $I$	Init. Rate $R$ (mm/min.)	$R/I^*$	$t$ for $\Delta p=0.525$ mm (min.)
1.00	0.072	0.072	0.85
0.15	0.012	0.072	5.20
0.68	0.053	0.072	1.05
0.38	0.028	0.065	2.00
1.00	0.083	0.072	0.70
Upper limit, $p_{PH_3}=0.127$ mm, $p_{O_2}=10.0$ mm			
Intensity	$t$ for $\Delta p=0.064$	$t \times I$	
0.38	1.65	0.63	
0.68	0.90	0.61	
1.00	0.55	0.55	
0.15	3.70	0.56	
0.51	1.24	0.63	

\* Corrected for the increase in the intensity during the series.

intensity and therefore cases 2 and 5 may at once be eliminated. For a given pressure of phosphine, it is known from the experiments of Dalton and others<sup>9</sup> that by increasing the pressure of oxygen, the lower limit may be approached, or if the oxygen pressure be decreased, the upper limit is reached. The upper limit must, therefore, be due to oxygen participating in some reaction which is negligible at low pressures. When chain initiation is brought about by mercury sensitization, it is probable that oxygen molecules account for a number of the chains started and it is therefore necessary to evaluate the magnitude of the coefficient  $A$  defined on p. 741. In Fig. 2,  $1/R$  and  $k^{-1}$  have been plotted against  $p_{O_2}$ , the dotted curve refers to the ideal case in which

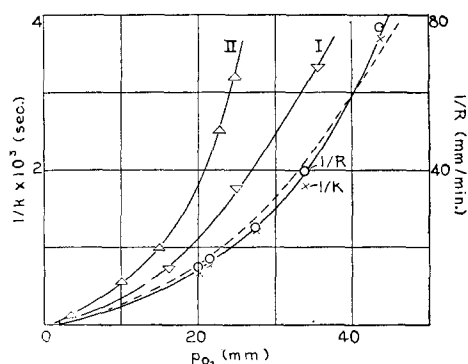


FIG. 2. Photosensitized reaction, curves I and II are for  $p_{PH_3}=0.120$  mm and different intensities.

<sup>9</sup> Dalton and others, e.g., Proc. Roy. Soc. A128, 263 (1930).

TABLE II.

$p_{\text{PH}_3}$ $p_{\text{O}_2}$ $t$	0.261 20.0		0.261 21.4		0.261 27.0		0.261 34.0		0.261 44.0	
	$\Delta p$	$k \times 10^3$ (sec. <sup>-1</sup> )	$\Delta p$	$k \times 10^3$ (sec. <sup>-1</sup> )	$\Delta p$	$k \times 10^3$ (sec. <sup>-1</sup> )	$\Delta p$	$k \times 10^3$ (sec. <sup>-1</sup> )	$\Delta p$	$k \times 10^3$ (sec. <sup>-1</sup> )
0.25	0.017	1.54	0.016	1.22	0.009	—	—	—	0.001	—
0.50	0.033	1.41	0.029	1.30	0.021	0.92	0.012	—	—	—
0.75	—	—	0.0430	1.23	0.029	0.81	0.017	0.51	—	—
1.00	0.066	1.51	0.055	1.19	0.041	0.92	0.025	0.52	—	—
1.50	0.092	1.40	0.079	1.23	0.056	0.84	0.042	0.61	0.016	—
2.00	0.118	1.73	0.097	1.09	0.073	0.81	0.047	0.54	0.026	0.26
3.00	0.162	1.28	—	—	0.104	0.78	0.071	0.54	0.035	0.26
4.00	—	—	—	—	—	—	0.094	0.54	0.055	0.29

$1/R$  and  $k$  vary as  $p_{\text{O}_2}^2$ . Table II contains the detailed runs and  $k$  is calculated assuming that  $-d[\text{PH}_3]/dt = k[\text{PH}_3]$ . The oxygen pressure may be regarded as constant during the reaction. Since these runs were not carried to completion, another series of experiments is given in Table III, where the pressure of oxygen was maintained

TABLE III. Effect of phosphine.

$p_{\text{PH}_3}$	0.260	0.190	0.129	0.132	0.066
$p_{\text{O}_2}$	9.4	10.5	9.2	10.0	10.0
Rate ( $R$ )	0.100	0.066	0.051	0.046	0.025
$R/p_{\text{PH}_3}$	0.038	0.035	0.039	0.035	0.038
$t(\Delta p = 0.066)$	0.65	1.15	1.55	1.86	2.95
$t \times p_{\text{PH}_3}$	0.169	0.22	0.20	0.24	0.20

constant and that of phosphine varied. The constancy of  $R/p_{\text{PH}_3}$  and of  $t \times p_{\text{PH}_3}$  shows that the rate is proportional to the pressure of the phosphine.

In Table IV, three series of results are listed for a constant oxygen pressure and for different argon pressures. First of all, it is seen that argon

TABLE IV. Effect of argon. Hg sensitized reaction.

