

THE FLAMMABILITY LIMIT OF PURE PHOSPHINE-AIR MIXTURES AT ATMOSPHERIC PRESSURE

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Abstract: The flammability limit of pure phosphine in air at 1037 ± 14 mb total pressure with 0.39% v/v water vapour was found to be 2.1% v/v phosphine at 10°C , falling to 1.85% v/v at 50°C . The limit value increased slightly with increasing water vapour concentration. The data is discussed in terms of the mechanism and kinetics of oxidation of phosphine. It is predicted on mechanistic grounds that most gases found in grain storages will increase the flammability limit, compared with that for simple phosphine-oxygen mixtures. Ammonia may be an exception possibly lowering the limit as it could interfere with the reaction by reducing the rate of termination. It is concluded that, under conditions normally found in grain storages, temperatures of up to 80°C do not substantially increase the risk from intrinsic phosphine flammability over that at 10°C . The value of the explosion limit concentration determined in this study is consistent with the currently accepted value of 1.79% v/v in air.

INTRODUCTION

Phosphine is often used as a fumigant against insects infesting stored durable commodities such as grain. It has many of the properties desirable for a fumigant (e.g. high penetrant ability, low sorption on foodstuffs, very low residue formation). However it has one major disadvantage: it is flammable and even explosive in mixtures with air at some concentrations and pressures.

It is remarkable that the fire and explosion risks associated with phosphine are still poorly defined. This is despite a long period of use of phosphine as a fumigant, the heavy reliance on the material for pest control in many situations and the recognition that any accident in which phosphine is involved, particularly in fires or explosions, could severely affect the acceptability of the material for use.

Though it can be said that the fumigant has been used safely for treating grain in the past, recent changes in application

methods for phosphine require a further assessment of the hazard. In particular phosphine-generating formulations are now sometimes applied onto the grain surface rather than distributed evenly throughout a grain bulk (e.g. Friemal, in press; Cook, in press). This method has the potential for producing much higher concentrations of the gas in the headspace of storages than normally encountered hitherto. Also forced recirculation of phosphine is being advocated (Cook, 1980), although in the past it has been recommended strongly that this not be done because of possible explosion hazard under reduced pressures (Monro, 1969 (p.251)).

The study presented here provides data on the flammability (or explosion) limits of pure phosphine-air mixtures at about 1 atm total pressure over the range of temperatures and relative humidities encountered in grain storages. The data is fundamental to assessment of flammability and explosion risks during the use of phosphine, as it provides a guide to the flammability of phosphine-air mixtures without complication from gaseous trace impurities, such as may be generated during decomposition of phosphine-releasing preparations. No reliable data has hitherto been available on the variation of the limits over the range of temperatures encountered in grain storages. The often-quoted figure of 1.79% v/v for the flammability limit of phosphine (Monro, 1969) in air is derived from a test carried out at 20°C and unspecified relative humidity with gas derived from a sachet-type preparation of aluminium phosphide (Anon., 1936). The data of Schantarovitsch (1937) and Trautz and Gabler (1929) can be extrapolated to suggest that the flammability limit might lie within the range of phosphine concentration encountered in fumigations at high temperatures (e.g. 50°C). This study was initiated specifically to check on this point since, if it proved to be correct, some procedures currently under consideration could be hazardous.

The mechanism and kinetics of gaseous oxidation of phosphine, summarised in Gmelin (1965), have received much study from Labillardière (1817) to the present. It was shown by van't Hoff (1884) that particular phosphine-oxygen mixtures were flammable or explosive below a certain pressure but were stable above the upper flammability limit (terms used here are explained in Fig. 1). This upper flammability limit can be described in terms of the minimum phosphine concentration in air or oxygen which is flammable at a fixed pressure (Fig. 1, point B'). Dalton and Hinshelwood (1929)

