59. *The Oxidation of Carbonyl Sulphide.*

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The oxidation of carbon disulphide has long been a subject of study (Bone and Townend, "Flame and Combustion in Gases," Chap. 33). In particular, experiments have been made upon the explosive reaction with a view to determine the mechanism of the process. The results obtained were somewhat discordant, and it was often supposed that this irregularity was due to the presence of varying amounts of impurities in the substances employed.

The process has certain characteristics of a chain reaction, since it shows limit phenomena often found in such reactions (Thompson, *Z. physikal. Chem.*, 1930, *B*, **10**, 280; Thompson and Kearton, *ibid.*, 1931, *B*, **14**, 359). There appears to exist a critical region of temperature and pressure within which spontaneous ignition of carbon disulphide–oxygen mixtures occurs, but outside which no measurable change can be detected. The relationships are very similar to those exhibited, *e.g.*, by mixtures of oxygen with phosphorus (Semenov, *Z. Physik*, 1927, **46**, 109; 1928, **48**, 571) or hydrogen (Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, **122**, *A*, 610; cf. *ibid.*, 1931, **130**, *A*, 640; 1931, **134**, *A*, 1; 1932, **138**, *A*, 311).

The influence of different factors upon the critical limits for explosion were examined, to obtain evidence, if possible, of a reaction chain which would accord with the facts. Although there seemed to be indications that the chains are broken by carbon disulphide itself, and although it was to some extent plausible to assume the initial production of some chemically active peroxidic compound, yet the nature of the chains was not fully elucidated.

For this reason, and also since the necessary experimental procedure was laborious, it seemed advisable to examine the very closely related process—the oxidation of carbonyl sulphide—in the hope that it might lead to an explanation of both reactions. No kinetic measurements upon the oxidation of carbonyl sulphide have previously been made, although it is recorded that its ignition temperature is higher than that of carbon disulphide–oxygen mixtures. (The latter ignition temperature may, however, be considerably affected by an alteration in the experimental procedure.)

The results to be described indicate that mixtures of carbonyl sulphide and oxygen exhibit the same general phenomena as those of carbon disulphide and oxygen, though there are differences in detail. There is no noticeable change below about 205°. Above this temperature explosion may occur if the pressure is above a certain value depending somewhat on the temperature. There may also be an upper pressure limit for the explosion, above which no change occurs, but this is rather indefinite and probably only exists over a narrow range of temperature. In the absence of explosion, no measurable reaction occurs. The effect of inert gases and other factors upon the conditions required for ignition is usually in agreement with that which would be anticipated if the phenomena were truly connected with the propagation of branching reaction chains; occasionally there are important differences.

Such chain hypotheses have recently been adversely criticised, but no more reasonable alternative explanation has been advanced adequately and unambiguously to cover the facts. Further, lack of validity of the theory in no way affects the reality of the facts: the two have often been confused, irregularities in the observations being considered to forbid the construction of explanatory hypotheses. Such irregularities, which occur, *e.g.*, in the two oxidations under discussion, are often probably inherent in the mechanism of the process; for example, they may arise from differences in the state of the surface of a reaction vessel in successive experiments. In these circumstances it is pointless to give detailed experimental data; accurate " absolute " values of the pressure limits for ignition in such cases only have a meaning if many more conditions are specified than is possible at present. The data given below represent averages of many experiments made to discover how the critical pressure limits for explosion vary with different factors, " blank " or control experiments being suitably interspersed, and the wall conditions maintained as fixed as possible.

EXPERIMENTAL.

COS, prepared by the action of dil. H_2SO_4 on NH_4NCS (Moser, " Die Reindarstellung der Gase "), contained H_2S, HCN, and CS_2; the bulk of the last was removed in a freezing mixture, the HCN absorbed by KOH aq., and H_2S by $Pb(OAc)_2$. The final traces of CS_2 were removed by a mixture of $PhNO_2$, $PhNH_2$, and PEt_3. The final product gave no test for H_2S or CS_2. Even if small traces of H_2S had been present, it seems very improbable that they would bring about the phenomena observed. To counter the (probably invalid) objection that traces of the PEt_3 used in the purification might cause the explosion phenomena, the purifying mixture was subsequently dispensed with. Careful control of the conditions of the preparation and the freezing mixture used to collect CS_2 made it possible to obtain samples of COS free from this substance: the results were the same.