$p_{\text{PH}_3}$	$p_{\text{O}_2}$	$p_A$	$R$	$(1/R - 1/R_0)$ $p_A^*$	$t$ for $\Delta p$ $= 0.039$	$k_{10}/k_6$
0.260	25.0	55.0	0.0086	1.5	4.50	1.00
0.260	24.6	—	0.0285	—	1.45	—
0.263	25.7	14.6	0.0193	1.3	2.20	0.8
$\Delta p = 0.039 \quad \Delta p = 0.131$						
0.263	14.9	16.1	0.051	0.52	0.82	3.68
0.262	15.0	—	0.093	—	0.41	2.00
0.258	15.6	26.4	0.033	0.74	1.18	4.60
0.262	15.5	7.7	0.066	0.57	0.64	3.05
$\Delta p = 0.0655$						
0.261	14.6	44.9	0.0201	0.82	4.00	0.7
0.262	15.8	16.4	0.0283	1.00	2.47	0.9
0.261	15.8	—	0.0533	—	1.27	—

\*  $R_0$  is the rate in absence of inert gas.

inhibits the oxidation, although in comparison with oxygen it does not quench mercury resonance radiation. The inhibition must therefore be due to chain termination and since the value of  $(1/R - 1/R_0)/p_A$  is approximately constant, the inhibition term in the kinetic equation may be expressed in two ways *viz.*,  $k_{10}[\text{X}_0][\text{A}]$  or  $k_{11}[\text{X}_0][\text{O}_2][\text{X}]$ .

Similarly, there is inhibition by nitrogen (Table V) and again according to the same law.

TABLE V. Effect of nitrogen.

Direct reaction, Zn spark $p_{\text{PH}_3} = 0.254, \quad p_{\text{O}_2} = 12$					
$p_{\text{N}_2}$	12	26	18	6	0
$t$ for $\Delta p = 0.064$	2.62	3.84	3.37	1.62	1.17
$k_{10}/k_6$	1.2	1.1	1.2	0.80	—
Hg reaction, constant $p_{\text{O}_2} + p_{\text{N}_2}$					
$p_{\text{PH}_3}$	$p_{\text{O}_2}$	$p_{\text{N}_2}$	$R$	$t$ for $\Delta p = 0.131$	
0.262	39.0	—	0.066	2.22	
0.256	11.0	32.0	0.074	2.16	
0.271	20.4	20.3	0.104	1.47	
0.259	10.8	30.5	0.131	1.06	
0.271	26.7	13.3	0.090	1.75	

Until a decision is made about the mechanism of termination, no calculation can be made of the coefficients  $k_{10}$  and  $k_{11}$ .

The kinetics of the reaction are, therefore, that

$$-d[\text{PH}_3]/dt = \text{const.} [\text{PH}_3]/[\text{O}_2]^2.$$

This does not decide the matter unequivocally, since case 3 and case 6 lead to the same equation if initiation in the first is due to oxygen and in the second to phosphine. Further, both cases allow the introduction of an inhibitory term containing oxygen, and argon and nitrogen. The inhibition by inert gases practically excludes cases 1 and 4

for it is probable, although the evidence is as yet indirect, that the chain carriers are not excited molecules of very short life and hence collision of  $X_O$  or  $X_P$  with argon or nitrogen should not lead to destruction.

### Direct photo-oxidation

The number of mechanisms has now been reduced to two. Fortunately, the kinetic equations for the direct oxidation are quite different for cases 3 and 6 and thus it should be possible to decide which is the more probable. Intensity measurements were not considered to be necessary in view of the definite answer given by the photosensitized experiments. In Table VI the

TABLE VI. Effect of phosphine.

$p_{PH_3}$	$p_{O_2}$	$t$ for $\Delta p = 0.025$ (sec.)	$t \times p_{PH_3}^2$
0.130	17.3	108	18.2
0.535	17.7	7	20.0
0.275	17.4	26	19.7
0.131	17.2	85	14.6
0.391	17.3	10	15.3
0.261	17.3	20	13.6

complete data are given for varying oxygen and phosphine pressures. In Fig. 3,  $1/R$  and  $t$  for  $\Delta p = 0.100$  mm have been plotted against  $p_{O_2}^2$  and also against  $p_{O_2}$ , the pressure of  $PH_3$  being 0.26 mm. The straight line obtained with the  $p_{O_2}^2$  plot and also the constancy of the product  $t \times p_{PH_3}^2$  in Table VI, indicates that the kinetics in this pressure range can be summarized by the equation,

$$-d[PH_3]/dt = \text{const. } [PH_3]^2/[O_2]^2.$$

Referring back to the theory given above, it will be observed that this equation only agrees with case 3 (18) and therefore the conclusion which may be drawn is that, above the upper limit, the chains are terminated by a triple collision between the chain carrier  $X_O$ , which normally reacts with phosphine, and with two oxygen molecules.