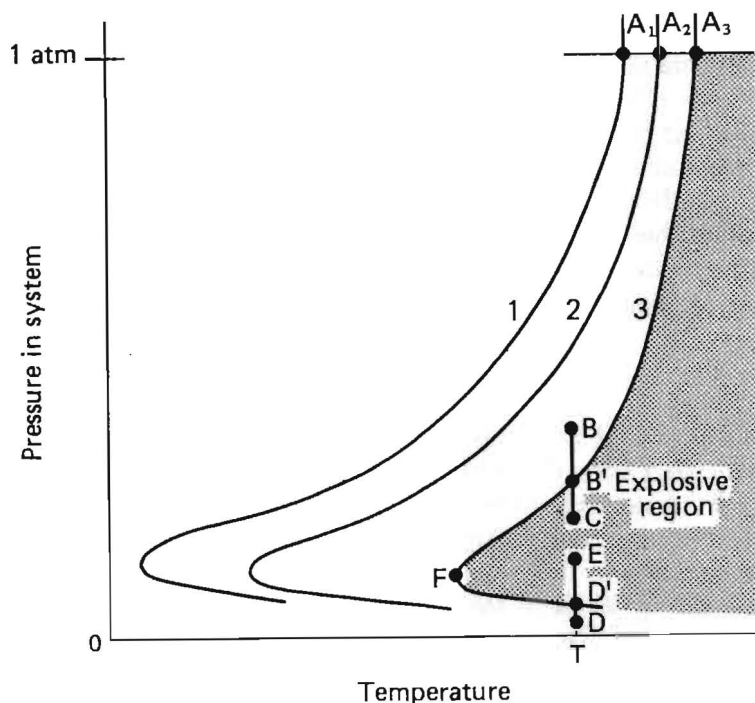


Fig. 1. Explanation of terms relating to phosphine explosibility, used in this paper. Curves 1, 2, and 3 define the boundary between the explosive and stable regions of phosphine-air mixtures for three decreasing phosphine-oxygen ratios for particular temperature system pressure combinations (adapted from curves of Schantarovitsch, 1937). Points A_1 , A_2 and A_3 give the temperature at which a particular phosphine-oxygen ratio is flammable at 1 atm pressure. At temperature T and composition corresponding to curve 3, lowering the system pressure from B to C brings the system within the explosive region. Point B' defines the upper or second explosion or flammability limit. Similarly, raising the pressure from D to E produces explosive conditions, with point D' being the lower or first flammability limit. Point F , the absolute flammability limit, defines the maximum temperature at which the composition corresponding to curve 3 is stable, irrespective of system pressure.

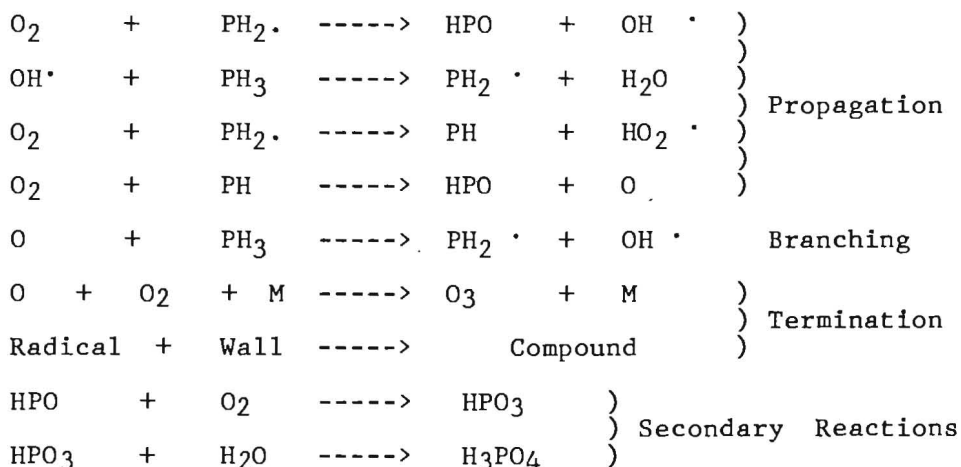
found that there was a second critical value (Fig. 1, point D') for pressure below which a flammable mixture became stable again. The second critical value is very low (< 5 kPa) and is unlikely to be of significance in grain storage practice. With decreasing phosphine-oxygen ratios, the upper critical pressure value falls rapidly and the lower one rises, but at a slower rate (Fig. 1). These two values converge at a particular phosphine-oxygen ratio (Fig. 1, point F). This composition, equivalent to about 0.11% v/v phosphine in air at 15°C , the highest temperature studied (Dalton, 1930;

Schantarovitsch, 1937), defines the absolute flammability limit. Mixtures at less than this phosphine-oxygen ratio are not flammable irrespective of pressure.

