CCLIV. *The Phosphorescent Combustion of Sulphur.*

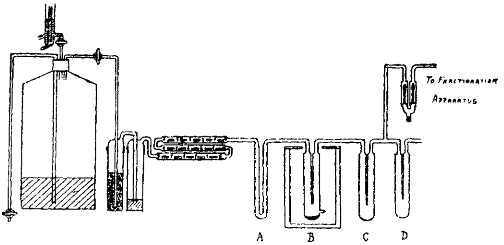
By Harry Julius Emeléus.

The temperature at which sulphur ignites in oxygen varies between 285° and 325° according to the conditions (Moissan, *Compt. rend.*, 1903, **137**, 547). Just below the ignition point the oxidation is accompanied by a bluish-white luminescence (Joubert, *ibid.*, 1874, **78**, 1853) persisting only so long as heat is supplied; at lower temperatures the reaction is non-luminous. The phosphorescent flame changes into the normal flame as the temperature is raised. Heumann showed that its products were sulphur dioxide and a little sulphur trioxide (*Ber.*, 1883, **16**, 139). Bloch found that no ionisation occurred, but stated (without giving details of his experiments) that ozone was formed (*Compt. rend.*, 1909, **148**, 782). The phosphorescent flame was also investigated by Watson (*Chem. News*, 1913, **108**, 187). The main aim of the present investigation was to search for any oxide of sulphur more volatile than sulphur dioxide (such as the still unknown sulphur monoxide might be expected to be), by methods which would enable a very small percentage of such a substance to be isolated. The alleged formation of ozone and the action of inhibiting substances on the phosphorescent flame were also examined.

The Products of the Phosphorescent Combustion of Sulphur.

The production and maintenance of the phosphorescent flame was most readily accomplished by using mixtures of oxygen and nitrogen (obtained from cylinders) with an oxygen content varying between 5—15%, according to the temperature at which the flame was being maintained. All tendency for normal burning to occur was eliminated in this way. The apparatus used for collecting the oxidation product is shown in Fig. 1. The gas mixture from the storage bottle was passed over soda-lime and dried by sulphuric acid and phosphoric oxide, residual condensable impurities being then removed in the U-tube *A* cooled in liquid air. Recrystallised sulphur (Merck's), which had been maintained in a vacuum at its melting point for ½ hour to remove solvent, distilled in a vacuum, and broken up, was distilled in a vacuum directly into *B* from a side tube, before the apparatus was assembled. *B* was heated in an electric furnace (10 cm. internal diameter), temperatures being recorded by a mercury thermometer in contact with the outside of the bulb. The flame in a gas stream under these conditions was invisible, except in a dark room, and remained steady over long periods. Its temperature was approximately 5° above that of the

FIG. 1.



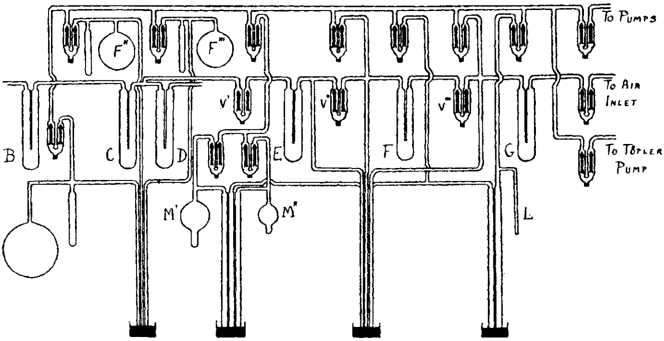
furnace. The oxidation product was frozen in C, which was cooled in liquid air, and it is assumed that none of the product escaped condensation under such conditions. The guard-tube D was similarly cooled. Connexion was made between C and D to an apparatus for the subsequent examination of the oxidation product.

Combustion was always incomplete, as shown by the following values for the oxygen content of the gas issuing at D for various temperatures of B. The ingoing gas contained 8·2% of oxygen, and was passed at the approximate rate of 1 l. per hour.