It is now possible to return to the question of inhibition by argon and nitrogen. The plots of  $1/R$  against  $p_{A(N_2)}$  are straight and hence the inhibition term will contain a factor  $[N_2]$  or  $[A]$ . It is of importance to note that a quadratic term  $[N_2]^2$  or  $[A]^2$  need not be introduced. The most

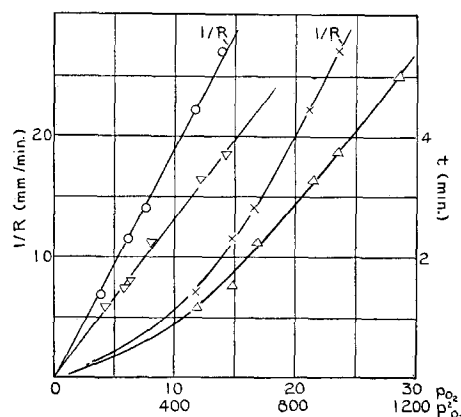


FIG. 3.

probable mechanism of the termination is that  $X_O$  must collide with a nitrogen molecule and an oxygen molecule. The function of the inert gas may simply be to stabilize the complex  $X_O + O_2$  and thus prevent  $X_O$  further propagating the chain. Let the inhibition term be  $k_{10}[O_2][N_2][X_O]$ , then  $k_{10}$  may be evaluated in the following way. Inserting this term in the equation for  $X_O$  in addition to the term required by case three (oxygen initiation)

$$\frac{d[PH_3]}{dt} = \frac{k[PH_3]I_n \cdot A}{[O_2]\{k_6[O_2] + k_{10}[N_2]\}}.$$

Hence

$$(1/R)/(1/R_0) = 1 + k_{10}[N_2]/k_6[O_2], \quad (28)$$

where the subscript 0 refers to the runs made in absence of foreign gas. From this equation the values of  $k_{10}/k_6$  have been calculated and are given in Tables IV and V. Argon and nitrogen are about as efficient as oxygen in promoting the stability of the complex.

The next question is to determine the absolute values of  $k_6$  and also of  $A$ . For this purpose, the ratio of the rates of oxidation to the rate of decomposition for the photosensitized and for the direct reaction were measured. The data are collected in Table VII.

Some notes about experimental procedure may be mentioned here. Since the ratio of the rates was large, the rate of decomposition was measured by a McLeod gauge and a filter was employed to cut down the intensity of the light during the oxidation experiments. In the direct reaction, comparison was made directly on the oil



TABLE VII. Photosensitized experiments.

$p_{\text{PH}_3}$	$p_{\text{O}_2}$	$d[\text{PH}_3]/dt$	Ratio of rates	Chain length ( $\nu$ )	$\nu$ for 5 mm $\text{PH}_3$ and 50 mm $\text{O}_2$
<i>Above the upper limit</i>					
1.98	37.5	$0.93 \times 10^{-2}$ mm/min. in 85 cc <i>I</i> 0.15	19.2	38	53
2.00	—	$5.3 \times 10^{-4}$ mm/min. in 514 cc <i>I</i> 1.00			
8.0	81.0	$3 \times 10^{-2}$ mm/min. in 85 cc <i>I</i> 0.15	10.4	21	34
8.0	—	$3.2 \times 10^{-3}$ mm/min. in 514 cc <i>I</i> 1.00			
6.8	68	$8.4 \times 10^{-2}$ mm/min. in 85 cc <i>I</i> 0.15	8.4	17	43
6.7	—	$11 \times 10^{-3}$ mm/min. in 514 cc <i>I</i> 1.00			
<i>Below the lower limit</i>					
0.85	0.36	$67 \times 10^{-2}$ mm/min. in 85 cc <i>I</i> 0.15	480	10	$\nu$ for 0.5 mm $\text{PH}_3$ 0.5 $\text{O}_2$ 820
0.79	—	$0.93 \times 10^{-2}$ mm/min. in 514 cc <i>I</i> 1.00			
0.83	—	$0.93 \times 10^{-2}$ mm/min. in 514 cc <i>I</i> 1.00	504	10	830
0.83	0.36	$2.52 \times 10^{-2}$ mm/min. in 85 cc <i>I</i> 0.0054			
At the lower limit explosion occurred with 0.83 mm $\text{PH}_3$ and 0.45 mm $\text{O}_2$ .					
<i>Direct reaction</i>					
$p_{\text{PH}_3}$	$p_{\text{O}_2}$	Rate*	Chain length ( $\nu$ )	$\nu$ for 0.5 mm $\text{PH}_3$ and 0.5 mm $\text{O}_2$	
<i>Below the lower limit</i>					
0.254	—	0.075	310	1200	
0.254	0.337	11.6			
0.267	—	0.070	400	800	
0.254	0.513	14.0			
<i>Above the upper limit</i>					
8.23	121.4	54.0	72	210	
8.64	—	1.5			
8.35	138.1	38.8	47	220	
8.40	—	1.65			

\* Multiply by  $1.27 \times 10^{-2}$  to give mm/min.

manometer. The rate of decomposition of phosphine was determined by measuring the pressure of hydrogen after the phosphine had been condensed out by liquid air. The ratio of the rates is doubled to give the chain length, for the quantum yield of the dissociation is 0.5.

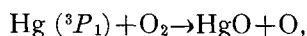
First of all, it will be seen that, below the lower limit, the chain lengths for the direct and photosensitized experiments are nearly the same. Above the upper limit, however, the chain length (calculated from the relative velocities) in the

direct reaction is about five times that obtained in the sensitized oxidation. This confirms the kinetic results about initiation by oxygen and moreover gives the value of  $A$ , the number of chains started per excited Hg atom deactivated by oxygen; it is 0.2. The kinetic experiments also yield information about the nature of initiation by oxygen. There is some doubt as to the products of reaction when a  $^3P_1$  Hg atom collides with an oxygen molecule. If the low efficiency of initiation were due to the deactivation, by

collision or by radiation, of an excited oxygen molecule of very short life and if initiation be brought about by collision of this excited molecule with phosphine, then it may easily be shown that the initiation factor will assume the form  $[PH_3]/[O_2]$  and hence the kinetic equation would become

$$-d[PH_3]/dt = \text{const. } [PH_3]^2/[O_2]^3,$$

which does not agree with experiment. Some atom or molecule must emerge from the collision which is not subject to such easy removal as an excited  $O_2$  molecule; the most probable reaction is



the O atom reacting with the first  $PH_3$  molecule it encounters.