We assume here that it is unnecessary to restrict the phosphine concentration in grain stores to below this absolute limit since mixtures at this composition are only flammable at low pressure (approx. 10 kPa, estimated from Schantarovitsch (1937) with allowance for the presence of nitrogen in air). However, to avoid possible explosion risks, we assume that the phosphine-oxygen ratio in the atmosphere of grain storages should not exceed the upper flammability limit at normal atmospheric pressure and, if reduced pressures are to be encountered, the composition of the atmosphere must not be such that it is brought into an explosive range by the reduction in pressure. The latter problem is currently under investigation. The upper flammability limit at normal atmospheric pressure is estimated here.

MECHANISM OF PHOSPHINE OXIDATION

A mechanism has been proposed (Norrish and Oldershaw, 1961) for the oxygen-phosphine reaction system under flash photolysis that is consistent with the observations of Dalton (1930), Melville and Roxburgh (1934) and others. The postulated mechanism is a chain reaction, involving free radicals in the following steps:



The condition for flammability or explosion occurs when the rate of branching exceeds the rate of termination. Similar mechanisms can be expected for any process producing free radicals in a phosphine-

oxygen or -air mixture. The initiation process studied in this work, spark ignition, gives a localised source of radicals and can be taken as similar to that which might occur in grain storages (electrostatic discharge, electrical faults) at atmospheric pressure.

In this reaction scheme there is only one branching reaction. Consequently the rate of branching, r_b , can be defined as

$$r_b = k_1 \cdot P_{PH_3} \cdot P_O \quad (1)$$

where k_1 is the forward rate constant and P_{PH_3} and P_O are the partial pressures of phosphine and oxygen atoms. Since it has been shown by Dalton (1930), that wall effects are negligible at the upper explosion limit, the termination rate, r_t , is given by

$$r_t = \sum_M k_2^M \cdot P_O \cdot P_{O_2} \cdot P_M \quad (2)$$

where P_{O_2} and P_M are the partial pressures of oxygen molecules and the third body M , and k_2^M is the rate constant for this termolecular collision involving M . The flammability limit, where the rate of branching is equal to the termination rate, is therefore defined as

$$k_1 \cdot P_{PH_3} = \sum_M k_2^M \cdot P_{O_2} \cdot P_M \quad (3)$$

The Equation (3) is analogous to that derived for the upper limit by Norris and Oldershaw (1961). At the limit the concentration of radicals is generally small compared with the stable species present and thus termination by collision between two radicals may be ignored. For damp air, Equation (3) may be then written as

$$k_1 \cdot P_{PH_3} = k_2^{O_2} \cdot P_{O_2} \cdot P_{O_2} + k_2^{N_2} \cdot P_{N_2} \cdot P_{O_2} + k_2^{PH_3} \cdot P_{PH_3} \cdot P_{O_2} + k_2^{H_2O} \cdot P_{H_2O} \cdot P_{O_2} \quad (4)$$

where P_i is the partial pressure of the species i . The temperature dependence of the rate constant, k_2^i , is given by

$$k_2^i = r_i e^{E_2^i/T} \quad (5)$$

where r_i is the termolecular collision rate of species i , and for k_1

$$k_1 = r_b e^{E_1/T} \quad (6)$$

where T is the absolute temperature and E_n the activation energy for the n th process.

The presence of gases which cannot give rise to additional radicals, thus enhancing the branching reaction rate, will inhibit the reaction by increasing the terminating termolecular reaction rate.

EXPERIMENTAL

A schematic diagram of the apparatus used for the determination of flammability limits is shown in Fig. 2. The explosion chamber and mixing apparatus were placed inside an environmental chamber which controlled the temperature and water content of the experiment. An explosion chamber of approximately 8L capacity was filled with a mixture of air and water vapour of known composition from the controlled environment chamber. After closing the valves to the environmental chamber and mixing apparatus, the temperature of the explosion chamber was raised to the experimental temperature. This procedure permitted observations to be made over a range of relative humidities and water concentrations.