Oxygen in outgoing gas, %	7·6	5·8	5·2
Temperature	257°	326°	350°

After a number of trials, three experiments were carried out at 275°, 300°, and 325° respectively. The oxidation product condensed in C was examined by a process of fractionation in the apparatus shown in Fig. 2 (compare Stock, *Ber.*, 1914, **47**, 154; 1917, **50**, 989; 1918, **51**, 983). C being cooled in liquid air, B and D were sealed off, the mercury valve V' (Stock, *Z. Elektrochem.*, 1917, **23**, 33) was opened, and the whole apparatus evacuated with a single-stage quartz diffusion pump, backed by a Cenco Hyvac pump. All the valves except V', V'', and V''' were then closed, and the U-tubes E, F, and G were cooled in baths at −85°, −124°, and in liquid air respectively; C was then allowed to warm slowly to room temperature. Its contents thus underwent a process of fractional condensation in E, F, and G (time, 20 minutes); the valves V'' and V''' were closed, and the residual solid in C was sublimed into E, which was cooled in liquid air, V' being then closed.

FIG. 2.



Examination of the Volatile Product.—The condensate in G (which was always very small) was distilled into L (of known volume), where its volume was determined by allowing it to vaporise and observing the pressure produced at a known temperature; the vapour pressure at a suitable temperature was also determined. It was then distilled back into *G* and stored. The condensate in *F* was divided into three fractions in order of descreasing volatility by allowing evaporation to occur at −56° to −58°. The volume of each of these in turn was determined in the gas measuring flask *M''*, of known volume, and the vapour pressure–temperature curve of each was determined in *L*, after which the fractions were stored in *M'*, *F''*, and *F'''*.

Results.

(All recorded gas volumes are reduced to 0° and 760 mm. of mercury.)

Experiment 1. Temperature, 275° (± 3°). Approximately 17 l. of an oxygen–nitrogen mixture containing 13·7% of oxygen were passed at the rate of 1 l. per hour.

Fraction in G : Volume = 0·1 c.c.; vapour tension at 99° = 0·7 mm.

Fraction in F :

Most volatile fraction. (Volume = 41·7 c.c.)		Middle fraction. (Volume = 58·5 c.c.)		Least volatile fraction. (Volume = 91·6 c.c.)	
Temp.	Vap. press.	Temp.	Vap. press.	Temp.	Vap. press.
−57·6°	38·0 mm.	−56·4°	41 mm.	−72·6°	10·5 mm.
−47·2	77·0 ,,	−48·3	70 ,,	−54·6	44 ,,
−37·1	151 ,,	−38·0	144 ,,	−40·0	123 ,,
−27·7	266 ,,	−28·2	260 ,,	−27·9	259 ,,
−17·6	470 ,,	−16·9	484 ,,	−17·5	459 ,,

The small fraction in *G* had a vapour tension consistent with its being sulphur dioxide which had escaped condensation in *F*. Any more volatile oxidation product would have collected in *G*, and its absence is a conclusive proof that no such product is formed in the phosphorescent flame. The experiment would not, however, have detected any substance not condensed in liquid air. It was shown in a separate experiment that no substance more volatile than sulphur dioxide and reacting with mercury was present.

The above vapour-tension measurements for the three fractions obtained from the condensate in *F* fall on one curve, indicating that a homogeneous substance was present. They agree with the values for pure sulphur dioxide obtained by use of the same pentane-filled thermometers, showing the condensate to be pure sulphur dioxide. The experiments at 300° and 325° were carried out in precisely the same manner, and led to the same conclusions. Unless special precautions were taken to avoid contamination of the sulphur by dust, a small quantity of carbon dioxide (varying from 0·6 c.c. to 0·2 c.c.) was formed during the oxidation, and was readily isolated from the condensate in *G*, and identified by vapour-tension measurements.

The less volatile reaction product. A small quantity of solid was always found in *C* and *E*. In some experiments it was white, but in others it contained a deep blue material which disappeared after 48 hours and was not isolated. Its colour and behaviour suggested that it was sulphur sesquioxide. Its formation always occurred where solid sulphur dioxide had melted in the condensing tube, and was most pronounced at higher temperatures and with faster gas streams—two conditions favouring the sublimation of sulphur. It is concluded that this lower oxide was produced in a secondary reaction between sulphur trioxide (see below) and sulphur.

