CCLI.—*Experiments on the Oxidation of Phosphorus Vapour.*

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THE oxidation of phosphorus vapour by oxygen has recently been shown to be a " chain " reaction by considerations of its general kinetics (Bäckström, *Medd. K. Vetenskapsakad. Nobel-Inst.*, **6**, No. 16, 40), and by experiments on its upper and lower critical limits of oxygen pressure (Rayleigh, *Proc. Roy. Soc.*, 1924, *A*, **106**, 1; Semenov, *Z. Physik*, 1928, **46**, 109). A small proportion (Bowen and Pells, J., 1927, 1096) of the activated molecules produced in the chain mechanism are deactivated by the emission of light, producing the glow. The experiments to be described consist of measurements made on the variation of the intensity of the glow with (*a*) temperature and oxygen pressure, and with concentrations of (*b*) ozone, (*c*) chlorine or sulphur dioxide, and (*d*) ether added to the system.

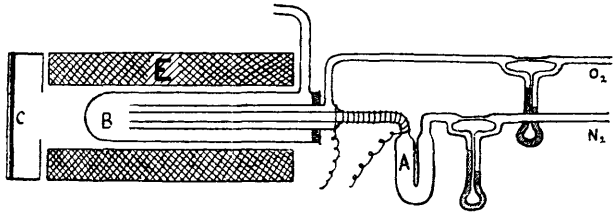
EXPERIMENTAL.

The white phosphorus was purified by treatment with acidified potassium dichromate solution, washing, and drying.

The intensity of the glow was measured by exposing a panchro-

matic plate to the glow for a fixed time. On every plate a photograph through an Ilford neutral gelatin wedge was taken by the light of a standard electric lamp running at a carefully controlled voltage, and placed a definite distance away. The light passed through a filter to make its spectral distribution approximately equal to that of the glow. The plates were measured with a pinhole photo-electric cell photometer kindly lent by Mr. Griffith, of the Clarendon Laboratory (see Dobson, Griffith, and Harrison, "Photographic Photometry," Chap. III, Clarendon Press). This instrument eliminates errors due to variations in the intensity of the measuring light source, and has other advantages over older types. The intensity of the glow was determined by finding with the photometer the position on the wedge photograph where the blackening was equal to that due to the glow. By this means variations between the degrees of development of different plates and

FIG. 1.



the complications due to the laws of photographic plates were avoided. No obvious change of colour of the glow was noticeable in the different experiments, so there is no reason to suspect errors due to differences in the spectral distribution of the glow under different conditions.

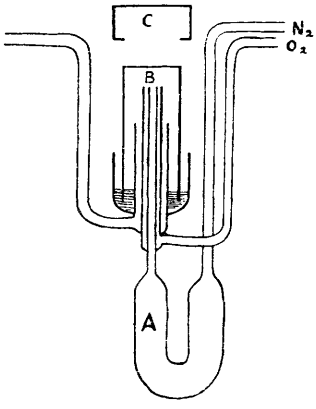
(a) *The Effect of Temperature and of Oxygen Pressure on the Intensity of the Glow.*—White phosphorus was contained in the U-tube, A (Fig. 1), kept at 26·7° in a thermostat. A current of nitrogen, freed from oxygen by passage through a long heated silica tube containing copper, and dried with sulphuric acid, passed through a flow-meter and over the phosphorus. The nitrogen and phosphorus vapour then passed through a tube, wound with nichrome wire electrically heated to prevent condensation, into a wider glass tube in an electric furnace, E. Oxygen was led through a flow-meter into an annular tube as shown in the figure, so that both gases were heated before mixing to produce the glow at B. The photographic plate was placed in the box, C. The temperature of the furnace was found by a calibrated thermocouple placed near the point B. The results are given in Table I.

TABLE I.

Temp.	Partial press. of oxygen (mm.).	Intensity of glow.	Temp.	Partial press. of oxygen (mm.).	Intensity of glow.
59°	243	6·43	212°	118	5·65
67	195	5·6	319	38·5	5·64
105	335	5·58	328	335	5·73
115	118	5·68	354	195	5·75
115	355	5·70	355	355	5·56
130	249	6·24	357	118	5·55
179	235	5·37	377	195	5·61
192	195	5·60	380	243	5·67
204	38·5	5·64			

It appears that between temperatures of 60° and 380° and oxygen pressures of 40—350 mm. of mercury the intensity of the glow does not vary appreciably. Plates taken at higher temperatures showed darker glow photographs, but this was traced to the radiation coming from the hot furnace. This independence of the intensity of the glow over so large a range of temperature and pressure is in agreement with the "chain" mechanism of the oxidation. The amount of phosphorus oxidised in each experiment is the same, and a rise of temperature, by increasing the collision frequency, merely increases the speed of propagation of the chains. The ratio of activated molecules producing light to the total activated molecules in the chains, which is about 1/2000 (Bowen and Pells, *loc. cit.*), is not greatly affected by temperature, as the energy of an activated molecule in the oxidation chains is about 150,000 cals. (Bäckström, *loc. cit.*), and the factors determining it are operating on molecules not of ordinary low energy, but of this very high energy.