Phosphine was generated by the action of water on phosphonium iodide. This method is known to give phosphine of high purity (Fluck and Novobilsky, 1969). The gas was stored over water in a glass bell jar. The phosphine was transferred by a pneumatically operated syringe from the storage jar to the explosion chamber. Mixing was helped by a low velocity recirculating fan in the explosion chamber. Preliminary experiments had shown that the gases were well mixed ($\pm 5\%$) after about 1 minute. The temperature and pressure of the experiment were sensed by a thermocouple and pressure transducer in the explosion chamber. A high capacity spark was used to ignite the mixture to ensure that the limit was not dependent on the ignition energy supplied. If the mixture did not ignite additional phosphine was added, the mixture was then sampled by syringe for gas composition analysis, the spark was applied again and the process repeated until flame propagation occurred. Ignition was indicated by a white mist rolling through the explosion chamber. The rate of temperature and pressure rise observed and the delay in ignition were used as qualitative measures of how close the mixture strength was to the flammability limit. Ignition near the limit occurred only after a long delay, up to two minutes, and with a

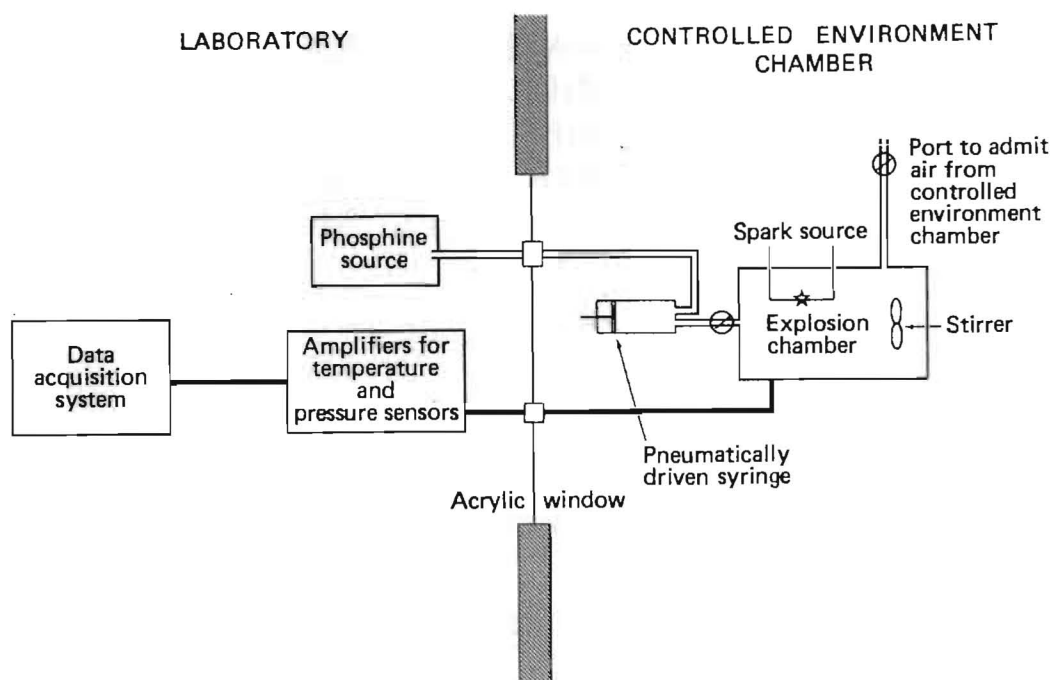


Fig. 2. Schematic diagram of apparatus used to determine the flammability limit.

small rise in temperature and pressure, while an explosion well above the limit gave a rapid and strong reaction.

Gas samples for analysis were taken from the region surrounding the spark electrode prior to applying the spark to the gas mixture. The gas samples were analysed for nitrogen, oxygen and phosphine. The water concentration was not estimated directly, but was controlled by adjusting the water content in the air of the environmental chamber and thus the water concentration in the air admitted to the explosion chamber prior to introduction of the phosphine.

