149. *The Kinetics of the Reaction between Oxygen and Sulphur. Part II. The Frigescent Oxidation of Sulphur.*

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It has been shown (Part I; Sayce, J., 1935, 1767) that saturated sulphur vapour and oxygen between 50 and 400 mm. and 200° and 280° react on quick cooling, producing in this rapid " frigescent " reaction more sulphur dioxide than is formed during long periods of steady heating at the same temperature range. The phenomenon is frequently accompanied by a flash of light. The normal slower reaction taking place at 240—280° has already been studied (see Part I) by adopting an experimental technique for circumventing the frigescent reaction, the detailed investigation of which is now described.

Visible reaction occurs only in presence of condensed sulphur which has been rapidly cooled to approx. 160° and is due to the explosion of sulphur vapour and oxygen at this temperature. The explosion appears to be initiated by energy liberated in a transition in the liquid sulphur, a portion of which is itself oxidised, and to occur only when this is liberated suddenly after a hysteresis resulting from rapid cooling. This hypothesis is supported by the fact that the reaction is suppressed by small amounts of iodine and chlorine, the former of which profoundly affects the physical properties of sulphur at about this temperature by an interference in the transition $\lambda S \rightleftharpoons \mu S$.

Experimental.

The experimental work was done in Pyrex glass, for the most part in sealed bulbs of 50—100 c.c. capacity. The sulphur used was carefully purified (Aynsley and Robinson, *Chem. and Ind.*, 1935, **54**, 392), weighed on a microbalance, and dispersed uniformly over the walls of the vessels by sublimation in a vacuum. The oxygen, generated by electrolysis of dilute sulphuric acid and freed from traces of acid spray, hydrogen, and ozone, was passed over potassium hydroxide and phosphoric oxide before use. The charged bulbs were heated in a thermostatic oil-bath, and after the prescribed treatment the amount of sulphur dioxide formed was estimated by opening them under 0·001*N*-iodine. More than a trace of the trioxide was found only in exceptional cases. As was anticipated from the earlier work, a high degree of concordance between the individual results was not obtained, and for that reason experiments were normally repeated several times.

Influence of Initial Temperature.—Bulbs containing saturated sulphur vapour and oxygen at 180 × 10^{-6} g. per c.c. (equivalent to a pressure of approx. 100 mm. Hg at 15°) were heated for 5 mins. at $T°$ and allowed to cool, in the air, to room temperature. From the sulphur dioxide formed (see below), it is evident that for sulphur to take part in the frigescent reaction it must have been above an initial temperature of 200°, and further, that the maximum reaction is attained when it has been heated to approximately 220°.

T	180°	190°	200°	210°	220°	230°
SO_2 yield per 100 c.c. (g. × 10^{-6}) ...	17·6	12·5	40·0	838	3240	2912

Influence of Sulphur Concentration.—Bulbs containing the above concentration of oxygen and various amounts of sulphur were heated at 250° for 5 minutes and cooled as before. In Table I are recorded the sulphur concentration, yield of sulphur dioxide (g. × 10^{-6}), the temperature ($T°$) at which the sulphur vapour became saturated, and the cooling period (P secs.) after which the flash, if any, occurred. Two features emerge : (i) that there is no visible inflammation and appreciably less sulphur dioxide is produced when the sulphur vapour reaches saturation below a specific temperature, *ca.* 174°, and (ii) that when saturation is reached above this temperature the probability of incandescence is high, and although the amounts of sulphur dioxide vary somewhat they range about a constant figure and are not greatly altered by a considerable excess of sulphur. The period after which the flash takes place is fairly uniformly 55 secs., pointing to a critical temperature at which incandescence is initiated. It is notable that the flash is always seen *after* the appearance of condensed sulphur upon the walls of the reaction vessel.

TABLE I.