One of the consequences of the theory of branched chains is that the explosion limit curve is a line of equal chain length. Therefore if the chain length be calculated below the lower limit and above the upper limit, and the results extrapolated to these limits employing the appropriate equations, then similar values should be obtained. Such a calculation has been made and the results are given in the last column of Table VII. Although the values of  $\nu$  are of the same order of magnitude, it must be pointed out that at the upper limit, the chain length is five times shorter than at the lower limit.

The chain length measurements above the upper limit provide the material for a calculation of  $k_6$ . From the equation already given, the chain length is represented by

$$\nu = \frac{-d[PH_3]/dt \text{ (oxidation)}}{-d[PH_3]/dt \text{ (decomp.)}} = \frac{k[PH_3]}{k_6[O_2]^2}.$$

Substituting from Table VII,  $\nu = 200$ ,  $[PH_3] = 8.4$  and  $[O_2] = 138.1$  mm  $k/k_6[O_2] = 3300$ . Since the propagation collisions are nearly 100 percent efficient, 3300 represents the ratio of the number of bimolecular to trimolecular collisions at 146 mm. Now it is generally assumed that at atmospheric pressure this ratio is  $10^3$ , at 146 mm, it will be  $760/146 \times 10^3 = 5200$  and therefore every second ternary collision is effective in destroying  $X_O$ . This result may be arrived at in another way. If the kinetics of the stable reaction and of the explosion are exactly similar, then

from the above analysis the corresponding equation for the upper limit may easily be deduced by placing the probability of branching  $(\alpha - 1)$  in the equations for the stationary concentration of the carriers

$$d[X_O]/dt = I + \alpha k[X_P][O_2]$$

$$-k[X_O][PH_3] - k_6[X_O][O_2]^2 = 0,$$

$$d[X_P]/dt = k[X_O][PH_3] + k[X_P][O_2] = 0,$$

therefore

$$[X_O] = I / \{ (1 - \alpha)k[PH_3] + k_6[O_2]^2 \}. \quad (29)$$

The condition for explosion is that

$$(\alpha - 1)k[PH_3] = k_6[O_2]^2, \quad (30)$$

which is exactly in agreement with Dalton's experiments except at high phosphine pressures and also with experiments made during this investigation. To calculate  $k/k_6[O_2]$ , it is necessary to know  $(\alpha - 1)$ . The chain length is  $10^3$  at the lower and  $2 \times 10^2$  at the upper limit, the probability of branching is, respectively,  $10^{-3}$  and  $5 \times 10^{-3}$ . At the upper limit, 5 mm  $PH_3$  and 50 mm  $O_2$ ,  $k/k_6[O_2]$  is  $10^4$  and  $2 \times 10^3$ . At 55 mm, the ratio of bi- to trimolecular collisions is  $1.5 \times 10^4$ . The agreement is not quite so good with  $(\alpha - 1)$  obtained from the upper limit results.

A third method, however, obviates the necessity of determining  $(\alpha - 1)$  and  $k$ . At the lower limit

$$(\alpha - 1)k[PH_3] = K/[O_2] \quad (31)$$

and at the upper limit

$$(\alpha - 1)k[PH_3] = k_6[O_2]^2 \quad (32)$$

or

$$K/[O_2]^3 = k_6, \quad (33)$$

$K$  can be calculated from the dimensions of the reaction tube and mean free path of the chain carriers in the gas.  $k_6$  may then be evaluated and from it the efficiency of the trimolecular collisions. Semenov<sup>10</sup> has made the calculations using Dalton's results and finds that 0.4 ternary collisions are effective.

Another check on the interrelationships between the stable and explosive reaction can be

<sup>10</sup> Semenov, Phys. Zeits. d. Sow. 4, 714 (1934).

made. The whole explosion curve may be represented by the equation

$$(\alpha - 1)k[\text{PH}_3] = K/[\text{O}_2] + k_6[\text{O}_2]^2, \quad (34)$$

obtained on adding (31) and (32). For  $[\text{PH}_3]$  to be a minimum, then by differentiating (34) with respect to  $[\text{O}_2]$ .

$$[\text{O}_2] = 3(K/2k_6)^{1/2}. \quad (35)$$

From the results shown in Fig. 4, the minimum occurs at 4.6 mm  $\text{O}_2$ . Similarly,  $\nu$  below and above the limit is given by

$$\left. \begin{aligned} \nu_{\text{lower}} &= k/K \cdot [\text{PH}_3][\text{O}_2], \\ \nu_{\text{upper}} &= k[\text{PH}_3]/k_6[\text{O}_2]^2 \end{aligned} \right\} \quad (36)$$

or

$$\nu = k[\text{PH}_3]([\text{O}_2]/K + 1/k_6[\text{O}_2]^2).$$

Hence

$$d\nu/d[\text{O}_2] = k/K \cdot [\text{PH}_3] - 2k[\text{PH}_3]/k_6[\text{O}_2]^3 = 0$$

or

$$[\text{O}_2] = (K/2k_6)^{1/2}$$

is the condition for the chain length to be maximum. Thus the maximum in the chain length curve should occur at the same oxygen pressure as the minimum in the explosion curve. Fig. 4 shows that these anticipations are realized. In the figure of the preliminary notice of this