RESULTS AND DISCUSSION

Determination of the flammability limit

The compositions of the gas mixtures in experiments showing flame propagation, together with those having the highest phosphine concentrations that did not result in flame propagation, are shown in Table 1.

The phosphine-oxygen ratios investigated that just did or just did not give an explosion are shown in Fig. 3 as a function of temperature at each of three water concentrations. The flammability limit lies between the points of explosion and no explosion, at each temperature. Although the gas analysis system will give concentrations to an accuracy of 1%, local variations within the explosion chamber lead to an estimated uncertainty of about 5%. The error bars given in Fig. 3 represent this 5% uncertainty.

Calculation of the forward rate constant for oxidation

Equation (4), the equation for the flammability limit, may be written in an alternative form involving the collision frequencies relative to those of oxygen for the termolecular reaction:

$$k_1 \cdot P_{PH_3} = k_2^{O_2} \cdot P_{O_2} (P_{O_2} + aP_{PH_3} + bP_{H_2O}) + k_2^{N_2} \cdot P_{O_2} \cdot P_{N_2} \quad (7)$$

where a and b are the relative collision frequencies for phosphine and water respectively. Arnold and Comes (1979) have accurately measured the parameters required for calculation of the reaction rates $k_2^{O_2}$ and $k_2^{N_2}$ according to Equation (5). These parameter values, given in Table 2, have been used to calculate these rate constants and thus the forward rate constant, k_1 , according to Equation (7). The rates for other third bodies have not been explicitly measured although relative collision frequencies at 300K can be inferred for some species. The available data for chemical species of interest in phosphine flammability are collated in Table 3.

In calculating k_1 , a value of $a = 2.5$ has been assumed. This value is similar to that given by Dalton (1930) and Kassel (1932). Values of k_1 and b for this work were estimated from the variation of $\ln k_1$ against $1/T$. The best overall fit was obtained with a value of $b = 3$ (Fig. 4), giving the rate constant k_1 value and temperature dependence shown in Table 4. The maximum and minimum deviations are also plotted in Fig. 4. The phosphine-oxygen ratio for the calculated limit is shown in Fig. 3 using these values.

Comparison with literature data on flammability

The value of k_1 determined in this work with those obtained by similar calculations using data in the literature are compared in Table 4. The values of k_1 at 300K and the likely uncertainty

TABLE 1.

Composition of near limit mixtures of phosphine, air and water vapour.

T°C	Total Pressure (mb)	Mole fraction				% r.h.	Occurrence of Explosion	Quality of Explosion
		N ₂	O ₂	PH ₃	H ₂ O			
12.4	1036	0.78	0.20	0.0188	0.0036	25	No	
12.3	1039	0.77	0.20	0.0253	0.0036	25	Yes	Violent (some way beyond limit)
11.4	1049	0.79	0.21	0.0204	0.0040	30	No	
11.3	1048	0.77	0.21	0.0214	0.0040	30	Yes	Very mild (close to limit)
28.9	1043	0.77	0.21	0.0173	0.0040	11	No	
28.9	1043	0.77	0.21	0.0209	0.0040	11	Yes	Very mild (close to limit)
50.2	1047	0.77	0.20	0.0180	0.0039	3	No	
50.0	1048	0.77	0.20	0.0200	0.0039	3	Yes	Mild
19.6	1032	0.78	0.19	0.0197	0.0037	16	No	
20.9	1033	0.77	0.20	0.0184	0.0037	15	Yes	Very mild (very close to limit)
40.7	1035	0.78	0.20	0.0155	0.0040	5	No	
40.8	1035	0.77	0.20	0.0186	0.0040	5	Yes	Mild
25.2	1031	0.77	0.21	0.0189	0.0040	13	No	
24.7	1031	0.77	0.21	0.0215	0.0040	13	Yes	Strong
20.3	1023	0.76	0.20	0.0205	0.0187	80	No	
20.3	1023	0.75	0.20	0.0293	0.0187	80	Yes	Very severe (some way beyond limit)
29.8	1028	0.76	0.20	0.0156	0.0206	50	No	
29.9	1025	0.76	0.20	0.0176	0.0206	50	Yes	Mild
40.2	1039	0.76	0.21	0.0198	0.0197	27	No	
39.6	1037	0.76	0.21	0.0188	0.0197	27	Yes	Mild
49.4	1047	0.76	0.20	0.0159	0.0211	17	No	
50.3	1049	0.76	0.20	0.0183	0.0211	17	Yes	Very mild
29.9	1027	0.74	0.20	0.0184	0.0390	94	No	
29.8	1027	0.74	0.20	0.0201	0.0390	94	Yes	Very mild
40.0	1039	0.74	0.20	0.0190	0.0408	56	No	
40.2	1039	0.74	0.19	0.0207	0.0408	55	Yes	Strong
49.9	1051	0.74	0.20	0.0209	0.0370	31	No	
49.8	1049	0.75	0.20	0.0193	0.0370	31	Yes	Mild