FIG. 2.



(b) *Experiments with the Addition of Ozone.*—The apparatus for these experiments is shown in Fig. 2. Nitrogen passed at a measured rate over the phosphorus contained in the tube A, while oxygen and an oxygen–ozone mixture, generated electrolytically (Griffith and Shutt, J., 1921, **119**, 1948) and dried with sulphuric acid, passed at a measured rate through a concentric tube as shown. The ozone concentration was varied by altering the current passing through the generator, and measured by passing it into a neutral solution of potassium iodide, acidifying, and titrating with thiosulphate solution. The glow was formed in the region B, surrounded

by the wider tube sealed with sulphuric acid at the lower end and closed at the top with a plane glass plate. The photographic plate was placed at C. The whole of the glass apparatus was immersed in a light-tight thermostat to eliminate condensation and to keep the partial pressure of the phosphorus vapour constant. The results are shown in Tables II and III.

TABLE II.

Lower ozone concentrations.

Ozone, %.	Intensity of glow.
0	5·15, 5·14, 5·12, 5·16
0·0225	5·12
0·0227	5·28
0·048	5·06
0·07	5·25
0·095	5·10
0·128	5·06
0·137	5·13
0·195	5·15, 5·19, 5·07

TABLE III.

Higher ozone concentrations.

	Intensity of glow.	
Ozone, %.	Obs.	Calc.
0·559	6·07	6·24
0·75	6·72	6·8
1·0	7·59	7·54
1·35	8·52	8·57
1·37	8·52	8·63
1·53	9·11	9·1

From these results it appears that up to 0·14% of ozone there is no increase of glow intensity. Above this point the glow intensity increases linearly with the percentage, according to the expression $5 + 2{\cdot}95\ (a - 0{\cdot}14)$, where a is the percentage of ozone, as shown in the " calculated " column. This effect is independent of the oxygen pressure.

The effect of ozone in increasing the glow intensity is due either to the suppression of some inhibitor or to the appearance of a new chain mechanism. If it is due to the latter cause, the critical percentage of 0·14 may be the lower pressure limit for the new mechanism, below which it is not self-propagating.

(c) *Experiments with the Addition of Chlorine or Sulphur Dioxide.* —The same apparatus as in (b) was used, except that chlorine, generated from potassium permanganate and concentrated hydrochloric acid, was introduced into the oxygen stream instead of ozone. Chlorine was found to decrease the glow, and at high concentrations to extinguish it. The results are given in Table IV, the partial pressure of chlorine being expressed as a fraction of that of oxygen.

In these three series of measurements, the amount of phosphorus carried over per second remained constant, whilst the oxygen flow was varied from 0·039 to 0·996 c.c./sec., and the Cl_2/O_2 ratio from 0 to 2·74. The whole of the results are closely represented by the equation, Intensity $= 6{\cdot}7\ (1 - 0{\cdot}433\ Cl_2/O_2)$, as shown in the " calculated " columns. This equation, although simple, does not seem to be easily explicable in terms of a reaction mechanism. It is different in type from that found by Bäckström (*loc. cit.*) for

TABLE IV.

(i) Rates of flow : N_2, 1·91 c.c./sec. O_2, 0·996 ,,

Cl_2/O_2.	Intensity. Obs.	Calc.
0	6·58, 6·81	6·7
0·0547	6·48	6·54
0·269	5·95	5·92
0·403	5·40	5·53
0·534	5·35	5·15
0·605	5·03	4·95
0·617	4·9	4·91
0·703	4·9	4·67
1·02	3·86	3·74
1·055	3·61	3·64
1·066	3·6	3·61
1·074	3·41	3·58
1·173	3·15	3·30
1·193	3·45	3·24
1·454	2·75	2·49
1·48	2·38	2·40
1·506	2·49	2·33
1·52	2·25	2·29
2·07	1·05	0·70

(ii) Rates of flow : N_2, 1·91 c.c./sec. O_2, 0·188 ,,

Cl_2/O_2.	Intensity. Obs.	Calc.
0	6·81, 6·7	6·7
0·170	6·05	6·2
0·178	6·29	6·18
0·362	5·23	5·65
0·372	5·81	5·62
0·413	5·56	5·50
0·496	5·34	5·26
0·521	5·11	5·19
0·526	5·08	5·17
0·537	5·1	5·14
0·710	4·58	4·64
0·91	4·3	4·06
1·365	2·6	2·74
1·574	2·3	2·14