O_2 was taken from a cylinder and dried by P_2O_5; it gave the same results as O_2 obtained by heating $KMnO_4$. The P_2O_5 was not specially purified. It has been suggested that traces of phosphines thereby introduced vitiate the results. This is very improbable, for the phenomena with COS fall into line with those of CS_2, and if phosphines were present very much lower ignition temps. would be noticed. Moreover, this objection would cast doubt on many of the expts. on reaction kinetics during the past few years.

Since, in the explosion of COS with O_2, complete oxidation involves a volume change, $COS + 1\frac{1}{2}O_2 = CO_2 + SO_2$, it seemed convenient to follow the reaction statically. It is unfortunate that the interesting phenomena observed occur predominantly in a region of low press., but experience and analyses indicate that no serious errors are introduced by the necessity of measuring small press. changes.

The apparatus consisted of a cylindrical or spherical Pyrex reaction vessel held within an electric furnace. An oil-bath often replaced the furnace with the same results, so that variations of temp. in the furnace can be disregarded. The gases, which were stored in glass globes, were introduced *via* capillary tubing. Pressure changes were recorded on a Hg manometer. The apparatus could be evacuated by means of a Hg-vapour pump backed by a water pump. For the expts. in which a mixture of the two reacting gases was employed, a mixing vessel was inserted into the apparatus. Inert gases were introduced from filled globes in a similar manner; N_2 and A were from cylinders, SO_2 from the liquid, and CO_2 was obtained by heating $MgCO_3$. Reaction vessels of various diameter (2—5 cm.) were employed.

In other expts. used to determine the conditions of temp. and press. necessary for explosion, mixtures of COS and O_2 were sealed in cylindrical glass tubes of known diameter and these were immersed successively in an oil-bath maintained at the desired temp.

RESULTS.

Several important conclusions are already established. The inferences drawn from them made it desirable to re-examine certain features of the oxidation of COS.

It is impossible in any circumstances to observe a slow reaction between O_2 and COS. Mixtures of the two substances either explode spontaneously under the prevailing conditions of temp. and press., or do not react measurably at all. The explosion is accompanied by a bluish flash, and the resulting contraction in vol. is approx. 80% of that required by the equation $COS + 1\frac{1}{2}O_2 = CO_2 + SO_2$. The deficiency might arise in one of two ways. Either all the COS is partially oxidised to CO as well as CO_2, or part of it is completely burnt in accordance with the idea of a " residual pressure " suggested by some expts. of Semenov and others. For a variety of reasons the first of these alternatives is favoured. In the second case the % press. contraction would vary with different initial concns., but actually there is no appreciable variation. Moreover, analysis shows that CO is produced in the explosion. Complete analysis of these mixtures is difficult, but after complete absorption of COS, CO_2, SO_2, and O_2 with KOH, and alk. pyrogallol, the residue was absorbed by Cu_2Cl_2, and this could only be CO. In different analyses the % of this residue varies slightly but is in fair accord with the requirements for 80% complete combustion. Very little solid is deposited from the explosions.

Analyses similar to these were subsequently made with CS_2–O_2 mixtures, and the results were essentially the same. In testing for CO, PEt_3 was used to absorb CS_2, and CO_2 and SO_2 were absorbed in KOH aq. as before.

The possibility that a slow reaction occurred without press. change in the absence of explosion was excluded by keeping a $1COS + 1\frac{1}{2}O_2$ mixture in the heated reaction vessel for a considerable time, removing it by means of a vacuum pipette, and treating it with KOH aq.; the residue (O_2) was still approx. 60% of the whole, showing that no CO_2 or SO_2 had been formed.