The white reaction product dissolved in water, giving a fog, and the solution contained sulphuric acid and was without reducing properties on indigo solution. It appeared to be sulphur trioxide, confirming an observation by Heumann (*loc. cit.*). Its vapour attacked mercury, giving sulphur dioxide and a sulphate. In the experiment at 275° already described, 2·2 c.c. of sulphur dioxide were formed in this way. Assuming an equal quantity of sulphur to have combined with the mercury, the quantity of sulphur trioxide formed in the phosphorescent combustion was approximately 2% of the quantity of sulphur dioxide. The value given for the formation of the trioxide in the normal combustion is approximately the same (Hempel, *Ber.*, 1890, **23**, 1455).

Formation of Ozone in the Phosphorescent Flame of Sulphur.—At the temperature at which sulphur glows, the thermal decomposition of ozone takes place rapidly. Bloch's report of its production is not accompanied by sufficient experimental detail to enable his conditions to be reproduced. Those chosen in testing for ozone were, therefore, (*a*) the oxidation of sulphur in a **U**-tube, as already described, and (*b*) the conditions described by Heumann (*loc. cit.*), sulphur being heated in a silica dish supported in a nickel dish (18 cm. diameter). Under these conditions the sulphur vapour oxidises near the heated surface, giving tongues of phosphorescent flame, from which gas may be withdrawn by inserting a funnel attached to a pump. In each instance the oxidation products traversed two narrow, thin-walled **U**-tubes, cooled to −124° to remove sulphur oxides, and the gas stream then passed over a drop of freshly distilled mercury, the tailing of which was used as a test for ozone.

With method (*a*), the glow being produced at temperatures between 200° and 300° by gas streams containing 8% of oxygen and passing at the rate of 2 l. per hour, no tailing of the mercury drop was observed (10 tests of 1—3 hours' duration each). Using method (*b*) and the same duration of test, negative results were obtained in each of six tests. Under these conditions, therefore, no ozone is formed in the phosphorescent combustion of sulphur.

Experiments to determine whether a "Glow Pressure" exists in the Oxidation of Sulphur.—Observations on the rate of oxidation of arsenic at different pressures have shown that for each temperature there is a "glow pressure," above which the oxidation is non-luminous, and below which luminescence occurs (Emeléus, J., 1927, 783). A similar examination of the oxidation of sulphur gave negative results. The same method as for arsenic was employed, the apparatus being modified by the addition of a bulb tube immersed in liquid air to a constant depth to freeze out the sulphur dioxide. By this means the rate of oxidation could be followed manometrically. In a series of experiments at 300—340° there was no sudden increase in the oxidation rate as the pressure was reduced, corresponding to the initiation of the glow. Apparently the inhibiting action of sulphur dioxide on the phosphorescent flame is very strong (see below), and the conditions employed did not provide for its sufficiently rapid removal, even at reduced pressures.

The Inhibition of the Phosphorescent Flame of Sulphur.

The large influence of sulphur dioxide in raising the ignition point of sulphur has long been known (compare Moissan, *loc. cit.*). Recently, White (J., 1927, 793) has shown that pentane, acetylene, and methane act similarly. The influence of inhibitors on the phosphorescent stage of the combustion has not, however, been considered, and the experiments described below were directed towards this aspect of the problem. It is suggested that inhibition of the phosphorescence is the primary cause of the raising of the temperature of normal ignition.

Inhibition by Sulphur Dioxide.—In studying the influence of inhibiting substances on the phosphorescent flame, the latter was produced by heating sulphur in a U-tube in a stream of an oxygen–nitrogen mixture, as already described. The depth to which the U-tube was immersed in the furnace was made as small as possible to minimise the formation of sulphur dioxide in the non-luminous oxidation occurring in the tube above the luminous zone. With an 8% oxygen–nitrogen mixture, the influence of varied additions of sulphur dioxide on the temperature of extinction of the glow was first examined, the sulphur dioxide being introduced into the gas stream from a side tube, and the gas composition determined by counting the bubbles in previously calibrated bubblers. The glow was first obtained at a temperature at which the sulphur dioxide concentration being examined was too small to inhibit it, and the temperature of the furnace was then allowed to fall slowly. The point could thus be found at which the glow disappeared, the observation being made in a dark room with well-rested eyes. The following readings were obtained with a gas stream of 30 c.c. per min. :

Conc. of SO_2 (% by vol. of total gas stream)	0	9·2	19	30	36	44
Temp. of extinction of glow	195°	235°	267°	295°	309°	328°

If, when the glow had disappeared, the temperature was again raised, the luminosity was first observed at a temperature 5—10° higher.