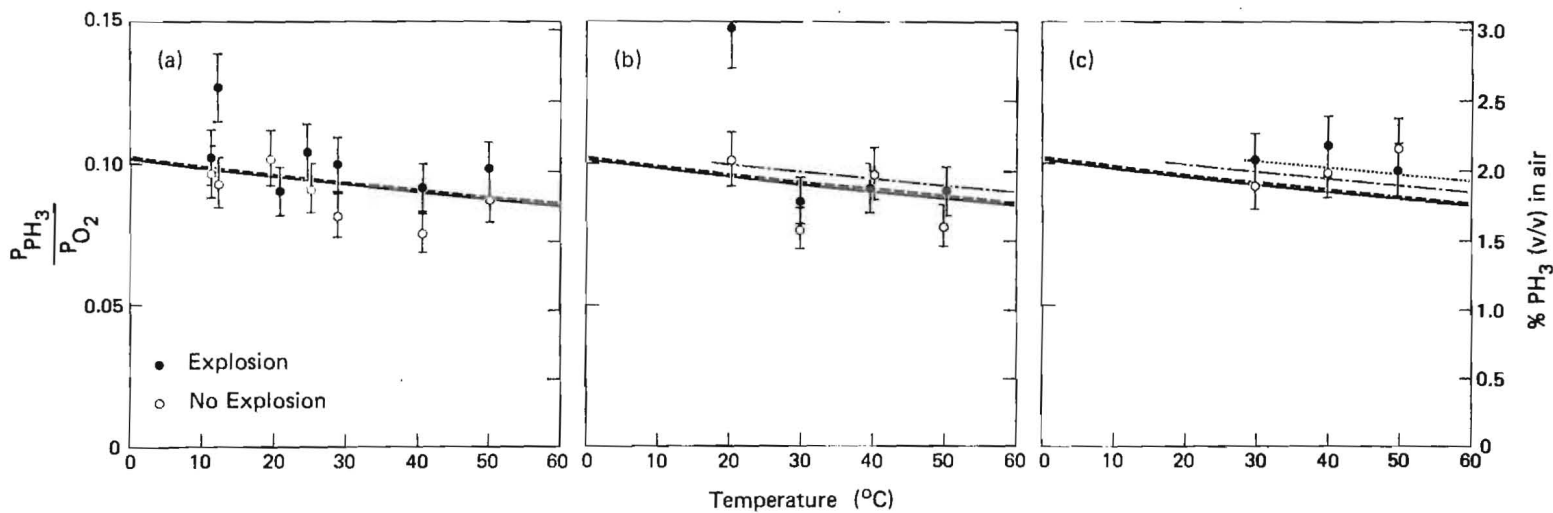


Fig. 3. Variation in flammability of phosphine-air mixtures with temperature at about (a) 0.4%, (b) 2% and (c) 4% v/v water vapour with calculated trends for the dry mixture (—) and with 0.39 (-----), 2.0 (— · —) and 3.9 (·····)% water vapour.

TABLE 2.

Reaction rates for the formation of ozone (Arnold and Comes, 1979).

Gas (M)	r_2^M cm ⁶ molec. ⁻² s ⁻¹	E_2^M K ⁻¹
O ₂	$(6.75 \pm 0.43) \times 10^{-35}$	635 ± 18
N ₂	$(1.82 \pm 0.23) \times 10^{-35}$	995 ± 37

TABLE 3.