An induction period, extending from secs. to many mins. in different expts., usually precedes explosion, and is found whatever method is used for carrying out the expts., *i.e.*, whether the gases are introduced successively into the heated vessel, or whether they are premixed. It is not certain whether a similar induction period occurs when COS–O_2 mixtures in clean glass tubes are immersed in an oil-bath at a temp. such that explosion occurs; the time required for the heating of the system in these circumstances can be only roughly estimated. It is probable, however, that with the clean vessels, the induction period, if it occurs, is more reproducible.

The duration of the induction period varies with the press. of the gases. It might be expected to decrease with increasing pressure. At lower pressures this is so, but at higher pressures the reverse is observed, the induction period eventually becoming so long that explosion does not occur. The existence of such an upper crit. press., below which spontaneous ignition occurs and above which there is no observable change, is, however, unlike the case of CS_2, confined to a very small range of temp.

The foregoing facts indicated the existence of a press. region for explosion of the type found for CS_2 and O_2; attempts were therefore made to discover the temp. and press. limits bounding this region.

Lower Limiting Critical Pressure.—To determine the lower crit. press. limit at any temp., a $1COS + 1\frac{1}{2}O_2$ mixture was introduced into the heated evacuated reaction vessel to successively different pressures. Below about 205°, no change was observed with total press. up to 600 mm. over long periods. At higher temps. explosion occurred, *e.g.*, at 217°; as the following table shows, the lower limit is approx. 37 mm. in a vessel of 4 cm. diam. (expl. = explosion):

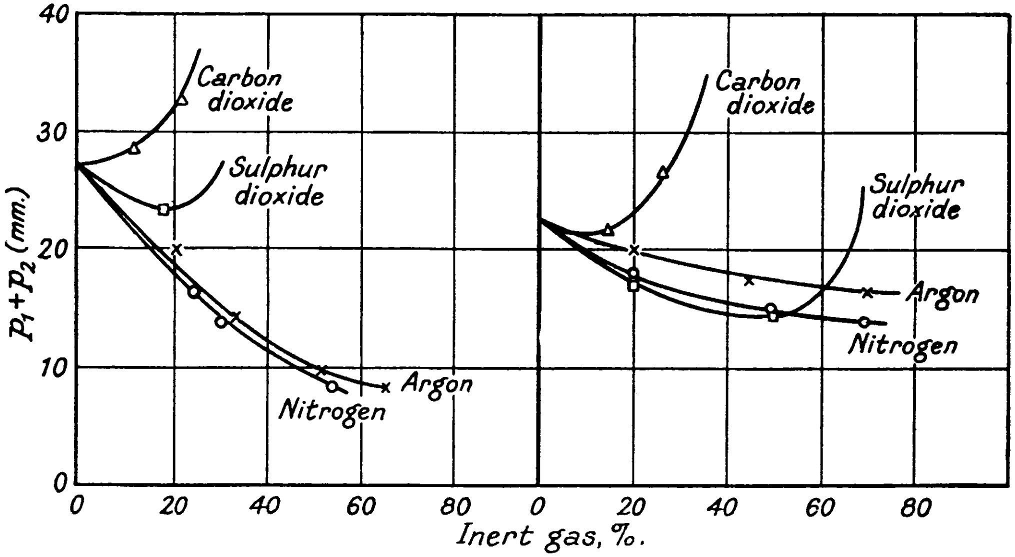
p_{COS}.	p_{O_2}.	Result.	Induction period.	p_{COS}.	p_{O_2}.	Result.	Induction period.
13	20	No expl. (4′)	—	35	53	Expl.	7″
13	20	No expl. (5′)	—	45	69	,,	7″
16	23	Expl.	7″	47	71	,,	10″
21	32	,,	12″	72	108	,,	15″
24	35	,,	11″	78	119	No expl. (4′)	—
27	40	,,	20″	96	145	No expl. (3′)	—
32	48	,,	12″				