Influence of Organic Vapours.—The action of the vapours of a number of organic liquids was examined by heating the sulphur in a U-tube in a stream of an oxygen–nitrogen mixture (8% oxygen), observing the glow, and then diverting the gas stream through a bubbler containing the liquid in question. It could thus be seen whether the glow diminished in intensity or was extinguished. When inhibition took place the glow invariably reappeared on restoration of the normal gas stream, and could be put out at will, showing that no permanent change in the sulphur surface had taken place. The vapours of the substances tabulated below all inhibited the glow completely over the temperature range stated (temperature of bubblers, 14°). The effect of further increasing the temperature could not be studied, because charring took place, and also because much sulphur dioxide would have been formed in the non-luminous oxidation.

Benzene	270—350°	Ethyl alcohol	300—325°
Toluene	280—325	Ethyl acetate	290—320
Chlorobenzene	270—290	Amyl acetate	295
Pyridine	310	Chloroform	280—300
Ethylene dibromide	280—320	Acetone	220—300

The influence of the concentration of the organic vapour on its effectiveness was not investigated in detail, but the general nature of the result was shown in the case of methyl salicylate, which has a low vapour pressure at room temperature and accordingly has only a weak action on the glow. It was possible to find the temperature at which the luminosity was just inhibited at different concentrations by maintaining the bubbler containing the inhibiting substance at a series of temperatures. The method of observation was the same as that used in the experiments with sulphur dioxide. When the bubbler was maintained at 12°, 24°, and 38°, the glow was extinguished at 243°, 258°, and 268° respectively. Increase in the concentration of the inhibitor, therefore, raises the temperature at which the glow occurs, as in the oxidation of phosphorus.

Tests were made when the luminous oxidation was inhibited by benzene to determine if any non-luminous oxidation was occurring. A small amount of sulphur dioxide could always be detected by the decoloration of potassium dichromate solution.

Discussion.

As far as can be judged from the nature of the reaction products, the chemical change in the phosphorescent combustion of sulphur is the same as in the normal flame. It is a significant fact that no evidence whatever of the formation of sulphur monoxide was obtained, though the conditions were such that, by analogy with, say, the glow of phosphorus, lower oxidation products would have been produced if they existed. The negative results of the ozone tests show that in this respect, too, the chemiluminescent oxidations of sulphur and phosphorus differ.

Consideration of these inhibition phenomena emphasises the two distinct stages in the oxidation of sulphur, *viz.*, the luminous and the non-luminous oxidation. The dynamics of the latter were investigated by Bodenstein and Caro (*Z. physikal. Chem.*, 1911, **75**, 30), who showed that the reaction rate was proportional to the sulphur surface, and hence, presumably, that the reaction was taking place at this surface. It was also found to be uninfluenced by sulphur dioxide. The slow luminous oxidation is, on the contrary, on the basis of visual observation, a gas reaction, and has been shown to be sensitive to the presence, not only of sulphur dioxide, but also of many other substances. In this, the analogy with the oxidation of phosphorus appears to be very close, and hypotheses as to the mechanism of inhibition of the latter phenomenon have been put forward which may be applied here (*e.g.*, Bäckström, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, No. 16). All contain in essence the idea that " active " molecules are produced in limited numbers, and are essential for the maintenance of the luminous oxidation. The molecules of the inhibiting substances are supposed to be able to deactivate such molecules, and so to hinder the reaction. In the case of the oxidation of sulphur this explanation cannot yet be put in more precise terms.

The author wishes to express his gratitude to Professor H. B. Baker, F.R.S., for his interest and advice throughout this research. It is also a pleasure to thank Professor A. Stock for the opportunity afforded to the author of studying the vacuum technique used in his laboratory in Karlsruhe. The research was carried out during the tenure of an 1851 Senior Studentship. Apparatus and materials were purchased from a grant by Imperial Chemical Industries, Ltd., to the Chemical Department of this College, and from the Dixon Fund.

IMPERIAL COLLEGE OF SCIENCE,
SOUTH KENSINGTON, S.W. 7.

[*Received, April 23rd,* 1928.]