Expt. No.	1	2	3	4	5	6	7	8	9	10	11	12
S, mg.	0·236	0·382	0·417	0·624	0·651	1·024	1·038	1·14	1·36	2·10	3·01	3·36
SO_2 yield (g. × 10^{-6})	0·0	208	288	512	864	1440	1506	1472	944	2114	1792	1840
T	154°	160°	164°	173°	174°	185°	186°	188°	192°	203°	214°	217°
P	Nil	Nil	Nil	Nil	58	54	51	56	59	58	52	51

Expt. No.	13	14	15	16	17	18	19	20	21	22	23
S, mg.	3·72	3·99	4·11	4·38	4·54	4·71	5·01	5·93	6·75	10·00	12·40
SO_2 yield (g. × 10^{-6})	2560	2175	1569	2115	1218	2337	2369	1378	1137	2210	3135
T	220°	222°	223°	225°	226°	227°	229°	234°	239°	253°	260°
P	47	64	58	74	56	46	47	Nil	Nil	60	51

Temperature of Bulb at which Flash Occurs.—Bulbs fitted with thermocouples of low heat capacity constructed of fine chromel-eureka wires thinly coated with glass, and with the junction situated either at the centre or touching the wall, were charged with excess of sulphur and oxygen as before, heated to 250°, and allowed to cool in air. The mean temperature at which flashing occurred was found to be 170° irrespective of the position of the junction. By applying to the flash intervals, P, of Table I a cooling curve obtained with a typical bulb, the apparent mean temperature of flashing of the 23 cases was found to be 172°. Thermocouples of bare wire gave temperatures a few degrees lower, and there is reason to believe that an allowance of about 10° must be made on the above figures for the heat capacity of the couple and the lag of the galvanometer, so the true mean temperature of the reactants at which flashing occurs is approx. 160°. Hence, since no flashing occurs in bulbs in which the sulphur reaches saturation below about 174°, it is evident that it is consequent upon the presence of condensed sulphur.

Influence of Rate of Cooling.—It has already been shown (Part I, *loc. cit.*) that very slow cooling leads to the production of very small quantities of sulphur dioxide, and quick cooling in kerosene, water, or air to increasingly larger quantities. In the following experiments the range of temperature in which quick cooling is effective was investigated. Bulbs were placed in a bath at 240° for 5 minutes and quickly removed to a second bath at a lower temperature, wherein they were allowed to cool very slowly. Experience having shown negligible amounts of sulphur dioxide to be produced by such slow cooling, it follows that the sulphur dioxide found was mainly produced during cooling through the interval of temperature between the two baths. Individual results showed considerable variations, an occasional anomalously high yield of sulphur dioxide being obtained at each temperature; these anomalies being omitted, the means of many experiments gave the data recorded in Table II.

TABLE II.

Temp. of cooling bath	200°	180°	170°	160°	150°	145°	140°	130°
Average yield of SO_2 per 100 c.c. bulb capacity (g. × 10^{-6})......	66·0	76·0	80·5	83·2	424	789	1479	2490

With rapid cooling to below 160°, the temperature at which flashing occurs, the yield rises suddenly and continues to increase as the temperature drop is increased : this is believed to be due to a greater speed of cooling more favourable to hysteresis in the transition of μS to λS (see later).

Influence of Local Cooling.—An hour-glass-shaped bulb, containing sulphur and oxygen at the above concentrations and having a narrow constriction between its two chambers, was completely immersed in oil at 250° for 5 mins., after which the upper portion was drawn out of the bath until the constriction was level with the surface of the oil. After 48 secs., and in a second experiment 110 secs., a very brilliant flash occurred, filling both chambers of the bulb and accompanied by a distinctly audible click. Evidently, the frigescent reaction is initiated in the cooler part of the system, whence it spreads homogeneously. The especial brilliancy of the flash in these experiments is ascribable to the concentration of sulphur vapour maintained in the heated portion of the bulb.

That the flash of the frigescent reaction is, in fact, an explosion of sulphur vapour and oxygen was shown in another way. A bulb furnished with an internal spark-gap of tungsten wire and containing the two reactants was heated gradually in an oil-bath, a spark from an induction coil being passed across the gap at intervals of about 5°. The temperatures at which an explosion was seen to occur lay between 142° and 150°, mean 146°. If the spark was delayed until a higher temperature and a correspondingly higher concentration of sulphur vapour had been reached, the brilliancy of the flash was increased, and even at 250° the mixture exploded vigorously, showing that it was still much below the upper critical explosion limit.