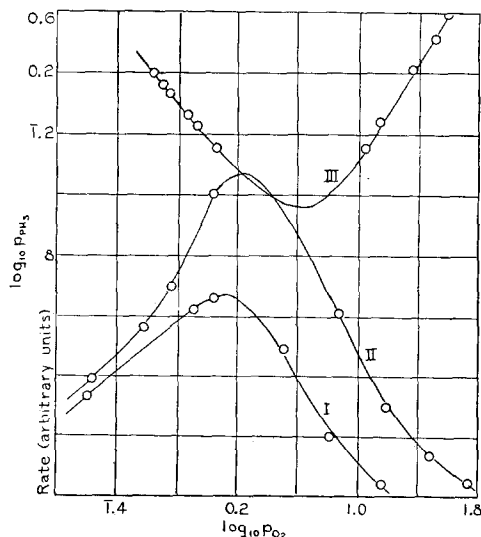


FIG. 4. Curve I, photosensitized reaction  $p_{\text{PH}_3} = 0.130$ ; II direct reaction  $p_{\text{PH}_3} = 0.260$  mm; III lower and upper limit, thermal explosion.

work,<sup>11</sup> the rate of reaction was plotted against the pressure of the oxygen, but it was also pointed out that the curve would have to be suitably corrected for deactivation of the mercury atoms by oxygen. On account of initiation by oxygen, however, the corrections to be made are small, so that the curve does represent the variation of chain length with oxygen pressure. This is more easily seen from Table VIII where the expression,  $Z = [\text{PH}_3]$

TABLE VIII. Variation of initiation factor with oxygen pressure.  
 $[\text{PH}_3] = 0.1$  mm

$[\text{O}_2]$	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0	50.0
Z	0.20	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20

$+0.5A[\text{O}_2]/\{[\text{PH}_3] + 0.5[\text{O}_2] + 37\}$  is evaluated for different oxygen pressures.

The photosensitized results are also plotted in Fig. 4. The position of the minimum in the explosion curve, which is 0.212 mm  $\text{PH}_3$  and 4.62  $\text{O}_2$ , was calculated from Eq. (34).

#### EFFECT OF RATE OF STARTING OF THE CHAINS ON THE POSITION OF THE LIMITS

Excepting for the moment the oxidation of phosphorus and of phosphine, there is abundant evidence that the position of both limits is dependent on the rate at which chains are started. In the hydrogen-oxygen reaction, for example, it has been established that hydrogen atoms produced photochemically,<sup>12</sup> thermally<sup>13</sup> and electrically,<sup>14</sup> oxygen atoms<sup>14</sup> and chlorine atoms<sup>15</sup> all reduce the ignition temperature. Moreover, even at room temperatures, conditions simulating the lower limit may be obtained with spark ignition.<sup>16</sup> The action of nitrogen peroxide in reducing the temperature of ignition of hydrogen, carbon monoxide, methane, etc., may also be a question of the rate of starting affecting the limits. Similarly, the limits in the oxidation of

<sup>11</sup> Nature **131**, 690 (1933).

<sup>12</sup> Farkas, Haber and Hartek, Zeits. f. Elektrochemie **36**, 711 (1930); Taylor and Salley, J. Am. Chem. Soc. **55**, 96 (1933).

<sup>13</sup> Haber and Oppenheimer, Zeits. f. physik. Chemie **B16**, 443 (1932).

<sup>14</sup> Semenov, Trans. Faraday Soc. **29**, 606 (1933); Phys. Zeits. d. Sow. **4**, 753 (1934).

<sup>15</sup> Norrish, Proc. Roy. Soc. **A135**, 334 (1931).

<sup>16</sup> Thompson, Trans. Faraday Soc. **28**, 308 (1932).

sulphur,<sup>17</sup> carbon disulphide<sup>18</sup> and hydrogen sulphide are considerably altered by suitable stimuli. Examples may be easily multiplied, but the situation can be summarized by the statement that, in those reactions where the limits are temperature dependent and where explosion occurs at elevated temperatures, the position of both limits is dependent *to some extent* on the rate of initiation. The chain hypothesis alone does not therefore wholly express the condition for explosion, in addition, some temperature dependent factor must be introduced to provide an adequate explanation for the phenomena. With phosphorus and phosphine, it is different, the propagating collisions are almost 100 percent efficient and the efficiency is so high that it cannot be dependent on temperature to any important degree. Similarly, the termination reactions at the walls and in the gas phase do not require activation. In these two examples, then, it is to be expected that the pure chain explosion would occur, and that the condition for explosion would be adequately expressed by the statement that the product of the probabilities of termination and of branching is equal to unity, from which it at once follows that the explosion pressure should be quite independent of the rate of starting. The test is rather a crucial one for some parts of the chain theory. Some time ago, it was applied to the lower limit of phosphine<sup>19</sup> and a very considerable lowering of the limit was obtained. The curious fact was that the effect persisted for a time much longer than the life of the reaction chains. Later it was shown<sup>20</sup> to be due wholly to an alteration of the surface upon which the chains terminated. In the experiments to be described below, the experiment has been repeated at the upper limit which is, of course, unaffected by wall conditions (more strictly the termination reaction only). Initiation was effected by the light from the mercury lamp (water-cooled).