This lower limiting press. decreases rapidly at first and then slowly with increasing temp.; at the lowest temps. for explosion in the vessel of 4 cm. diam., *i.e.*, about 205°, it is just below 100 mm.:

Temp.	235°	227°	220°	217°	215°
Lower limit, $p_{COS + 1\frac{1}{2}O_2}$ (mm. Hg)	30	35	37	38	41

Expts. were also made to determine the effect of alteration in vessel dimensions upon the lower crit. explosion press. At 240° in a vessel of 4 cm. diam. it was of the order of 30 mm.; in one of 2 cm. diam. no explosion occurred below about 240°, where the limit was *ca.* 200 mm. Decrease in the vessel dimensions therefore raises the lower limit.

FIG. 1. FIG. 2.



Addition of N_2 or A depresses the partial press. of COS plus O_2 required for explosion at any temp.; SO_2 behaves in the same way at first, but larger additions raise the limit rapidly. CO_2 raises the limiting press. even more effectively. These results are depicted in Fig. 1, and Fig. 2 shows that similar results are obtained with CS_2–O mixtures. CO_2 and SO_2 have a particular ability for decreasing the ease of ignition in both reactions; A and N_2 behave, qualitatively at least, as would be expected on the basis of other results (see p. 212).

Upper Limiting Critical Pressure.—The results in the above table suggested the possibility of determining an upper crit. press. for explosion at the lower temp. This is attainable because the induction period is long enough to allow the introduction of the mixed gases into the vessel up to the required press. above the upper limit, before the explosion consequent upon an overstepping of the lower limit occurs. For instance, at 217° in a vessel 4 cm. in diam. the upper limit appears to be about 180 mm. for COS + $1\frac{1}{2}O_2$. Another series of expts. at 220° in a 4-cm. diam. vessel is given below:

$p_{COS + 1\frac{1}{2}O_2}$	73	82	122	203	281
Result	Expl.	Expl.	Expl.	Expl.	No expl. (5′)
Induction period	1″	2″	1″	3″	—

At higher temps. the shorter induction periods made this procedure impossible, and other methods, which had been used in expts. upon the combination of H with O_2 (Thompson and Hinshelwood, *loc. cit.*), were therefore tried. In the first, one of the reactants was introduced into the heated reaction vessel to a definite press. and the other was then added in the requisite proportion. It was thought that with pressures of the first gas below a certain value, ignition would occur on introduction of the second, but with higher pressures no ignition would occur. The following table indicates that with 1COS + $1\frac{1}{2}O_2$ in a vessel of 4 cm. diam. the press. of COS (introduced first) at 220° is approx. 110 mm.

p_{COS}	76	100	104	119	134
p_{O_2}	122	150	161	185	203
Result, and induction period (if explosion)	Expl. (8″)	Expl. (2″)	Expl. (5″)	No expl. (10′)	No expl. (10′)

When O_2 is admitted first, the crit. press. has a different value.

Determinations of the upper crit. limit in this way show that it increases rapidly with temp., so that above about 230° it is not amenable to measurement.

Despite the arguments which have been raised against its validity, the " withdrawal " method of determining the upper limit was next tried, although accurate values could not be expected, especially in view of difficulties caused by the induction period. COS was introduced into the reaction vessel at such a press. that no explosion occurred on addition of O_2. The mixture was then slowly evacuated in order to determine whether explosion occurred at the upper limit. It is remarkable that explosion on withdrawal is very rarely observed, although it occurs in some cases. For example, at 215° in the larger reaction vessel, with press. of COS and O_2 of 186 mm. and 284 mm. respectively, no reaction took place after 30 min., but the mixture exploded on withdrawal at approx. 140 mm. In another expt., in which no press. change had been observed over many mins., the press. was somewhat reduced, and after an appropriate induction period the mixture exploded at the lower press. At 220°, with 112 mm. of COS and 168 mm. of O_2, no explosion occurred in 5 min.; on reduction to a total press. of 143 mm., the mixture then exploded after 15 sec.