Collision frequencies relative to oxygen at 300K estimated from various data sources

Gas (M)	Frequency relative to oxygen	Reference
O ₂	1	
N ₂	0.88	Baulch <i>et al.</i> (1972)
	0.85	Arnold and Comes (1979)
PH ₃	2.7	Dalton (1930)
	2.1	Kassel (1932)
	0.5	Trautz and Gabler (1929)
	4	Schantarovitsch (1937)
H ₂ O	8.8	Baulch <i>et al.</i> (1972)
	4	Trautz and Gabler (1929)
	3	This work
CO ₂	3.8	Baulch <i>et al.</i> (1972)
O	3	Baulch <i>et al.</i> (1972)
O ₃	3.0	Baulch <i>et al.</i> (1972)

factor are also given.

It is notable that the rate constants predicted from earlier work are generally some two orders of magnitude lower at 300K than we find here. There are a number of possible reasons for this difference. Most factors tend to provide a lower apparent value of k_1 . The literature data was obtained for relatively high phosphine concentrations and often with pressures below 8 kPa. The constants a and b will be temperature dependent. The early work was mainly concerned with phosphine-oxygen ratios above 0.1 and the

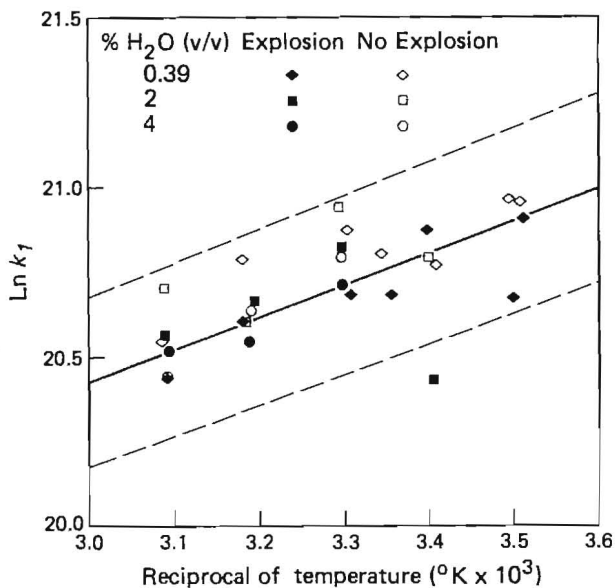


Fig. 4. Dependence of the rate constant for the branching reaction on temperature.

reported limits were those observed by reducing the pressure in the system until explosion occurred. These limits are indicative of the auto-ignition point and will depend on the initiation process and are unlikely to be lower than the spark-induced flammability limits.

There is a possibility that another reaction becomes important at higher pressures. The initiation process involves the formation of an H atom. It is possible for this radical to cause branching through the following reaction



This reaction is not very likely at low pressures (Dalton, 1930) as the hydrogen radical diffuses to the wall too quickly. However at higher concentrations of phosphine and higher total pressures this reaction is possible. The hydrogen atom concentration is dependent on the dissociation of phosphine to give PH_2^{\cdot} and H^{\cdot} . The use of a spark ignition source or photolysis facilitates this process, leading to higher hydrogen atom concentrations, produced locally in the former case and throughout the system in the latter. The additional term to the rate of branching would be

$$k_3 \cdot k_4 \cdot P_{\text{PH}_3} \cdot P_{\text{O}_2} \quad (8)$$

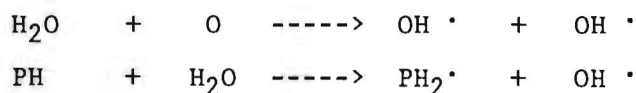
where k_3 is the forward rate constant for the above reaction and

k_4 is the rate constant of the dissociation. This term is the same form as the termolecular termination involving phosphine. The net result would be an additional variation in the value of a with pressure and temperature.

The reasons for the differences between the flammability observed in spark and auto-ignition experiments is currently under investigation.