Influence of Iodine and Chlorine.—Bulbs containing sulphur and oxygen as before and, in some cases, small amounts of iodine were heated to 240° and cooled in the atmosphere. The results (below) show that iodine to the extent of 1—3% of the sulphur is enough entirely to inhibit the reaction, such sulphur dioxide as was formed in bulbs containing iodine being entirely attributable to oxidation during the period of initial heating. High accuracy is not claimed for the amounts of iodine which were weighed into the reaction bulbs, since its appreciable vapour pressure led to some loss on evacuation.

S, mg.	4·145	3·102	3·483	4·883	3·710	5·499
Iodine, mg.	—	—	—	0·102	0·113	0·054
SO_2 yield (g. $\times 10^{-6}$)	1229	1033	1182	68	78	78
Flash after, secs.	40	51	45	—	—	—

The effect of lower concentration of halogen was conveniently studied by mixing chlorine with pure oxygen in a storage bulb and introducing the mixture into the reaction bulbs which were heated to 240° for 5 mins. and cooled in air. Each column in Table III represents the mean of several experiments : evidently chlorine behaves like iodine, since traces of it have a marked effect on the amount of sulphur dioxide produced, as little as 0·01 mg. per 100 c.c. sufficing to reduce the yield of sulphur dioxide to one-tenth.

TABLE III.

S, mg.	5·88	6·23	6·61	6·93	6·48	5·81
Cl, mg.	0	0·0098	0·0133	0·0365	0·231	0·714
S : Cl ratio	∞	635	496	190	28·0	8·13
SO_2 yield (g. $\times 10^{-6}$)	2432	240	215	134	42·5	11·8

It remained to be discovered whether the inhibition is upon the visible homogeneous reaction or upon the change in the condensed sulphur which initiates it. Experiments to observe the minimum temperature at which an electric spark ignites mixtures of oxygen and sulphur vapour, already described, were repeated in presence of various amounts of chlorine (Table IV), and it was found, within the limits of experimental error, to be unaffected by concentration of chlorine up to 0·014 mg. per 100 c.c. At low concentrations chlorine does not impede the homogeneous reaction between sulphur and oxygen once it is started, and the observed inhibition (Table III) must be due to its effect upon the condensed sulphur. Concentrations of 0·2 mg. and more cause an increase in the minimum temperature for explosion (Table IV), and also reduce the yield of sulphur dioxide (Table III) below that expected from the initial heating at 240° (see above). As was subsequently demonstrated by direct experiment, chlorine at such concentrations also poisons the normal wall reaction described in Part I.

TABLE IV.

Cl, %	0	0·013	0·035	0·093	0·59	1·6
Cl, mg. per 100 c.c.	0	0·00509	0·0137	0·0365	0·231	0·627
Min. temp. for explosion	142—150°	151°	152°	160°	170—180°	170—175°

DISCUSSION OF RESULTS.

Sulphur dioxide is produced in considerable quantities when mixtures of sulphur vapour and oxygen are cooled rapidly from temperatures over 210°, usually with the emission of a momentary flash of light. Once started by cooling a portion of the reaction vessel, the flash is capable of passing through a narrow tube into a region which is still uncooled, from which it appears that the particular reaction made visible by flashing is initiated by a cooling of the reactants and then proceeds homogeneously throughout the system. The production of sulphur dioxide is uninfluenced by the concentration of the sulphur, provided that this be more than sufficient to saturate the vapour when the reaction vessel is between 170° and 180°. With lower concentrations of sulphur there is no visible phenomenon accompanying the reaction, and the production of sulphur dioxide falls with diminishing sulphur content. The temperature of the vessel when flashing takes place is approximately 160°; hence, it depends on the presence of condensed sulphur. With very slow cooling the phenomenon is never observed, and even with rapid cooling it does not arise unless the range of rapid temperature change includes the region 150—160°. The temperature limit of 160°, above which the visible homogeneous reaction does not occur, might be attributable to an upper critical explosion limit to the reaction were it not that mixtures of saturated sulphur vapour and oxygen at the concentration used in the preceding experiments can be ignited electrically at all temperatures from 146° to 250°. If it be contended that the energy of ignition is greater when electrical means are employed than under the normal conditions of flashing, we have the experiments with the hour-glass-shaped bulb to prove that the homogeneous reaction initiated by cooling can, in fact, pass into a region where the concentration of sulphur is relatively high.