The failure to explode on withdrawal was noticed in the original expts. with CS_2–O mixtures. It seems probable that gaseous deactivation processes are operative at the upper limit, but there are other complications. An entirely independent investigation on the oxidation of CO suggests that the starting of the chains may be affected by " poisoning " processes at the vessel walls (Hadman, Thompson, and Hinshelwood, *Proc. Roy. Soc.*, 1932, **137**, *A*, 87; **138**, *A*, 297). It may well be that similar processes are in play here too, so that no ignition is observed on evacuation. In this connexion another phenomenon was observed : when a COS–O_2 mixture is introduced into the reaction vessel to a press. below the lower limit, no explosion occurs, and if after an interval of some secs. more of the mixture is introduced, no explosion occurs on passing the lower limit. This must indicate the occurrence of some " poisoning " process.

Other General Results.—Although the method of heating mixtures of CS_2 and O_2 in sealed tubes was expected to give entirely reproducible values for the press. limits, since a " clean " surface was used in each expt., yet perfect regularity was not obtained. Several facts can, however, be deduced from the results. First, the crit. press. region for explosion, though of the same form, lies at higher temps. than those found by the other method : the reason for this is not known, but the tubes used in these expts. were narrower than the larger reaction vessel employed in the earlier ones. Again, no upper limit could in general be observed. This may be either because the upper limit increases rapidly with temp. or because " metastability phenomena " are operative (see Hadman, Thompson, and Hinshelwood, *loc. cit.*).

Attempts were made to obviate the occasional erratic results by " washing out " the reaction vessel with COS or O_2 between successive runs. In the expts. with CS_2, this was similarly used. The procedure did not give more satisfactory results, but in the expts. with CS_2 the lower press. limit for explosion was raised, *i.e.*, the ignitability was decreased.

DISCUSSION.

The principal facts are illustrated by Fig. 3. The absence of a measurable reaction between carbonyl sulphide and oxygen, and the sudden transition under certain conditions from this state to that of explosion, are probably to be interpreted by assuming the propagation of branching reaction chains. The alternative would be that it is the result of a " thermal " process starting on the active points on the vessel walls; but for a variety of reasons this is thought to be improbable.

The relationships would therefore appear to be similar to those found in the oxidation of carbon disulphide. There is a lower critical pressure limit only slightly dependent upon temperature. Whereas, however, in the latter case the upper critical pressure bounding the explosion region is quite definite, yet with carbonyl sulphide it is very uncertain and may only exist over a narrow range of temperature. The difference in the two processes may be due to the difference in the gaseous deactivation processes occurring. In the oxidation of carbon disulphide the chains are broken by the carbon disulphide

FIG. 3.

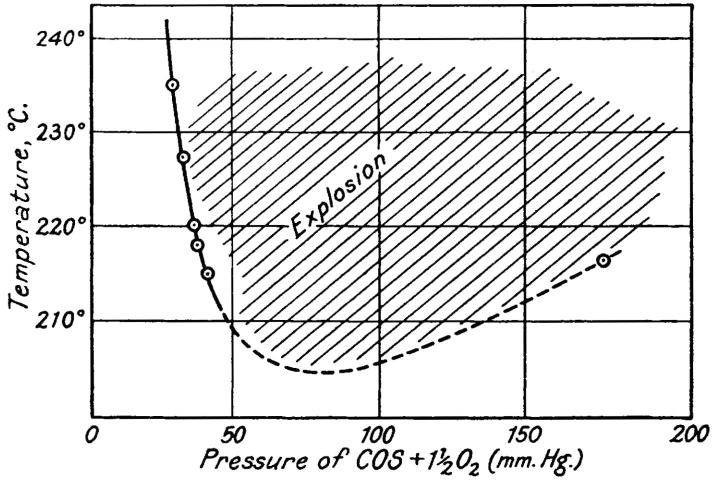


FIG. 4.