Effect of other gases on flammability limit

The presence of water vapour reduces the flammability of the mixture. Although the data is consistent with the expected termolecular termination, additional branching reactions involving water could take place:



The first reaction is unlikely to be important as the rate constant at 300K is some 10 magnitudes (Baulch *et al.*, 1972) smaller than the reaction of O with $\text{PH}_2 \cdot$. We do not have sufficient data to assess conclusively the possibility that the second reaction occurs. The rate constant for this reaction has a complex dependence on the rates of propagation of the chain reaction, but since the flammability limit falls with increasing $[\text{H}_2\text{O}]$, these reactions are unlikely to be significant.

Commercial phosphine-releasing agents release other gases in addition to phosphine. In general these gases would tend to reduce the flammability of a phosphine air mixture due to the species acting as an inert gas in the termolecular collision process. However, products which release ammonia could lower the flammability limit via the reaction (Olszyna and Heicklen, 1972):



a reaction analogous to the branching reaction of the reaction scheme of Norrish and Oldershaw (1961).

Implications for phosphine fumigation

The data presented in Fig. 3 shows that there is only a slight effect of temperature on the explosion limit for phosphine in air. By extrapolation, it can be expected that the explosion limit will be $> 1.5\%$ v/v even at 100°C . Limited extrapolation of this kind is reasonable as the kinetic model used here is well founded and the observations show a linear trend when transformed as for Fig. 4.

TABLE 4.

Estimated value and temperature dependence of k_1 , the rate constant for the branching reaction.

Ignition source	k_1	k_1 at 300K	Uncertainty factor	Reference
	$\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	$\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$		
Spark	$(5.9 \pm 0.6) \times 10^{-15} \exp \frac{(950 \pm 50)}{T}$	1.4×10^{-13}	10	This work
Auto-ignition under reducing pressure	$7.2 \times 10^{-11} \exp \frac{(-2590)}{T}$	1.3×10^{-15}	200	Schantarovitsch (1937)
	$2.5 \times 10^{-11} \exp \frac{(-2800)}{T}$	2.2×10^{-15}	200	Trautz and Gabler (1929)
		4.4×10^{-15}) 1.49×10^{-15})	10	Dalton (1930)
		4.6×10^{-15}	200	Kassel (1932)

TABLE 5.

The explosion limits for phosphine-air mixtures at 1 atm pressure and 0.39% v/v water vapour at various temperatures

Temperature (°C)	Phosphine concentration	
	% v/v	g m ⁻³
10	2.10	31.9
20	2.04	31.0
30	1.98	30.1
40	1.92	29.1
50	1.85	28.2
60*	1.80	22.3
70*	1.74	26.4
80*	1.68	25.5

* extrapolated values on the basis of the relationship shown in Fig. 4.

In most fumigations, as now carried out, the concentration of phosphine is unlikely to exceed the flammability limit values given in Table 5, except possibly in the vicinity of a phosphine-generating preparation. However in fumigation carried out where the added preparations are concentrated in a restricted space, such as the headspace of a well-filled vertical cell, it may be possible to exceed those levels in a significant volume of the storage, with the possible hazard from ignition. Clearly such situations are to be avoided either by restricting the total quantity added or by ensuring by some means that there is an adequate rate of gas dispersion from the region in which the preparation is placed so that build-up of a hazardous concentration is prevented.

The upper flammability limit, measured here, refers to that in a free space, such as a storage headspace or in ductwork. In a filled grain storage, much of the storage atmosphere is within the bulk. The upper limit is not sensitive to the size of the reaction vessel in which it is measured, at least down to less than 4 mm for the smallest dimension of the vessel (Dalton 1930). This scale is similar to the distance between some grains. Thus it is possible that the flammability limit in grain will not differ substantially from that in a free space. However, inasmuch as wall effects become significant in very small spaces and the temperature rise during propagation of a flame is inhibited by grain, the upper limit within grain will not be lower than in free space and the free space value can thus be used as a conservative estimate for the total storage atmosphere for safety assessments.

This study has dealt with the limits of flammability of pure phosphine-air mixtures. Further work is in hand to determine the sensitivity of the upper explosion limit to total pressure and to determine experimentally the influence, if any, that gaseous trace components (e.g. diphosphine), generated from phosphine-generating formulations, may have on the limit.

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