Some indication of the behavior to be expected has already been given, since it has been shown that the chain lengths at the lower and

upper limit are not identical. Apparently the explosion can occur more easily at high pressures in that such a long chain is not necessary.

Preliminary experiments showed at once that there was a considerable displacement of the upper limit to higher pressures, provided the tube was illuminated during expansion. Several experiments were carried out in which the gases were illuminated for a considerable time (min.) and allowed to stand for intervals of from 0.5 to 10 min. before expansion, but no displacement could be detected. Table IX contains a number of typical results.

TABLE IX.

Expt. No.	Initial press. $p_{\text{PH}_3}$ $p_{\text{O}_2}$		Total press. at explosion	Conditions of illumination
561	6.5	103	72	during expansion
562	6.4	99	26	none
563	6.6	99.5	26	see text
565	5.3	103	57.3	during expansion
566	6.4	112	65	" "
567	4.7	95	56.5	" "

Expt. No.	Initial press. $p_{\text{PH}_3}$ $p_{\text{O}_2}$		Total press. at explosion	Intensity
570	7.5	113	63.5	1.00
571	7.5	113	43.5	0.15
572	6.5	100	38.5	0.15
574	7.4	100	56.5	0.15
575	7.3	106	63.5	1.00
577	4.8	111	42.3	1.00
578	8.1	101	80.0	1.00

\* Rate of stable reaction at initial pressure 0.13 mm/min.,  $I = 1.00$ .

Experiments 561 to 563 may be particularly mentioned. The initial pressures were all practically the same, but the explosion pressure has been increased by illumination from 26 to 72 mm. In experiment 563 illumination was continued during expansion until the pressure was only 2 mm above the upper limit (72), the light was cut off and the expansion continued, but the pressure had to be reduced to 26 mm to obtain explosion. The time for the pressure to fall 2 mm was not more than 2 sec. so that the lifetime of the effect cannot exceed 2 sec. It is therefore quite different from the lower limit phenomenon which persists for several minutes. The effect of intensity was further investigated in the following way. Instead of plotting upper limit curves for different intensities two mixtures of constant composition were employed. Since expansion does not alter the composition, the displacement of the ex-

<sup>17</sup> Semenoff and Rjabinin, Zeits. f. physik. Chemie **B1**, 192 (1928).

<sup>18</sup> Ritchie and others, Proc. Roy. Soc. **A137**, 511 (1932).

<sup>19</sup> Clusius and Hinshelwood, Proc. Roy. Soc. **A129**, 589 (1930).

<sup>20</sup> Melville, Proc. Roy. Soc. **A138**, 389 (1932).

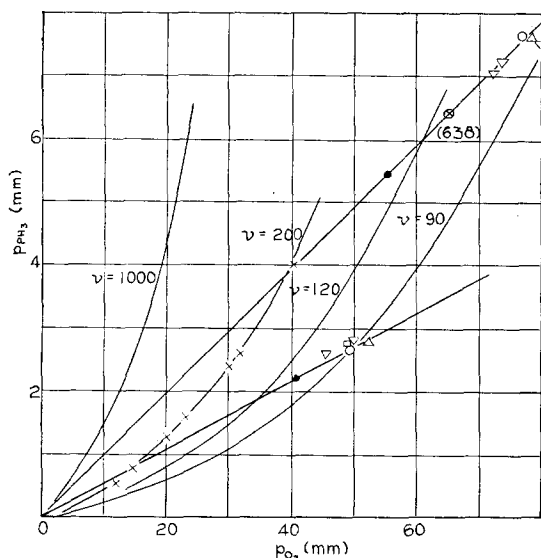


FIG. 5. Displacement of upper limit by illumination. Rate,  $\bullet = 5 \times 10^{-5}$  mm/sec. ( $2.0 \times 10^{10}$  quanta per sec.)  $\oplus = 10^{-4}$ ,  $\odot = 1.7 \times 10^{-4}$ ,  $\Delta = 3.3 \times 10^{-4}$ ,  $\square = 5.4 \times 10^{-4}$ ,  $\nabla = 37 \times 10^{-4}$ .

plosion limit along the expansion line can be regarded as a measure of the effect. The data are plotted in Fig. 5.

The intensity could not be increased to higher values since the velocity of the reaction was then sufficient to remove considerable amounts of phosphine and oxygen.

These results then prompt a further question as to whether, at the lower limit, in addition to the ordinary displacement owing to the change in surface, there is a transient effect similar to that at high pressures. The procedure adopted was to use a constant pressure of phosphine and allow oxygen to leak in through the needle valve and record the explosion pressure on the oil manometer. The intensity of the light was 0.15 on the same scale as that given in Table X. The results listed in Table X show the conditions of illumination and are recorded in the order in which the experiments were carried out.