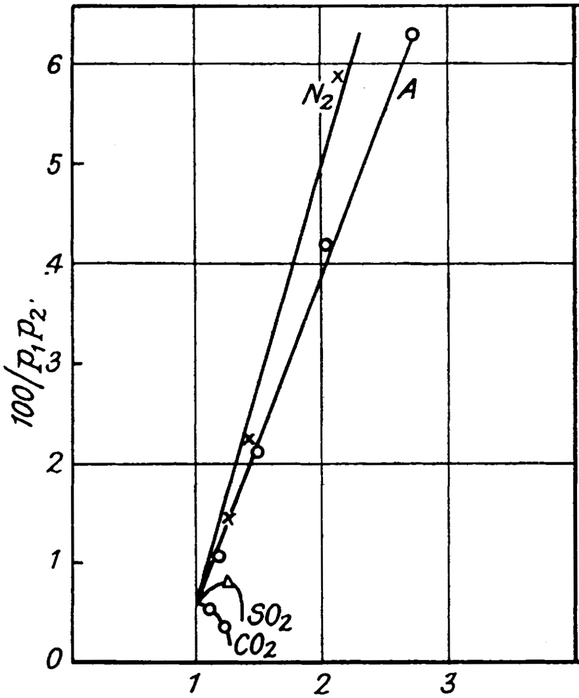
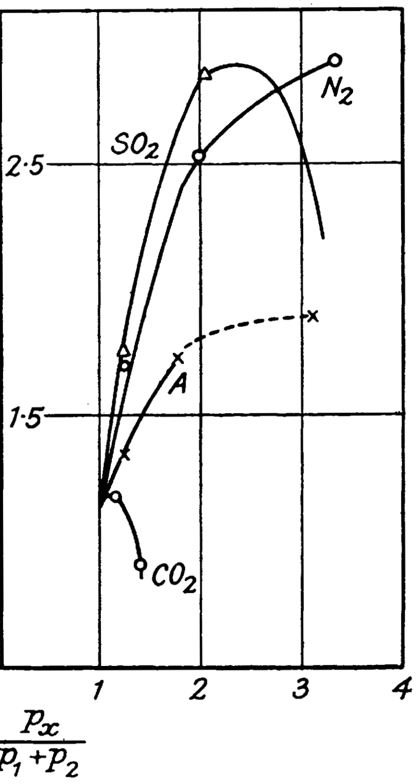


FIG. 5.



itself; this may be true of carbonyl sulphide too, but to a much smaller degree. The existence of the induction period and the way in which it varies with pressure in the neighbourhood of the limits suggest that a finite time is necessary for the establishment of branching chains in the gas.

Recently, data on lower limits of this type have been applied as a test of the relationship $p_1p_2[1 + p_x/D(p_1 + p_2)]d^2 = \text{const.}$ which is derived on the basis of the theory of reaction chains; p_1 and p_2 are the pressures of the reactants and p_x that of the inert gas at the limit; D is the diffusion coefficient of active centres through the reaction mixture, and d the diameter of the vessel (Melville and Ludlam, *Proc. Roy. Soc.*, 1931, **132**, *A*, 108; Thompson, *Trans. Faraday Soc.*, 1932, **28**, 300; J., 1932, 933; Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc.*, 1932, **138**, *A*, 311; Melville, *Trans. Faraday Soc.*, 1932, **28**, 814). In the absence of inert gases the following relationships should then hold: $p_{\mathrm{COS}}p_{\mathrm{O_2}} \,.\, d^2 =$ const., and $p_{\mathrm{CS_2}}p_{\mathrm{O_2}} \,.\, d^2 =$ const. It is difficult to test these equations, for two reasons: (1) the lower limit depends more upon temperature than is usually the case; (2) the pressures are rather small and variations due to the erratic nature of the process may mask the observations. For carbonyl sulphide–oxygen mixtures, mean values for the total limiting pressures in vessels of 4 and 5 cm. diameter are respectively 33 and 27 mm., whence

	p_{COS}.	$p_{\mathrm{O_2}}$.	d.	k.
(i)	13	20	4	4160
(ii)	11	16	5	4400

The agreement is good but may be fortuitous.