(iii) Rates of flow : N_2, 1·91 c.c./sec. O_2, 0·039 ,,

Cl_2/O_2.	Intensity. Obs.	Calc.
0	6·7	6·7
0·0647	6·6	6·51
0·118	6·15	6·35
0·251	6·16	5·97
0·346	5·74, 5·76	5·70
0·659	4·80	4·79
0·741	4·84	4·55
0·831	4·51	4·29
0·99	3·73	3·82
1·06	3·51	3·62
1·21	3·20	3·19
1·26	3·00	3·05
1·28	3·10	2·99
1·71	1·55	1·74
2·49	0	0
2·74	0	0

the effect of inhibitors on the benzaldehyde–oxygen reaction, which is of the form : Rate $= k/(a + c)$, where a and k are constants and c is the inhibitor concentration. The intensity of the glow decreases linearly with increase in the Cl_2/O_2 ratio, and by extrapolation appears to become zero when this is about 2·3. It was noticed by visual observation, however, that the glow persisted up to a ratio of 6·8, where it flickered faintly, being sharply extinguished at a ratio of 6·9. The effect of chlorine on the glow is therefore linear with respect to the Cl_2/O_2 ratio over a large range, but when the glow is reduced to less than one-fifth of its intensity, further additions of chlorine do not exert the same quenching power.

Measurements were made with sulphur dioxide in place of chlorine. The diminution of intensity produced by this gas is very much less than that produced by chlorine, and in this case the effect appears to be approximately linear with respect to the SO_2/O_2 ratio over almost the whole range to the extinction point. Visual determinations of the extinction point showed that it occurred at a ratio of 140, whilst that determined by extrapolation is about 200. At high concentrations of sulphur dioxide the glow spread from its small flame-like appearance so that it filled the whole vessel. Table V gives the results, SO_2/O_2 denoting the ratio of the partial pressures of the two gases.

The effect of the two inhibitors chlorine and sulphur dioxide is therefore similar in that a straight line is obtained when glow

TABLE V.

Rate of flow of oxygen, 0·190 c.c./sec.

SO_2/O_2.	Intensity.	SO_2/O_2.	Intensity.	SO_2/O_2.	Intensity.
0	4·18	2·40	4·19	23·4	3·51
	4·41	3·98	3·99	24·0	3·18
	4·25	10·7	3·86	24·5	3·47
	4·35	10·9	3·75	25·4	3·13
	4·43	18·1	3·6	25·5	3·29
0·876	4·14	20·6	3·56	28·7	3·15
2·14	4·02	21·6	3·45	32·6	2·01

intensity is plotted against the (inhibitor)/O_2 ratio, although the curve for chlorine ceases to be linear at very high chlorine concentrations. This may be due to the fact that chlorine, in combining with phosphorus, can stimulate the formation of some oxygen reaction chains, whilst sulphur dioxide acts as a simple inhibitor. Data on the effect of other inhibitors are necessary before a full explanation of the results can be given.

(d) *Experiments with the Addition of Ether.*—In these experiments nitrogen was led over ethyl ether contained in a long tube at constant temperature, and passed with the oxygen to the phosphorus vapour, the total pressure being atmospheric. The concentration of ether vapour was calculated from its vapour pressure at different temperatures. From the results in Table VI, in which the column

TABLE VI.

Ether/O_2.	Intensity.	Ether/O_2.	Intensity.	Ether/O_2.	Intensity.
0	5·25	7·38	5·06	23·7	5·18
	5·05	7·8	5·18	24·1	4·47
	4·97	11·0	4·71	29·6	4·73
	4·87	15·6	5·12	41·3	4·83
	4·91	15·8	4·71	52·1	5·14

"Ether/O_2" denotes the ratio of partial pressures, it appears that even when the ether concentration is 50 times that of the oxygen the glow intensity is not changed. This is a very remarkable result in view of the great effect of ether in lowering the maximum glow pressure in moist oxygen (Centnerszwer, *Z. physikal. Chem.*, 1898, **25**, 1). In these experiments the gases were dried with sulphuric acid, which eliminates the phenomenon of the maximum glow pressure. Under these conditions, then, ether has no effect on the reaction chains, even when present in enormous quantities.

Summary.

(1) Within the temperature range 60—380°, there is no appreciable change in the intensity of the glow of the oxidation of phosphorus vapour. This is in agreement with the "chain" mechanism of the oxidation.

(2) Small quantities of ozone do not affect the glow, but beyond a certain concentration its intensity is increased linearly with the concentration.

(3) Chlorine and sulphur dioxide diminish the glow intensity linearly with the (inhibitor)/O_2 ratio over a large range, the former being much more effective than the latter. There is an indication that the reaction of chlorine with phosphorus can stimulate the production of chains involving oxygen.

(4) Ether vapour has no effect on the glow intensity, even when present at a partial pressure 50 times that of the oxygen (dried with sulphuric acid). This is in curious contrast to the great effect of small quantities of ether on the upper glow pressures of moist oxygen–phosphorus mixtures.

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