Comparing Nos. 625, 626 and 633 with the remainder, it will be seen that the explosion pressures, in which there has been illumination, are somewhat lower than those in its absence, thus confirming previous results. It does not appear to matter whether the light is switched off sometime before the explosion or whether it is left on right up to the explosion limit. It will also

TABLE X. Lower limit, silica surface.

No.	$p_{\text{PH}_3}$	$p_{\text{O}_2}$ at explosion	$p_{\text{PH}_3} + p_{\text{O}_2}$	Conditions of illumination
622	0.74	0.61	1.35	continuous
623	0.81	0.54	1.35	until $p_{\text{PH}_3} + \text{O}_2$ 1.26
624	0.80	0.49	1.29	" " 1.26
625	0.80	0.79	1.59	none
626	0.77	0.76	1.53	none
627	0.80	0.49	1.29	until $p_{\text{PH}_3} + \text{O}_2$ 1.26
628	0.78	0.48	1.26	continuous
629	0.76	0.44	1.20	until $p_{\text{PH}_3} + \text{O}_2$ 1.18
630	0.76	0.64	1.40	" " 1.12
631	0.76	0.48	1.24	" " 1.18
632	0.76	0.64	1.40	" " 1.12
633	0.77	0.74	1.51	none

be observed that if illumination be stopped at a low pressure of oxygen (expts. 630 and 632) the explosion limit is a little higher than that where illumination has been continued up to higher oxygen pressures. The conclusion then is that the transient effect, obtained at the upper limit, is not in evidence at the lower limit.

To demonstrate more clearly the sensitiveness of the upper limit to the stationary concentration of  $\text{X}_0$ , the following experiment (638) and calculations were made. A mixture of 12.0 mm, phosphine and 114 mm oxygen was prepared, illuminated during expansion when explosion occurred at 71 mm. Thus the intensity of the light was a somewhat greater (0.30) than 0.15 in the experiments in Table X, as is seen if the explosion point is placed on the upper expansion line of Fig. 5. A second mixture was then prepared and pumped down to 75 mm. At this pressure, the rate of oxidation of phosphine was  $9.3 \times 10^{-5}$  mm/sec. in a volume of 85 cc: the calculated chain length is 110. The number of quanta entering the reaction tube is thus  $4 \times 10^{10} \text{ sec}^{-1}$ . At 75 mm, a molecule experiences about  $10^6$  ternary collisions per sec., or the interval between such collisions is  $10^{-6} \text{ sec.}$ , which is therefore the mean life of  $\text{X}_0$ . The rate of production of  $\text{X}_0$  may be taken as the rate of dissociation of phosphine or  $9.3 \times 10^{-5} / 110 \text{ mm/sec.} \doteq 10^{-6} \text{ mm/sec.}$  and the stationary concentration is thus  $10^{-12} \text{ mm.}$  According to Table X, when the stationary concentration of  $\text{X}_0$  attains  $10^{-11} \text{ mm.}$  the limit ceases to be affected. When such a small concentration of

carriers displaces the limit so much, it is not at all surprising that traces of water vapor and possibly other gases and also changes of temperature<sup>9</sup> exert a comparatively large influence. This, in turn, suggests that the displaced limit is really the true explosion limit and that the one observed in the thermal reaction is particularly low because of the fact that a sufficient number of chains do not start to fulfill the conditions required by the chain theory. If this were the case, the chain length at the displaced limit would be  $10^3$ , whereas it is only  $10^2$ . Both the probability of branching and of termination are processes involving the reaction of only one carrier and thus should be unaffected by variations in the concentration of that carrier.

The following theory may be advanced to account for these observations. As a result of a slow thermal reaction above the upper limit ozone is formed. Likewise in the stable photo-reaction ozone is produced in much larger amounts as a consequence of the termination of the chains. Ozone increases the explosion pressure for every collision between  $X_P$  and  $O_3$  gives rise to two  $X_O$ 's, i.e., the probability of branching is increased. Ozone is destroyed by reaction with phosphine, but this is a comparatively inefficient reaction. In the photoreaction ozone is also decomposed photochemically. No chains are started, however, by these two processes. Expressing all these assumptions in the usual manner, the following equations are obtained

$$\left. \begin{aligned} d[O_3]/dt &= k_6[X_O][O_2]^2 - k[X_P][O_3] \\ &\quad - k_{10}I_0[O_3] - k_{11}[PH_3][O_3] = 0, \\ d[X_O]/dt &= I_T + I_P + \alpha k[X_P][O_2] \\ &\quad + 2k[X_P][O_3] - k[X_O][PH_3] \\ &\quad - k_6[X_O][O_2]^2 = 0, \\ d[X_P]/dt &= k[X_O][PH_3] - k[X_P][O_2] \\ &\quad - k[X_P][O_3] = 0, \end{aligned} \right\} (37)$$

where  $I_0$  is proportional to the intensity of the light decomposing the ozone,  $I_T$  and  $I_P$  are the thermal and photo rates at which chains are started. Solving and simplifying these equations, the condition for explosion is that

$$(\alpha - 1)k[PH_3] + 2k[O_3]/[O_2] = k_6[O_2]^2, \quad (38)$$

from which it is evident that ozone facilitates

explosion. The quantity required to exert a large effect is small. From Fig. 5, with 2 mm  $PH_3$ , the pressure of  $O_2$  at the limit should theoretically be 12 mm; experimentally it is 26 mm and therefore if  $(\alpha - 1) = 10^{-3}$  solution of (38) gives  $[O_3] = 10^{-2}$  mm. On solving (37) for  $[O_3]$  above the explosion limit