The inert-gas effect is best examined by plotting $1/p_1p_2$ against $[1 + p_x/(p_1 + p_2)]$ for one vessel and one temperature. Such curves (Figs. 4 and 5) are based on the calculations shown in Table I.

TABLE I.

Carbonyl Sulphide–Oxygen Mixtures.

Temp. 230°. Vessel 5·0 cm. diameter.

Inert gas, and %.		p_{total}.	p_1.	p_2.	p_x.	$100/p_1p_2$.	$p_x/(p_1 + p_2)$.
Argon	0	27	11	16	0	0·568	0·00
	20·1	25	8·0	12·0	5·0	1·04	0·25
	33·5	21	5·5	8·5	7·0	2·14	0·50
	51	20	3·9	5·9	10·2	4·35	1·04
	65·6	23·5	3·2	4·9	15·4	6·37	1·90
Nitrogen	0	27	11	16	0	0·568	0·00
	25·0	22	6·6	9·9	5·5	1·52	0·33
	31·0	20·5	5·6	8·5	6·4	2·10	0·46
	53·0	20	3·4	5·0	10·6	5·88	1·26
Sulphur dioxide	0	27	11	16	0	0·568	0·00
	19·6	28·5	9·1	13·7	5·7	0·804	0·25
	28·0	—	—	—	—	—	0·38
Carbon dioxide	0	27	11	16	0	0·568	0·00
	12·0	32·0	11·2	17·0	3·8	0·526	0·14
	20·5	40·0	12·8	19·2	8·0	0·406	0·25
	25·0	—	—	—	—	—	0·33

Carbon Disulphide–Oxygen Mixtures.

Temp. 170°. Vessel 2·5 cm. diameter.

Argon	0	22	5·5	16·5	0	1·10	0·00
	20	25	5	15	5	1·33	0·25
	46·5	33	4·4	13·3	15·3	1·71	0·87
	71·0	58	4·2	12·6	41·2	1·89	2·45
Nitrogen	0	22	5·5	16·5	0	1·10	0·00
	20·4	22	4·4	13·1	4·5	1·73	0·26
	50·0	29	3·6	10·9	14·5	2·55	1·0
	70·0	45	3·4	10·1	31·5	2·91	2·33
Sulphur dioxide	0	22	5·5	16·5	0	1·10	0·00
	21·1	22	4·3	13·05	4·65	1·78	0·27
	52·0	28·5	3·4	10·3	14·8	2·86	1·08
	70·0	—	—	—	—	—	2·33
Carbon dioxide	0	22	5·5	16·5	0	1·10	0·00
	15·1	25	5·3	15·9	3·8	1·18	0·18
	25·0	35	6·3	19·95	8·75	0·795	0·33
	40·0	—	—	—	—	—	0·66

The relationships are not obeyed closely. Argon and nitrogen are qualitatively in agreement, but carbon dioxide and sulphur dioxide show a fundamental discrepancy. These gases appear to have a peculiar ability to break reaction chains. The effect of the former is most marked and at once suggests a possible reason for some of the erratic results; for traces of this substance remaining in the reaction vessel owing to incomplete evacuation might introduce error.

The selection of a cycle of changes which might occur in the process is necessarily difficult, but a few possible chains are given below: they may be either " material " or " energy " in type, or a combination of both. Spectroscopic investigation of the flame of burning carbon disulphide indicates the presence of SO and S_2 radicals (Fowler and Vaidya, *Proc. Roy. Soc.*, 1931, **132**, *A*, 310). These might well arise here too. Again, carbonyl sulphide, like carbon disulphide, may be, in part, a chain-breaker. The experiments of Harteck and Kopsch show furthermore that oxygen atoms bring about rapid oxidation of carbon disulphide (*Z. physikal. Chem.*, 1931, *B*, **12**, 327). In the oxidation of both the disulphide and the oxysulphide, carbon monoxide is formed.