It is, therefore, to the film of sulphur condensing on the walls of the vessel at 160—170° and to its previous history that particular importance attaches : it must have been above 210° and must have cooled therefrom to 160° at a sufficiently rapid rate. It is known that there is a gradual transition of λS to μS when the element is heated above 150°, and that the reverse change shows a hysteresis so great as to allow the formation of "plastic sulphur." It is presumed that in the condensate the transition from μS to λS occurs gradually under conditions of very slow cooling, but that with quick cooling the energy of transition is liberated suddenly at *ca.* 160°. If this assumption be true, two alternative explanations are possible to account for the initiation of the visible homogeneous reaction. On the one hand, the gas reaction may be activated by the energy of transition, or, on the other hand, this energy may cause a local oxidation of the condensed sulphur which, in its turn, may provide the energy necessary to start the gas reaction.

Support is given to the latter explanation by the results in Table I. In a typical experiment the total yield of sulphur dioxide is made up of at least two distinct reactions. First, there is oxidation during the 5 mins.' preliminary heating period at 250° which, from the evidence of Part I, amounts to approximately 400×10^{-6} g. of sulphur dioxide per 100 c.c. Secondly, there is, in all but two of the later experiments, oxidation in the gaseous phase accompanied by flashing. But in the absence of the visible reaction there is evidence of a third reaction, for in Expts. 20 and 21 there was considerable oxidation producing about 1258×10^{-6} g. of sulphur dioxide. After deduction from this figure of the contribution made during the heating period, there remains 858×10^{-6} g. of sulphur dioxide, which, from the evidence of Table II, must have been made in the region of temperature where flashing normally occurs, presumably by oxidation of condensed sulphur, a presumption justified by the fact that the mean total yield of sulphur dioxide in Expts. Nos. 10—19 and 22 and 23, in which flashing occurred, surpasses the total yield of Nos. 20 and 21 by 862×10^{-6} g. of sulphur dioxide. This corresponds to the complete combustion of 100 c.c. of saturated sulphur vapour (assumed to be S_8) at 164°.

The effect of small amounts of iodine and chlorine in preventing oxidation also favours the hypothesis that it is initiated by a transition of μS to λS, for halogens have long been known to interfere with this transition. The quantities of chlorine which suffice to inhibit the reaction are too small to be effective by removing sulphur as sulphur chloride, and below 0·0365 mg. of chlorine per 100 c.c. neither the high-temperature wall reaction nor the visible reaction is materially affected; yet as little as 0·01 mg. of chlorine per 100 c.c. prevents the visible reaction and reduces the total yield of sulphur dioxide to a tenth of its value with pure oxygen. It is believed that the inhibiting effect of chlorine operates upon the oxidation of condensed sulphur by affecting the transition which initiates it, and thereby denying the homogeneous reaction the necessary activation.

SUMMARY.

1. Mixtures of sulphur and oxygen of widely different compositions, when cooled rapidly from above 210°, react at *ca.* 160°.
2. The reaction is two-fold, and comprises the oxidation to sulphur dioxide of (*a*) condensed and (*b*) uncondensed sulphur. The latter is accompanied by the emission of light.
3. The first reaction is initiated by energy released in a transition in the liquid sulphur. There is reason to believe that the homogeneous reaction is activated by the oxidation of condensed sulphur rather than by the energy of transition.

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