$$[O_3] = (I_T + I_P) / (I_T + I_P + k_{11}[PH_3]),$$

which shows at once that in the photo-experiments when  $I_P \gg I_T$  and  $k_{11}[PH_3]$ , this expression is independent of intensity in agreement with observation. Moreover the displacement at high oxygen pressures should not be quite so much as at low pressures. Examination of Fig. 5 reveals that the explosion points on the upper expansion line lie somewhat to the left of the curve for  $\nu = 90$ . At low values of  $I_P$ ,  $k_{11}[PH_3]$  comparable with  $I_P$ , the displacement of the limit will be proportional to the intensity. In order to preserve the form of the explosion curve for the dark reaction it is necessary to assume that  $I_T \sim [PH_3][O_2]$  in which case the term containing  $[O_3]$  becomes independent of phosphine and oxygen pressure.

On account of the sensitiveness of the upper limit to the stationary concentration of chain carriers, an attempt was made to measure the rate of the thermal reaction outside the explosion limits. For this purpose a quantum counter sensitive to radiation of  $\lambda < 2800\text{\AA}$  and capable of detecting 50 quanta per minute was employed.<sup>21</sup> Two mixtures were made up (a) below the lower limit, 0.396 mm  $PH_3$  and 0.37 mm  $O_2$ ,  $\nu = 250$ , (b) above the upper limit 8.7 mm  $PH_3$ , 132 mm  $O_2$ ,  $\nu = 50$ , and the tubes placed in close proximity to the counter, but no radiation could be detected. It may of course be that there is reaction accompanied by radiation which does not affect the counter.

Elsewhere it has been suggested that oxidations brought by nitrous oxide instead of by oxygen cannot proceed explosively by branching chains, although straight chains are readily obtained. Experiments were therefore made with phosphine-nitrous oxide mixtures to see if chains could be started by the photodissociation of the phosphine, but no chain propagation occurred.

In view of these experiments and calculations,

<sup>21</sup> Ouellet, Trans. Faraday Soc. 29, 486 (1933).

there are consequently good grounds, though the evidence is not direct, for supposing that  $X_O$  is an oxygen atom. Furthermore, it is possible that the collision which gives rise to branching is that between  $X_P$  and  $O_2$ , yielding two oxygen atoms.

The existence of an upper limit can be attributed to two causes (a) removal of the chain carriers by a reaction of higher order than that of branching, e.g., phosphine, (b) a deactivating influence of the reactants on a collision complex which would otherwise give rise to two chains, e.g. hydrogen, (c) other causes not at present included in the theory. It will be a matter for further experiment to decide, by closely examining the relationship between the kinetics of the stable and explosive reactions, which mode of

deactivation causes the upper limit in other chain reactions. Such experiments may reveal whether, as in the case of phosphine, explosion occurs at the upper limit more readily than theory predicts.

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## The Disappearance of Hydrogen in the Presence of Potassium and Lithium Ion Sources

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The disappearance of hydrogen in the presence of iron-alkali catalysts, sources of  $K^+$  ions and a synthetic spodumene mixture, a source of  $Li^+$  ions, was investigated. In these experiments, like those previously reported by the authors, no gas phase reaction was detected which could be attributed to the bombardment of hydrogen by positive ions with speeds up to 565 volts. It was concluded that all cleanup effects could be accounted for by reactions on or within the materials used as ion sources.

**F**URTHER results on the cleanup of hydrogen in the presence of materials and mixtures used as ion sources clear up a number of points upon which apparent disagreement in results was reported and conflicting opinions expressed.<sup>1, 2</sup>

In the previous paper by the authors it was found that with the platinum-coated glass anode source of positive ions,<sup>3</sup> an effect was observed, which was found to be due, not to the positive ions but to a surface reaction intimately associ-

ated with the electrolysis of potassium through the glass anode.

The present paper deals with further results from similar tests with an iron alkali catalyst, a source of potassium ions, and with an artificial spodumene, a source of lithium ions.

The apparatus, Fig. 1, was essentially the same as in previous work,<sup>2</sup> except that in some of the experiments a grid was used to accelerate the ions to their full velocity as soon after leaving the filament as possible. Pressures were measured with a Pirani gauge.

The results from an Fe-K catalyst (No. 920, containing 0.2 percent  $K_2O$ ) source are shown in Fig. 2. These results were obtained after the catalyst had been reduced at about 650°C for a total time of 24 hours. No definite cleanup due to the positive ions was observed. On the

<sup>1</sup>Leipunsky and Schechter, *Zeits. f. Physik* **59**, 857 (1930). A. Schechter, *Zeits. f. Physik* **75**, 671 (1932). A. C. G. Mitchell, *J. Frank. Inst.* **210**, 269 (1930). *Zeits. f. Physik* **78**, 138 (1932).

<sup>2</sup>C. H. Kunsman and R. A. Nelson, *Phys. Rev.* **40**, 936 (1932).

<sup>3</sup>F. G. Cottrell, C. H. Kunsman and R. A. Nelson, *Rev. Sci. Inst.* **1**, 654 (1930).