A. *Oxidation of Carbon Disulphide*:

(1)	$CS_2 + O_2 \longrightarrow CS_2,O_2$	peroxide theory.
(2)	$\left\{\begin{array}{l} CS_2,O_2 + O_2 \longrightarrow CO_2 + 2SO \\ CS_2,O_2 + CS_2 \longrightarrow 2CS + 2SO \end{array}\right\}$	giving branching chains.
(3)	$CS_2,O_2 \longrightarrow CS + SO_2$	
(4)	$SO + O_2 \longrightarrow SO_2 + O$	O atoms (Harteck and Kopsch)
(5)	$O + CS_2 \longrightarrow CS + SO$	CS deposited.
(6)	$O_2 + CS + O_2 \longrightarrow CO_2 + SO_2$	
(7)	$CS + O_2 \longrightarrow CO + SO$	CO formed, preferred to (6)?
(8)	$SO + CS_2 \longrightarrow CO + 3S$	S formed? Breaking effect of CS_2.
(9)	$O + O + X \longrightarrow O_2$	upper limit?
(10)	$O + SO + X \longrightarrow SO_2$	end of chain.
(11)	$S + O_2 \longrightarrow SO_2$	" "

B. *Oxidation of Carbonyl Sulphide*:

(1)	$COS + O_2 \longrightarrow COS,O_2$	peroxide theory.
(2)	$COS,O_2 + COS \longrightarrow 2CO + 2SO$	giving branching chains.
(3)	$COS,O_2 \longrightarrow CO_2 + SO$	
(4)	$SO + O_2 \longrightarrow SO_2 + O$	cf. A(4).
(5)	$O + COS \longrightarrow CO + SO$	
(6)	$SO + COS \begin{array}{l} \nearrow CO_2 + 2S \\ \searrow CS + SO_2 \end{array}$	
(7)	$O_2 + CS + O_2 \longrightarrow CO_2 + SO_2$	cf. A(6).
(8)	$CS + O_2 \longrightarrow CO + SO$	cf. A(7).
(9)	$O + O + X \longrightarrow O_2$	cf. A(9).
(10)	$O + SO + X \longrightarrow SO_2$	cf. A(10).
(11)	$S + O_2 \longrightarrow SO_2$	cf. A(11).

The peculiar ability of carbon dioxide and sulphur dioxide to break the chains, however, rather suggests the presence of chains by which energy is transferred from " hot " molecules of these substances to the corresponding " cold " molecules. This process may occur with special ease. Such steps as the following may occur:

(1) $CS_2 + O_2 \longrightarrow CS_2,O_2$
(2) $CS_2,O_2 \longrightarrow CS + SO_2^*$
(3) $SO_2^* + O_2 \longrightarrow O_2^* + SO_2$
(4) $O_2^* + CS + O_2 \longrightarrow CO_2^* + SO_2^*$
(5) $CS + O_2^* \longrightarrow CO + SO$

SUMMARY.

The thermal oxidation of carbonyl sulphide is a chain reaction which exhibits discontinuities of the type observed in other similar processes. Explosion occurs under certain conditions of temperature and pressure; otherwise reaction is not noticeable. The influence of various factors, such as vessel size and addition of inert gases, agrees to some extent with that which would be expected, but with carbon dioxide and sulphur dioxide the inert-gas effect is abnormal. These substances have a peculiar power of breaking

reaction chains. Cycles of changes are suggested for the reaction and also for the closely related oxidation of carbon disulphide.

We thank the Chemical Society for a grant, and one of us (F. L. H.) is indebted to the Rhodes Trustees for a Scholarship.

UNIVERSITY MUSEUM, OXFORD. [*Received, July* 1*st*, 1932. *Amended, January* 9*th*, 1933.]